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*Review*

# Adhesion in Bitumen/Aggregate System: Adhesion Mechanism and Test Methods

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**Abstract:** A literature review of the five main theories describing the interaction mechanisms in the bitumen/aggregate system was conducted: theory of weak boundary layers, mechanical theory, electrostatic theory, chemical bonding theory, and thermodynamic theory (adsorption theory). The adhesion assessment methods in the bitumen/aggregate system are described, which can be divided into three main groups: determination of adhesion forces for bitumen with different materials, determination of bitumen resistance to the exfoliating action of water with different materials, and determination of adhesion as a fundamental value (contact angle measurements, interfacial fracture energy, adsorption capacity and others). It is proposed to evaluate the quality of adhesive interaction in the bitumen/aggregate system in two stages. The authors recommend using the adhesion determination methods for these two stages from the second group of methods the determination of bitumen resistance to the exfoliating action of water with different materials. In the first stage, the adhesion in the bitumen/aggregate system is determined by an accelerated technique in which the used bitumen binder and mineral material are considered as test materials. After the first stage, there are positive results in the second tests on compacted mixtures (indirect tensile strength test, Modified Lottman indirect tension test, immersion-compression test, and Hamburg wheel tracking test).

**Keywords:** adhesion; bitumen; aggregate; moisture damage; laboratory testing

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**Citation:** Pstrowska, K.; Gunka, V.; Sidun, I.; Demchuk, Y.; Vytrykush, N.; Kułażyński, M.; Bratychak, M. Adhesion in Bitumen/Aggregate System: Adhesion Mechanism and Test Methods. *Coatings* **2022**, *12*, 1934. https://doi.org/10.3390/coatings12121934

Academic Editor: Valeria Vignali

Received: 9 November 2022
Accepted: 3 December 2022
Published: 8 December 2022



## 1. Introduction

Asphalt pavements include two main ingredients: bitumen and aggregates (crushed stone). Bitumen performs the adhesive function that binds mineral material particles to form an asphalt concrete coating. Being non polar, bitumen has high water resistance properties. It is known that low-paraffinic oil is the most suitable for the bitumen production, but, due to the shortage of this type oil, almost any oil residues are used. This leads to the bitumen materials' low quality and, as a result, to the asphalt concrete pavement's low quality.

In general, asphalt concrete appears as a substantially water resistance material, but water can penetrate into the pores in different ways: impregnation (surface water), under the action of capillary forces (water from the bottom of the road base rises to the asphalt concrete), and water vapor (air moisture can penetrate into the asphalt concrete pores and condense). Furthermore, transport wheel pressure accelerates the water penetration into the asphalt concrete pores [1]. Therefore, both passive and active adhesion of bituminous binder to the asphalt concrete must be ensured.

Active adhesion is the ability of the binder to completely surround the particles of the aggregate and adhere to it during the mixing of the components of the asphalt concrete mixture (Figure 1). This type of adhesion arises due to the mutual attraction of positively charged surface-active substances of bitumen molecules to negatively charged aggregate molecules. This type of interaction makes it possible to displace water located at the interface of phases and ensures maximum bitumen coverage of the surface of the mineral material. In case of loss of active adhesion, this can lead to increased movement of moisture in asphalt concrete layers [2,3].

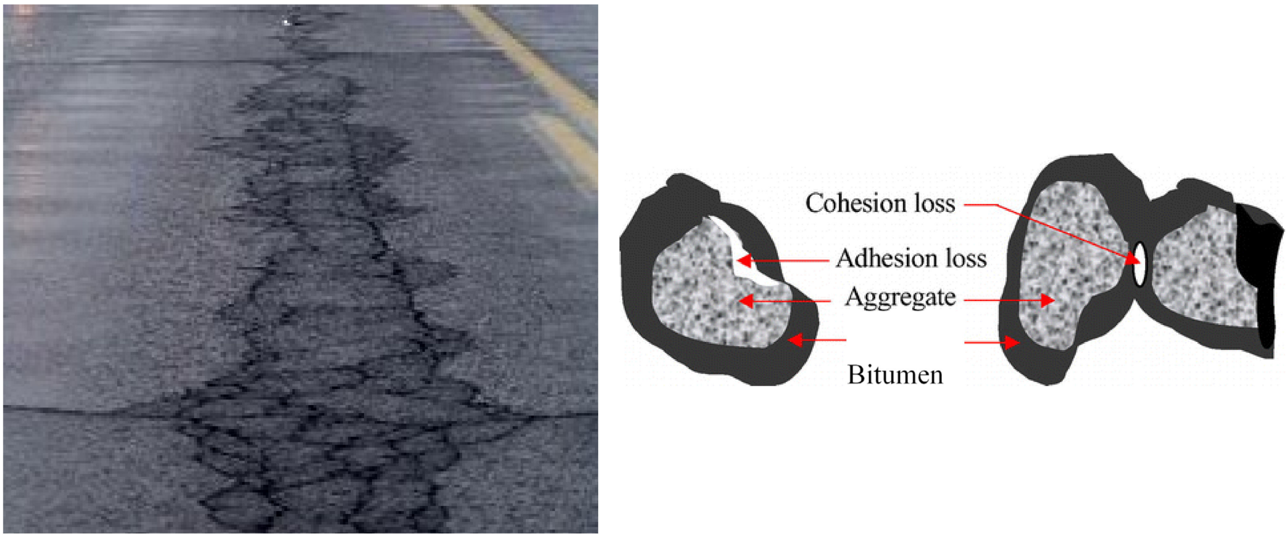



**Figure 1.** Fatigue cracks caused by low-adhesion in bitumen.

In contrast to active adhesion, passive adhesion occurs as a result of external forces, for example, due to increased pressure in the pores and can be described as the ability to resist the penetration of water into the asphalt mixture. Passive adhesion indicates the ability of bitumen to bind to the surface of the mineral material throughout the further service life of the asphalt concrete without the risk of destruction of these bonds under the action of vehicle wheels or water [4]. Loss or insufficiency of passive adhesion can cause premature appearance of cracks, potholes and ruts [5].

Poor adhesion between bitumen and aggregate leads to the binder stripping in the presence of water, which ultimately leads to the pothole formations (Figure 1). Moisture damage in asphalt concrete pavements is considered as primary cause of distresses in the asphalt pavement layers. The resistance of bitumen to stripping is determined by its adhesion to the aggregate surface: it must be not only high, but also stable over time, which is one of the conditions for the road surface durability. The situation is exacerbated by the traffic and car numbers constant increase on the roads. Therefore, to obtain high quality coatings, a key factor is high adhesion ensure between bitumen and the road pavement mineral components.

This work is devoted to fundamental knowledge related to adhesion in the Bitumen/Aggregate system, namely there is a need to explain and understand how bitumen adheres to the aggregate surface, show the most well-known tests that numerically evaluate the adhesion between bitumen and aggregate, and group them by common features.

The following section highlights the theories which explain the adhesion phenomena between bitumen and aggregate.

## 2. Adhesion Mechanism in Bitumen/Aggregate System

Researches in this area were conducted for more than 100 years, but the question about adhesion mechanism between bitumen and aggregate remains debatable. There were proposed many theories to explain the adhesion mechanism between bituminous and aggregate. The main theories explaining the adhesion mechanism in the bitumen/aggregate system are presented in the Table 1 and Figure 2.

**Table 1.** Theories explaining the adhesion mechanism in the bitumen/aggregate system.

| Theory | Interaction | References |
|---|---|---|
| Weak Boundary Layer | layering | Bikerman, 1961 [6] and other [7–11] |
| Mechanical interlocking | interlock | McBain and Hopkins, 1925 [12] and other [6–11] |
| Electrostatic | potential | Deryaguin and other, 1948 [7] and other [6,8–11] |
| Chemical bonding | covalent and ionic bonds | [6–11,13–16] |
| Thermodynamic (Surface free energy) | surface free energy | [6–11] |

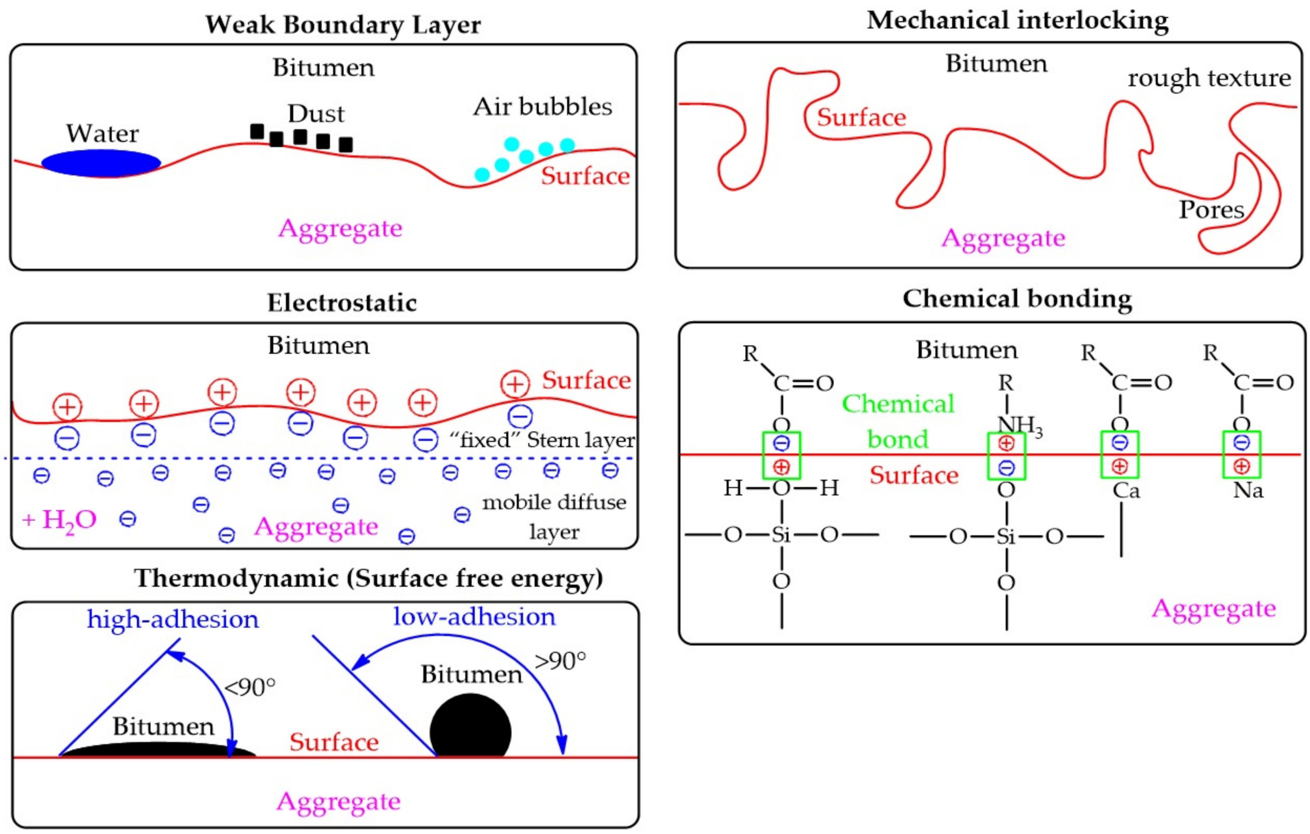



**Figure 2.** Representation of theories explaining the adhesion mechanism in the bitumen/aggregate system.

Let us briefly describe each of the theories.

*2.1. Theory of Weak Boundary Layers*

According to the weak boundary layer theory, the breakdown of adhesive bonds occurs either in the adhesive or in the substrate due to the presence of an interfacial region with low cohesive strength. While there is debate as to how common these layers are, they do exist and cannot be ignored. However, certain types of boundary layers, according to some researchers, are important factors for good adhesion. Common causes of weak boundary layers are low molecular weight (and therefore low cohesive strength), and surface contaminants such as organics and water. Dusty substrates can prevent effective wetting and close contact with the adhesive, and dust on aggregates is able to trap air, mixing with bitumen, and thus weaken the bitumen/aggregate bond (Figure 2).

### 2.2. Theory of Mechanical Interlocking

Adhesion occurs through the binder material penetration into the aggregate surface irregularities (pores and cavities). Adhesion occurs due to the "mechanical connection" between the binder and aggregate (Figure 2). Rough surfaces provide greater adhesion compared to a smooth surface. It should also be noted that rough surfaces are not the only reason for better adhesion. This may also be due to other factors (clean surfaces, highly reactive surface formation, or a contact area increase). The surface texture of an aggregate also affects its coat-ability, or wettability, in that a smoother surface coats easier than a rough surface. In addition, wettability, including pore filling, also depends on the viscosity of the bitumen and the chemical composition of the surface of both aggregate and bitumen. While many researchers claim that aggregate surface texture is the primary factor affecting adhesion, others report that chemical and electrochemical effects dominate. This theory simply explains the mechanical adhesive bond without taking into account the chemical interaction that can occur between the bitumen and the surface of the aggregate, so this theory has not found wide support among scientists.

### 2.3. Electrostatic Theory

Electrostatic theory is based on the presence of free charges in any material, where the opposite charges attract each other (Figure 2). The presence of free charges in the materials causes an electrochemical potential difference between two contacting materials and, thus, establish an electrical double layer. Most surfaces are charged in the presence of water. This is due to the high dielectric permeability of water, which makes it a good solvent for ions. When the bitumen/aggregate surface system is exposed to water, the mineral structure of the aggregate easily collapses and ionizes, and thus the adhesive structure of the bitumen film on the aggregate can be broken and ionized. Two layers are formed ("fixed" Stern layer and mobile diffuse layer), together they form an electric double layer. The electric potential at the shear plane between the fixed and mobile layers is measurable, and called the zeta potential ($\zeta$). The zeta potential value depends on two main factors: diffusion of external water to the bitumen/aggregate interface (the amount of moisture in the system) and the pH value of the water. The introduction of various substances can change the pH value of water into the bitumen/aggregate system (for example, mineral powders), which leads to a decrease in zeta potential. Researchers consider this approach to be of fundamental importance for quantifying adhesion in the presence of water, with knowledge of the pH effect. Determination of zeta potential can serve to quantify adhesion in the presence of water, especially taking into account the pH effect.

### 2.4. Chemical Bonding Theory

This theory is based on the formation chemical bonds in the system of bitumen and aggregate components. Although bitumen mainly consists non-polar and low-reactive hydrocarbons in relation to the aggregate, it also contains polar compounds that contain heteroatoms (O, S, N and others). The study of adsorption of bituminous model compounds containing specific functional groups is presented in the works [13–16]. Relative affinity of functional groups for aggregate surfaces and their relative displacement by water are presented in these studies.

Tests involving the adsorption affinity of the model compounds representing the various functional groups present in asphalt averaged over a series of aggregates (including granites, limestone, gravels, and greywacke) gave the following ranking [7]:

sulfoxide > carboxylic acid > nitrogen base > phenol >ketone > pyrrole > 4-ring aromatic > 2-ring aromatic

The order of desorption:

sulfoxide > carboxylic acid > pyrrole >ketone > nitrogen base > phenol

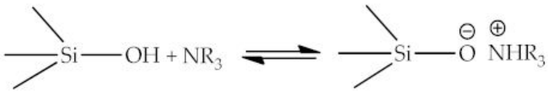
Functional groups that had the highest adsorption capacity for aggregates also had the highest sensitivity to water (sulfoxide and carboxylic acid), while nitrogen base and phenolic functionalities had the lowest sensitivity. The adsorption of bituminous components and their subsequent desorption by water depends on both the bitumen and aggregate (adsorbent) composition.

As an example of the interaction between organic and inorganic parts can be the following reaction equations [7,11]:

$$CaCO_3 + 2RCOOH \rightleftharpoons (RCOO^-)_2Ca^{2+} + CO_2 + H_2O \tag{1}$$

$$Ca(OH)_2 + 2RCOOH \rightleftharpoons (RCOO^-)_2Ca^{2+} + 2H_2O \tag{2}$$

(3)



(4)

### 2.5. Thermodynamic Theory (Surface Free Energy)

The physical and chemical adhesion between bitumen and aggregate can be seen as a thermodynamic phenomenon, which requires the removal of bitumen from the aggregate surface (bond failure), that is, the work or energy required to produce new units of area in a vacuum. The physical and chemical adhesion between bitumen and aggregate depends on the surface free energy (SFE) of the material. The higher surface free energy (adhesion work) indicates that the adhesion strength between the bitumen and aggregate interface is better. This theory, is the most widely used approach in adhesion science as indicated by most comprehensive references on this subject.

SFE is directly proportional to the contact angle (θ). The theory explains the adhesion phenomenon on base of wettability. The contact angle is the angle formed by a liquid with a solid surface when both materials are in contact. If the contact angle is >90°, the wettability is bad, and if <90° then wettability is good (Figure 2). Thus, if the wetting decreases, it leads to the adhesion decrease.

The aggregate wetting remains an important condition for good adhesion. Wetting is necessary for contact between materials, and thus the basic physical and chemical forces establishment that are ultimately responsible for adhesion. Without wetting, it is unlikely to establish the surface texture favorable impact by mechanical adhesion.

If you follow this theory, which is the most accepted and proven by researchers, adhesion in the bitumen/aggregate system can be numerically determined as derivatives of surface free energy or contact angle.

## 3. Test Methods for Adhesions

The term adhesion is widely used but its direct measurement is less evident. Far easier to define the lack of adhesion directly correlated with failure or in situ damage (e.g., raveling). Adhesion is considered as an important aspect of durability.

Directly in the bitumen/aggregate system the adhesion determination is difficult for several reasons: excess in the positive temperatures range of adhesive strength over cohesive; polymineralality of stone materials; results significant dependence on the temperature, strain (deformation) rate, binder layer thickness, etc. Therefore, for practical purposes, in laboratories usually perform an indirect adhesion assessment for the bitumen resistance assess to the exfoliating action of water (as the most significant destructive factor). The adhesion assessment indirect methods have a long history of use and are the most numerous and widely used in production conditions.

Currently there are a large number of adhesion testing methods for bitumen—more than 150 [16–23], and there are no generally accepted test methods, but the most popular are those regulated by European standards (EN) and US standards (AASHTO and ASTM).

This section provides an overview of the main laboratory test methods for adhesion in the bitumen/aggregate system in the world.

Based on the processed literature data, these methods can be divided into three groups:

1. Determination of adhesion forces for bitumen with different materials;
2. Determination of bitumen resistance to the exfoliating action of water with different materials;
3. Determination of adhesion as a fundamental value (contact angle measurements, interfacial fracture energy, adsorption capacity and others).

### 3.1. Determination of Adhesion Forces for Bitumen with Different Materials

The main methods in which the base principle is mechanical separation include: a group of methods—Peel test, Bitumen Bond Strength Test, Vialit Plate Test.

**Peel test.** The main principle of this group methods is the force determination required for the separation of a certain area bituminous film from the surface under study (Figure 3). The advantages of peel test methods are testing and devices design simplicity, ability to determine the adhesive strength of any binder, assessment of temperature effects, strain rate, stripping action of water and aggressive water environments. A similar method is the Bitumen Bond Strength Test (BBS Test) (Figure 4), which is based on the force determination generated by the pneumatic system of the device required for separation working fragment glued with bitumen to the tested surface [19,24,25]. The disadvantage of these methods is that during the test there is both adhesive and cohesive separation of the bituminous film, and also there can be inhomogeneity of values over the entire sample area [19,26,27].

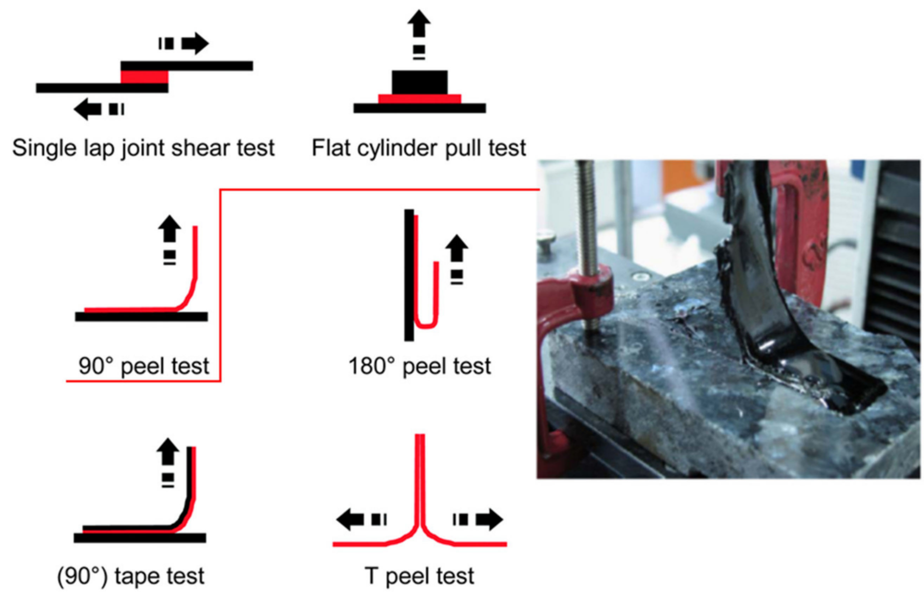



**Figure 3.** Possible schemes on peel test.

**Vialit Plate Test** [28,29] used in European countries is also one of the typical for the peeling methods. The essence of the method is that on a metal plate is applied a bitumen layer and then 100 or 50 grains of stone material are glued by the appropriate fractions. After that, the plate is fixed with the grains down and a weighing 500 g ball is thrown three times from a fixed height. After the third stroke, the sample on the plate is examined and the grains of crushed stone are counted as follows: the number of unstuck gravels, the surface of which is not covered with binder; the number unstuck gravels, the surface of which is partially covered with binder; the number of stuck gravels.

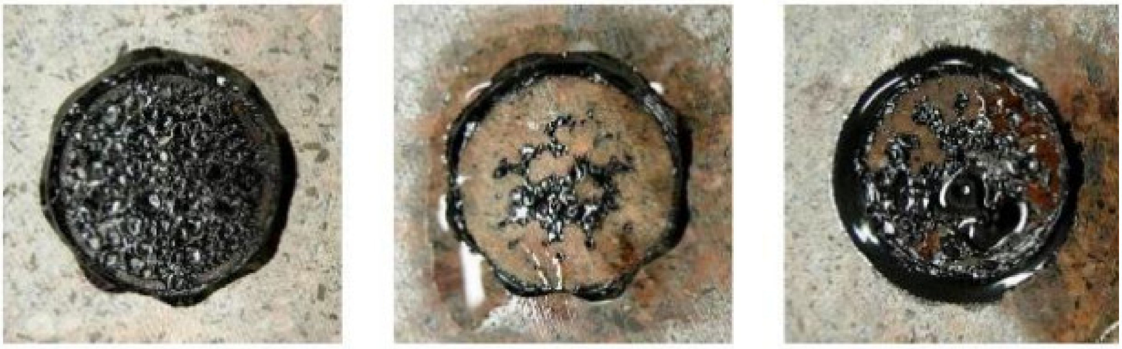


**Figure 4.** Tested surfaces after BBS Test, cohesive, adhesive and mixed separation (from **left** to **right**) Reprinted with permission from [26] Copyright Taylor & Francis 2010.

### *3.2. Determination of Bitumen Resistance to Exfoliating Action of Water with Different Materials*

Different surfaces are used for testing: stone, metal and glass plates; grains of stone materials that are treated with bitumen and after cooling (or immediately after the treatment) are immersed in distilled water or in an aqueous solution with a given temperature and kept for a certain time (from several minutes to several days). After an aqueous medium keeping, the exfoliation of bituminous binders from the surface of stone materials is estimated in percentages or points, usually by visual method.

Characteristic advantages this group of methods are:

- Easy implementation;
- No additional special equipment;
- Short test time in most methods (when boiling in water the test time does not exceed 1.0–1.5 h);
- Due to the use of grains of stone material of the same size it is possible to assess the influence on the adhesion value the bitumen film thickness on the surface of the grains.

At the same time, this group of methods has the significant disadvantages, which include:

- Visual evaluation of results, leads to significant errors;
- Results dependence on the size and surface of stone materials grains;
- In some methods, low sensitivity to the presence of modifying additives;
- Inability to compare the results obtained by different methods.

These methods adhesion assessment (exfoliating action of water) of bitumen with a mixture of stone materials were used the first in production laboratories.

The simplest methods of this group include adhesion to the glass surface [30–40]. A portion of bitumen 0.35 g is weighed on a scale and placed on a glass plate (70 mm × 24 mm). The bitumen is distributed by an even layer along the contour marked on the plate. Its overflow outside the rectangular contour marked on the glass plate should be prevented. This plate is kept for 30 min at a temperature 80 °C higher than the bitumen softening point. After that, the plate is cooled by air for 30 min at room temperature and photographed. Then, the glass plate with bitumen is kept in water at 85 °C for 25 min. After holding the bitumen plate, cold water is added to the water bath to make its temperature lower on 10 °C than the bitumen softening point. The plate is removed from the water and photographed a second time. After that, on the basis taken before and after test photos and by use the applied program software the bitumen film retained area on the glass is determined in percent (Figure 5).


**Figure 5.** The glass plates after testing two bitumen samples for adhesion to the glass surface, 33 and 87%, respectively.

The main disadvantage of the above method is the use a glass surface, which has much worse adhesion to bitumen than the surface of stone materials. This disadvantage is absent in the method of determining bitumen adhesion to gravel [31,41–48]. Gravel grain (not less than 10 mm) is tied with a thread and heated in an oven to a temperature depending on the technology. After 1 h heating, it is immersed for 15 s in bitumen (at the temperature according to the technology), then removed and hung on a tripod to drain excess bitumen. The tests are carried out not earlier than 1 h after the treatment of gravel grains with bitumen. Gravel grain is immersed in a glass and kept in boiling water for 30 min. Then remove and immerse in a glass of cold distilled water for 1–3 min to cool and fix the bitumen film left on the gravel surface. The gravel grains surface is checked and evaluated on a 5-point scale, with an interval of 0.5 points (Figure 6).

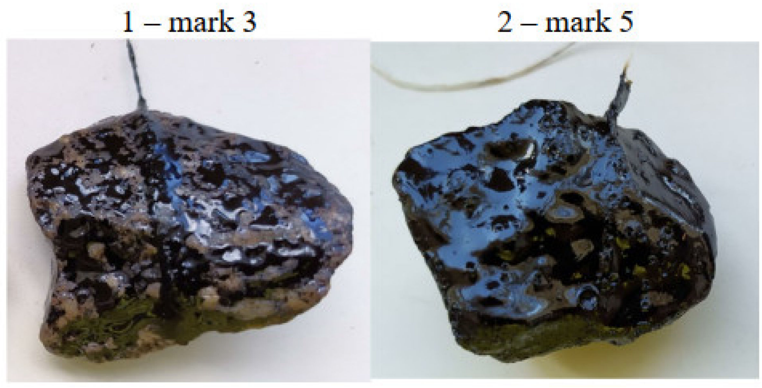



**Figure 6.** The gravel grains after testing two bitumen samples for adhesion to the gravel surface, 3 and 5 points, respectively.

A modification of this test, which is used in some laboratories in Ukraine, is that the stone material coated with bitumen is weighed before and after boiling, then according to the ratio of these masses the adhesion (in %) is calculated. That is, only the data interpretation is different, not in points, but in %. The main advantage of this method is a fairly high-test speed and it also allows to test the adhesion properties of bitumen on various stone materials.

Due to the detrimental effect of moisture damage, it is important to test the susceptibility of an asphalt mixture to moisture damage. The tests for asphalt mixes are divided into tests for loose mixtures and tests for compacted mixtures [6,19,23,49–51]. Despite the availability of tests for moisture susceptibility, none of them provides high correlation with field performance.

#### 3.2.1. Tests on Loose Mixtures

Moisture-susceptibility tests on loose mixtures are carried out on particles with an asphalt coating in the presence of water. The main advantages of these tests are their simplicity and low cost compared to the compacted-specimen test costs. The use of simple equipment and procedures to perform experiments is another advantage.

Tests on Loose Mixtures can be divided into:

- Static

  Static test [52];
  Static immersion test [53];
  Boiling water test or Texas boiling test [54,55];
  Boiling water stripping test [52,56];
  Chemical immersion test [57];
  Surface reaction test [58]; many others.

- Dynamic

  Rolling bottle test [41,52,59–62];
  Film stripping test [63];
  Dynamic immersion test [49,64];
  many others.

Conditions the most common main methods that use tests on Loose Mixtures are presented in Table 2.

**Table 2.** Conditions of the most common methods that use Loose Mixtures treated with bitumen.

| Parameter | Test | | | | | |
|---|---|---|---|---|---|---|
| | **Static** | **Static Immersion** | **Texas Boiling** | **Boiling Water Stripping** | **Rolling Bottle** | **Film Stripping** |
| | | | **Aggregate Coating** | | | |
| **Binder amount** | 4% (±x·0.5%) | 5.5 g (5.2%) | 2.3%–8% | 30 g (2.0%) | 16 g (3.0%) | 3.6% |
| **Aggregate (size)** | 150 particles (8/11.2 or 6/10 mm) | 100 g (6.3/9.5 mm) | 300 or 100 g (3/8 in) | 1500 g (8/11.2 or 6/10 mm) | 510 g for 3 sets (8/11.2 (5.6/8, 6.3/10) mm) | 60 g (3/8 in) |
| | | | **Amount for testing** | | | |
| **Loose Mixtures** | 150 particles | 100 g | 300 or 100 g | 200 g | 150 g | – |
| **Water** | full cover | 600 mL | 500 mL | 600 mL | 500 mL * | – |
| | | | **Water conditioning** | | | |
| **Conditioning type** | static | static | static | static | dynamic | dynamic |
| **Water temperature** | 19 ± 1°C | 25 °C | boiling water | 20 ± 5 °C | 25 °C | |
| **Conditioning time** | 48 ± 1 h | 16–18 h | 10 and 13 min | 10 min | 6 h and 24 h if necessary 48 h and 72 h | 15 min |
| | | | **Assessment of the coating degree** | | | |
| **Validation of the result** | number of not completely coated aggregates (visual) | visual estimation of the coating, less than or greater than 95% | visual estimation of the coating | visual estimation of the coating | visual estimation of the coating | validation of the result |

* including mixtures.

Most static methods of analysis on loose mixtures differ mainly from each other in:

- Bitumen/aggregate ratio;
- Aggregate size;
- Methods of bitumen and aggregate preparation and mixing (for example, mixing Temperature, cooling time and other);
- Water conditioning (test temperature from room to boiling; it should also be noted that as the water temperature increases, the test time decreases significantly; adding different amounts of $Na_2CO_3$ to distilled water during chemical immersion test [57];

- Coating degree assessment (it's usually a visual estimation of the coating, but digital image processing is possible [61].

The difference between the various dynamic methods of analysis on loose mixtures is the same as static methods, the only difference from static methods is that the bitumen/aggregate System is mixed in water. There are different ways of mixing (Figure 7).

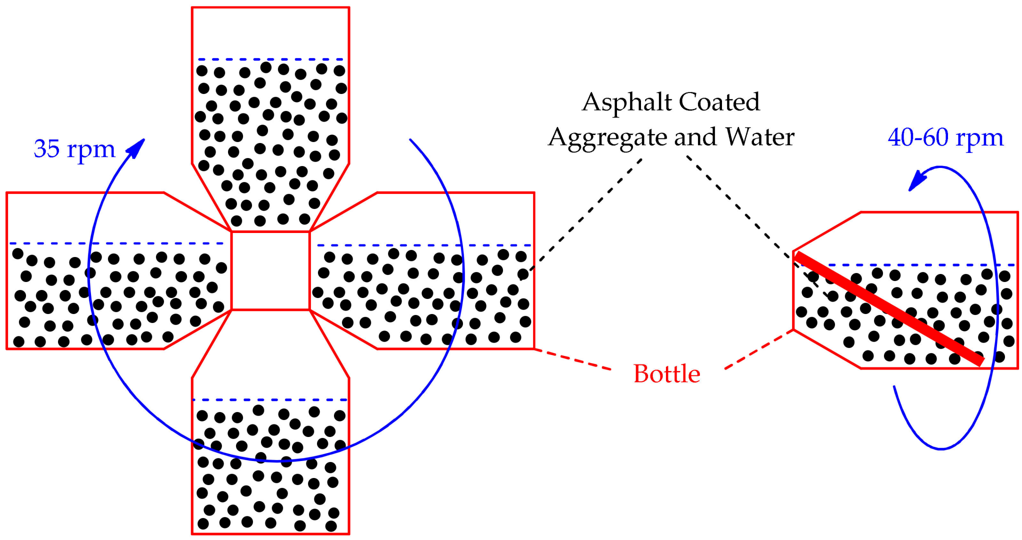



**Figure 7.** Rotating bitumen/aggregate mixture in a sealed bottle for film stripping test and rolling bottle test.

### 3.2.2. Tests on Loose Mixtures

Many researchers believe that the adhesion determination on loose mixtures is uninformative and does not reflect the real conditions of asphalt concrete in the coatings and prefer a group of test methods for compacted mixture. This group includes methods based on the characteristic changes of asphalt concrete samples (different shapes) before and after their deposition in water at different temperatures. A significant advantage of these methods is that they can be used to quantify the water impact on reducing the asphalt concrete adhesive properties. The disadvantages of these group methods are that they are used in different test conditions, which differ significantly from the actual operating conditions of asphalt pavements, and also have a relatively low results accuracy.

Mainly for this group of tests use compacted cylindrical mixtures:

- Indirect tensile strength test [65];
- Original Lottman indirect tension test [49,66];
- Modified Lottman indirect tension test [49,67,68];
- Tunnicliff–Root test [69,70];
- Compression strength test [71];
- Immersion-compression test [72,73];
- Marshall immersion test [74];
- Texas freeze-thaw pedestal test [49,75,76].

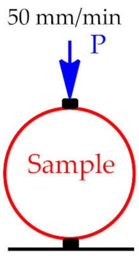
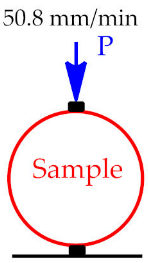
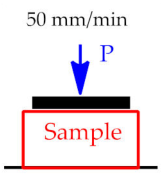
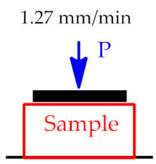
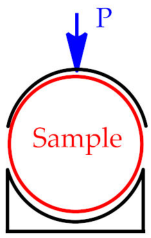
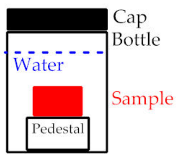
The Tunnicliff–Root test is comparable with modified Lottman indirect tension test. In both methods, the freeze cycle is optional. However, curing of the loose mixture in a 60 °C oven for 16 h is eliminated in the Tunnicliff-Root test procedure [23,49].

Therefore, most methods on compacted cylindrical mixtures differ mainly from each other in (Table 3):

- Size samples;
- Preparation the dry and wet samples;
- Determination of the different performance indicators for dry and wet samples (indirect tensile strength;

- Compressive strength;
- Marshall stability and other.

**Table 3.** Conditions the main most common methods on Compacted Cylindrical Mixtures.

| **Parameter** | **Test** | | | | | |
|---|---|---|---|---|---|---|
| | **Indirect Tensile Strength** | **Modified Lottman Indirect Tension** | **Compression Strength** | **Immersion-Compression** | **Marshall Immersion** | **Texas Freeze-Thaw Pedestal** |
| **Sample Size** | | | | | | |
| **Diameter** | 80, 100, 120, 150 and 160 mm | 63.5 and 150 mm | 80, 100, 120, 150 and 160 mm | 101.6 mm | 100 mm (cylinder height 75 mm) | 41.3 mm (cylinder height 19.5 mm) |
| **Preparation of dry samples** | | | | | | |
| | 20 °C (air) | 25 °C, 2 h (in plastic film, water) | 18 °C (air) | 25 °C, 4 h (air) | 25 °C, 4 h (air) | - |
| **Preparation of wet samples** | | | | | | |
| **Water saturation** | (1) 30 min(vacuum) | (1) 10 min (water, vacuum) | (1) 60 min (vacuum) | (1) 60 °C, 24 h or 49 °C, 4 days (water) | (1) 60 °C, 24 h (water) | (1) 3 days (air) |
| | (2) 40 °C, 68–72 h (water) | (2) 18 °C, 16 h (in plastic film, freezer) | (2) 120 min (water, vacuum) | - | - | (2) freeze-thaw cycles bottle (−12 °C, 24 h (freezer); 49 °C, 9 h (water)) |
| | - | (3) 60 °C, 24 h (in plastic film, water) | (3) 18 °C, 7 days (water) | - | - | - |
| **Testing** | | | | | | |
| **Cooling** | 2–4 h (water) | 2 h (in plastic film, water) | - | 2 h (water) | 2 h (water) | - |
| **Temperature** | 25 °C | 25 °C | 18 °C | 25 °C | 25 °C | - |
| **Method** | Indirect tensile strength (ITS; kPa) | Indirect tensile strength (ITS, kPa) | Compressive strength (CS; kPa) | Compressive strength (CS; kPa) | Marshall stability (MS; kN) | After each freeze-thaw cycle, the briquette surface is checked for cracks |
| |  |  |  |  |  |  |
| **Result** | | | | | | |
| **Index** | indirect tensile strength ratio (ITSR) | tensile strength ration (TSR) | index of retained strength (IRS) | retained compression strength (RCS) | retaining strength index (RSI) | the number of cycles required to induce cracking is a measure of water susceptibility (typically 10 freeze-thaw cycles) |
| **Calculation** | $\frac{ITSwet}{ITSdry} \times 100$ (%) | $\frac{ITSwet}{ITSdry} \times 100$ (%) | $\frac{CSwet}{CSdry} \times 100$ (%) | $\frac{CSwet}{CSdry} \times 100$ (%) | $\frac{MSwet}{MSdry} \times 100$ (%) | - |

One of the relatively recent methods for assessing the asphalt concrete samples on long-term adhesive strength without water use is developed in the UK at the end of the last century Saturation Aging Tensile Stiffness (SATS) test [77]. This method allows to estimate the complex influence of moisture and aging binder on the strength of asphalt concrete samples. The test is performed on five asphalt concrete samples with diameter 100 mm and height 60 mm, which are kept in the test chamber at pressure 2.1 MPa and temperature 85 °C for 65 h and then another 24 h with a gradual decrease in pressure to atmospheric and temperature to 30 °C. After keeping samples, their modulus stiffness is determined and the durability indexes are calculated by the modulus ratio of initial and sustained samples. The SATS method is standardized in the countries of the European Union [78].

In addition to the cylindrical samples the tests are performed on prismatic samples of asphalt mixture, as well as rods drilled out from aggregate rock and stuck together with bitumen film (Direct tensile strength ratio—DTSR). The unit axial direct tensile strength test was introduced for investigating adhesion strength properties in this study. Again, strength is determined before and after conditioning the test sample in a water bath according to [16,65].

The Hamburg Wheel-Tracking Device (HWTD) measures combined effects of rutting and moisture damage and is gaining popularity because of fast and reliable testing of various hot mix asphalt (HMA) mixes [23,78–82]. Two HMA beam samples, each measuring 260 mm wide, 320 mm long and 40 mm thick. It measures the effects of rutting and moisture damage using a steel wheel that runs over compacted beams immersed in hot water (usually 50 °C). HMA sample is loaded for 20,000 passes or until a final strain of 20 mm appears (Figure 8).

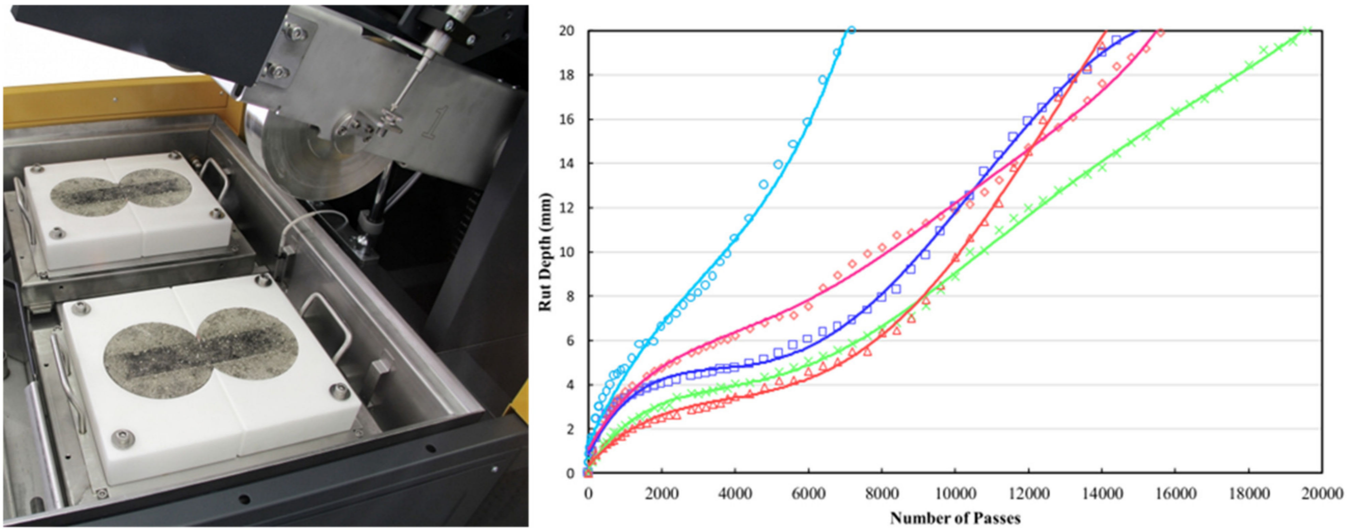



**Figure 8.** HWTD rutting curves of asphalt mixtures. Reprinted with permission from [79] Copyright Elsevier 2019.

### 3.3. *Definition of Adhesion as a Fundamental Value*

The main problem of the previously presented tests is the dependence on visual observation to detect stripping, low reproducibility and results accuracy. This group of tests allows to get rid of these shortcomings.

As already mentioned, the aggregate high wetting is essential for good adhesion. Therefore, the measurement of its derivatives—contact angle and surface free energy is important for the adhesion characterization in the bitumen/aggregate system. Many methods are based on the determination of these indicator.

For the analysis of bitumen, the contact angle measurement can be used in different ways. Three different approaches were covered in this study [16]: bitumen drop on glass, Pendant drop and water drop on bitumen surface. Contact angle measurements were conducted on a DSA100 (KRÜSS Ltd., Hamburg, Germany), a goniometric setup including an automated sample dosing device. The sample is illuminated by a strong light source and filmed and recorded with a high-resolution camera with manual zoom and focus.

It is known that the adhesion of bitumen to aggregate can also be determined based on the calculation of SFE [83–85] and its polar and dispersive components [83,86], by measuring the contact angle of liquids with different hydrophilicity on bitumen binder films under ambient conditions. Having determined the contact angle of the liquid (water, ethylene glycol, and others) to the bitumen (in the solid state), you can calculate the SFE of bitumen. To calculate SFE of bitumen, using the dispersion force component and polarity component (hydrogen bonding and dipole-dipole interactions) into the equation (using a modified Young-Good-Girifalco-Fowkes equation), which was adopted by Owens and Wendt [87,88]:

$$1 + cos(\Theta) = 2 \cdot \sqrt{\gamma_S^d} \cdot \left( \frac{\sqrt{\gamma_L^d}}{\gamma_{LV}} \right) + 2 \cdot \sqrt{\gamma_S^h} \cdot \left( \frac{\sqrt{\gamma_L^h}}{\gamma_{LV}} \right) \quad (5)$$

where $\theta$ is the contact angle between the interface (Figure 9); $\gamma_S^d$ and $\gamma_L^d$ is SFE of dispersion force component for solid and liquid, respectively; $\gamma_{LV}$ is SFE for liquid-vapor; $\gamma_S^h$ and $\gamma_L^h$ denotes the component of SFE due to hydrogen bonding and dipole-dipole interactions (polarity component) for solid and liquid, respectively.

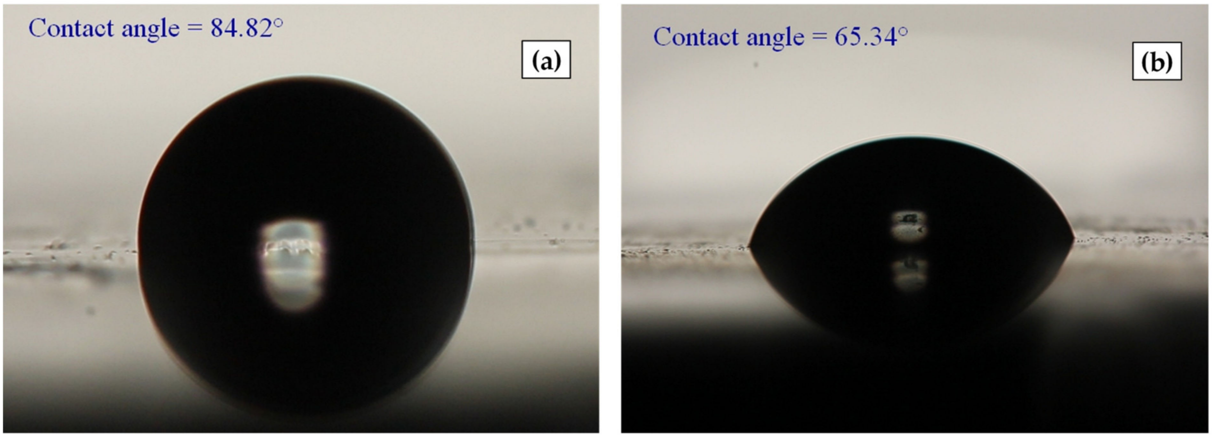



**Figure 9.** Photos of sessile drops (5 µL) in contact with a solid surface: (**a**) water drop on the bitumen; (**b**) ethylene glycol on the bitumen 70/100.

The samples were illuminated by a strong light source and recorded with digital camera Canon EOS 1100D equipped with macro lens (Canon Inc., Tokyo, Japan). Drop images were analyzed for CA measurement by open-access software ImageJ with plugins such as Low Bond Axisymmetric Drop Shape Analysis (LB-ADSA) technique [89] and Half-Angle technique [90].

Equation (5) is written in a condensed form relative to the known components and terms containing the values of the components (dispersive and polar) for the free energy of the solid surface for both test liquids (i = 1; 2, where water is index 1 and ethylene glycol is index 2):

$$0.5 \cdot \gamma_{LV-i} \cdot (1 + cos(\Theta_i)) = \sqrt{\gamma_S^d} \cdot \sqrt{\gamma_{LV-i}^d} + \sqrt{\gamma_S^h} \cdot \sqrt{\gamma_{LV-i}^h} \quad (6)$$

To form a system of two equations with two unknowns, the corresponding designations *X*, *A*, *B*, *C* were entered (the contributions from the dispersive and polar parts to the free energy of the solid surface):

$$X_1 = \sqrt{\gamma_S^d};\ X_2 = \sqrt{\gamma_S^h};\ A_i = \sqrt{\gamma_{LV-i}^d};\ B_i = \sqrt{\gamma_{LV-i}^h};\ C_i = 0.5 \cdot \gamma_{LV-i} \cdot (1 + cos(\Theta_i))$$

The values of the components (dispersive and polar) for the surface tension of both test liquids were taken from the work [84] and are represented in Table 4.

**Table 4.** Values of the components (dispersive and polar) for the surface tension of both test liquids.

| Liquid | $\gamma_{LV-i}^d$ (mJ/m$^2$) | $\gamma_{LV-i}^h$ (mJ/m$^2$) | $\gamma_{LV-i}^{total}$ (mJ/m$^2$) |
|---|---|---|---|
| Water | 21.80 | 51.00 | 72.80 |
| Ethylene glycol | 29.00 | 19.00 | 48.00 |

Solutions of the system of equations:

$$X_1 = \frac{B_1 \cdot C_2 - B_2 \cdot C_1}{A_2 \cdot B_1 - A_1 \cdot B_2};\ X_2 = \frac{C_1 - A_1 \cdot X_1}{B_1}$$

The SFE calculation is summarized in Table 5.

**Table 5.** Contact angles and SFE of bitumen 70/100.

| Contact Angle (°) | | Surface Energy Components (mJ/m$^2$) | | Total Surface Energy (mJ/m$^2$) |
|---|---|---|---|---|
| Water | Ethylene glycol | $\gamma_S^d$ | $\gamma_S^h$ | $\gamma_S^{total}$ |
| 84.82 | 65.34 | 14.90 | 9.21 | 24.11 |

Note: $\gamma$—surface energy (i.e., surface tension); subscript indices $s$ pertains surface energy of solids; superscript indices $d$ mean dispersion force component of SFE for solid; $h$ mean polarity component (hydrogen bonding and dipole-dipole interactions) of SFE for solid.

The determination of contact angle and SFE for bitumen characterizes their adhesive properties, the lower the value of contact angle and SFE, the higher the adhesion and properties of bitumen.

Labib at al. [91] report use of electrophoreses to investigate the proton transfer surface properties of both aggregate and bitumen in the presence water. Previous studies in the field have shown consistency with the results obtained in this study, proving that the zeta potential test can be a viable and accurate method for predicting aggregate-bitumen adhesion. The zeta potential test has the potential to act as an alternative to conventional adhesion tests with substantially shorter turnaround times [92].

The surface reaction test allows a researcher to quantify the level of stripping on loose asphalt mixtures [58]. The reactivity of calcareous or siliceous aggregates and the reaction to the presence of highly toxic and corrosive acids is assessed by the surface reaction test. The gas released during the chemical reaction creates a pressure proportional to the aggregate surface area. The basis of this test is the assumption that different levels (intensity) of stripping lead to exposed aggregate surface parts [49,58].

These group tests includes Net Adsorption Test [13,23] and Modified Net Adsorption Test [23,93]. These methods are based on physic-chemical adsorption of bitumen from solution (in toluene) by the mineral aggregate surface. Adhesion is estimated by the amount of adsorbed bitumen from the solution. These methods are not widely used because they are quite difficult to implement.

Blister test (interfacial fracture energy (IFE)) allows to determine the binder film elasticity modulus and the interfacial fracture energy, which corresponds to the adhesive strength. The principle of the test is to break the interface bonding by pressurizing the interface between the adhesive and adherent. The amount of pressure and the deformation of the adhesive before and during the debonding period are used to calculate the IFE [22].

Wilhelmy plate method [21] is to determine the thin plate weight and the depth at which it will sink into the liquid. At touching a thin plate (a plate is usually made from glass, filter paper, foil or platinum), suspended on a thin metal wire or spring, on the liquid surface there is retraction of this plate into the liquid. At the same time, retraction is accompanied by spring elongation and weight gain. The retraction is due to the surface tension force acting on the thin plate perimeter, and the force of the plate retraction into the liquid is determined by the appropriate formula.

## 4. Conclusions and Recommendations

Due to the excellent adhesion in the bitumen/aggregate system, scientists and technologists can use these two different materials together. Therefore, laboratory determination of the adhesion value between different bitumen and stone materials used in road construction is very important.

First, a review of the various mechanisms of interaction in the bitumen/aggregate system was conducted. There are five main theories why the interaction between these materials occurs, but to some extent the theories contradict each other. None of the theories is absolutely correct, because according to the authors, excellent adhesion depends on a number of factors listed in different theories.

The literature review analysis shows the absence of a single generally accepted adhesion evaluation method in the bitumen/aggregate system, which would allow the evaluation of the adhesion characteristics relatively quickly with high accuracy and reproducibility. A significant number of existing methods that evaluate the adhesion of bitumen, stone materials mixtures with bitumen, and asphalt mixtures differ in test conditions, and the obtained results are not comparable. At the same time, the number of adhesion evaluation methods increases constantly and the issue of assessing and predicting changes in the bitumen affinity to stone materials is relevant.

The article shows that the adhesion tests in the bitumen/aggregate system, according to the authors, can be divided into three groups: determination of adhesion forces for bitumen with different materials; determination of bitumen resistance to stripping action of water with different materials; and definition of adhesion as a fundamental value (contact angle, surface free energy, zeta potential, interfacial fracture energy, adsorption capacity and others). The most common tests to determine bitumen resistance to water stripping with different materials in turn are divided into: those that are conducted on loose bitumen/aggregate mixtures and those that are conducted on compacted mixes. The first evaluate the bitumen and aggregate compatibility and stripping potential, the second try to take into account various properties (as an example, tensile strength) of asphalt concrete on the water action. Many researchers believe that the determination of adhesion on loose mixtures is uninformative and does not reflect the asphalt concrete real conditions in the coatings and prefers a group of tests methods for compacted mixtures.

Therefore, today, there are no single common adhesion test in the bitumen/aggregate system that are regional. Thus, it is important to develop a single procedure for interpreting data in this area and the possibility of comparing them with each other. According to the authors, the test should consist of two successive stages: the first should be fast, which will confirm bitumen and aggregate compatibility (for example, "adhesion to gravel" test); the second should be the Compacted Mixtures test (indirect tensile strength test, Modified Lottman indirect tension test, immersion-compression test and Hamburg wheel tracking test).

**Author Contributions:** Conceptualization, V.G. and M.B.; methodology, I.S. and Y.D.; software, N.V.; validation, M.B., V.G., Y.D. and K.P.; formal analysis, M.B. and M.K.; investigation, V.G., I.S. and Y.D.; resources, Y.D. and N.V.; data curation, V.G. and Y.D.; writing—original draft preparation, V.G. and Y.D.; writing—review and editing, M.B., M.K. and K.P.; visualization, V.G.; supervision, M.B.; project administration, M.B. and V.G.; funding acquisition, M.B and K.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Research Foundation of Ukraine, Kyiv (Grant No. 2020.02/0038) and statutory activity subsidy from the Ministry of Science and Higher Education Republic of Poland for the Faculty of Chemistry of Wrocław University of Science and Technology.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data supporting reported results are stored by V. Gunka.

**Acknowledgments:** The paper is a part of the research done within the project 2020.02/0038 (National Research Foundation of Ukraine). KP gratefully acknowledge statutory activity subsidy support (2022) from the Ministry of Science and Higher Education Republic of Poland for the Faculty of Chemistry (Department of Advanced Materials Technologies) of Wrocław University of Science and Technology.

**Conflicts of Interest:** The authors declare no conflict of interest.

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