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Review

Adhesion Promoters in Bituminous Road Materials: A Review

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Featured Application: The adhesion between aggregate and bitumen is crucial in asphalt pavements and has a strong influence on the service time of the road. Thus, the addition of adhesion promoters is gaining importance, particularly with regard to emerging and more sustainable technologies for asphalt production, which aim to reduce the working temperature, save energy, and guarantee the safety of specialized personnel. The present work offers an overview on physical and chemical properties of most common types of adhesion promoters currently used in asphalt industry and tries to build a bridge between scientific research and technological application.

Abstract: This review focuses on certain classes of organic compounds known variously in the specific literature of asphalt as adhesion promoters, antistripping agents, wetting agents, antistrips, or adhesion agents. These kinds of organic additives are currently formulated to enhance the bitumen coating of mineral aggregates and improve the workability of asphalt mixtures. In this review, the term "adhesion promoters" includes both synthetic organic compounds as well as those extracted from natural resources, mixed in trace amounts to bitumen. Their main role is to alter the interfacial energy, so that the presence of water, even in trace, does not weaken the bitumen-aggregate bond and tends to favor adhesion. The report also considers the chemical functionalities that play a predominant role in bonding, as well as the effects of surface modification of the aggregate due to the presence of adhesion promoters in pre-blended bituminous mixtures. Although bitumen is widely used in road pavement construction and the discussion is mainly addressed to the improvement of adhesion in road materials, adhesion and wetting properties can also represent a general issue in various bitumen-based industrial products.

Keywords: asphalt concrete; adhesion promoters; antistripping agents

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1. Introduction

Bitumen (asphalt cement) is the most common petroleum product used in road construction industry thanks to its high adhesive and waterproofing power. [1,2]. The term "asphalt mixture" is a combination of mineral aggregate, bitumen, and some other inorganic and organic additives [3]. Conventional Hot Mix Asphalt (HMA), which is currently produced at elevated temperatures requiring high energy input, consists of crushed mineral particles that are bonded together by bitumen at working temperatures between 150 to 190 °C. However, current environmental regulations require a greater reduction in emissions caused by the pollution generated by asphalt production for road pavements. To address these challenging problems, Warm-Mix Asphalt (WMA) technology—which allows a reduction of 20–40 °C in the temperature at which asphalt mixes are produced and placed compared to conventional HMA mixtures, without lowering the mechanical performance, thus offering a wide range of potential for use in road construction projects—was developed [4,5]. A powerful variant of WMA technology makes uses of organic additives, provided as formulations based on surfactants, polymers, and adhesion promoters, which are able to enhance coating, workability, and compacting. The suitable amount of additives can be calibrated on the temperature reduction set by the WMA design. Those additives are generally mixed with bitumen before adding the binder into the asphalt mixer.

One disadvantage of using the WMA technology compared to HMA is connected with lower mixing and compaction temperatures, which make the asphalt more susceptible to residual moisture [5–7]. Hence, the possible presence of water in the mix, owing to incomplete drying of the aggregates, is detrimental to the adhesive properties of the binder, thereby giving rise to a reduction in adhesion and cohesion [8].

There are several consequences caused by water damage including shoving, loss of chippings from surface dressings, potholes, cracking due to freeze-thaw damage, and bleeding [9–13]. As a whole, the main problem on a microscale level is an irreversible failure of adhesion between the binder and the aggregate.

Additionally, it is very important in the production of WMA to ensure an efficient road-way performance and durability. Indeed, the reduction of the manufacturing temperature, which could not guarantee a complete drying of rocks, may have serious consequences on adhesion quality between asphalt and aggregates. As a contribution to this task, the present review reports highlights of past and present research regarding the effectiveness and application of adhesion promoters (APs), with particular emphasis to their anti-stripping behavior.

2. The Structure of Bitumen and Its Interaction with Mineral Aggregates

Bitumen is a dark, oily, and viscous residue of the vacuum distillation of petroleum, which is widely used in road paving, roofing membranes, and other waterproofing materials. Bitumen is also known to be a colloid in which asphaltenes (n-pentane insoluble) [14] form complex micelles dispersed into an oil phase of saturated paraffins, aromatics, and resins [1,15,16] with weak chemical affinity for aggregate, whereas the aggregate is characterized by a strong affinity for water. The result is that bitumen can be easily replaced by water. Several studies showed that bitumen polar functionalities, such as polynuclear aromatics, phenolics, pyrrolics, pyridinics, 2-quinolones, sulfoxides, sulfides, ketones, anhydrides, and carboxylics have different adsorption powers on aggregate active sites (see [1] and references therein). Adhesion is promoted by bitumen polar components, which are able to lower the interfacial energy between bitumen and mineral aggregates. The adhesive strength depends on the relative capacity of the functional groups to adsorb at the aggregate surface and the relative desorption by water.

As a matter of fact, due to the complex and variable composition of the materials involved, a few investigations have been reported on the identification of suitable physico-chemical factors able to describe the wetting behavior of the bitumen-aggregate interface [17,18]. Very recently, Vassaux et al. identified bitumen viscosity and rock heterogeneities as two indicators to consider for a good wetting quality [19]. For example, asphaltenes are mostly subjected to oxidation reactions owing to their aromatic structure, and may form heavier and more complex molecules whose result is an increased stiffness and decreased flexibility of the binder. Therefore, any physico-chemical phenomenon that leads to an asphalt composition modification may determine a change in bitumen viscosity. These consequences may also weaken the aggregate/asphalt bond because the binder would not satisfactorily wet the mineral substrate, hence the bond strength could not be optimal. This last effect may also partially depend on the chemical composition of mineral aggregates.

In the simplest case stripping, a type of dewetting, the bitumen film is detached from the surface of the aggregate. However, it can also show itself as a retraction of the bitumen film from the stone caused by water mobility within the film or coming out of the stone itself (see Figure 1). In addition, regarding the WMA technology, if the moisture included in the aggregate does not completely evaporate during mixing due to the relatively low mix temperatures, residual water may still be on the aggregate surface, which in turn could lead to an increased susceptibility to moisture damage.

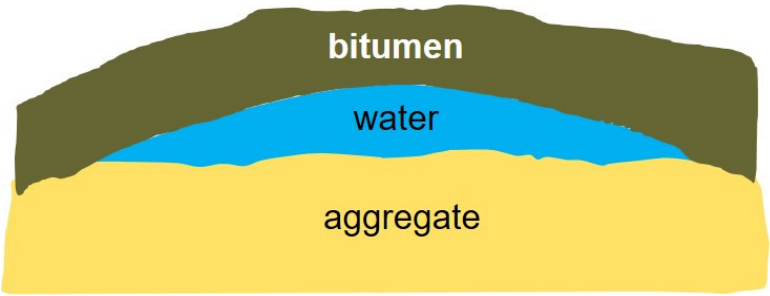

Figure 1. Adhesion failure at the aggregate-bitumen interface due to the penetration of water is termed "stripping".

The stripping phenomenon has been firmly attributed to the presence of residual water as a principal consequence of adhesion failure of bitumen onto aggregates [20–23]. It has also been ascertained that mineralogy (rock chemical composition), surface texture, absorption, surface ageing, surface coatings, and particle shape can affect the efficiency of an adhesive bond in an asphalt-aggregate mixture [24,25]. Aggregates are characterized by chemical heterogeneity resulting from several factors such as oxidation, coatings, adsorbed films, ledges, kinks, dislocations, and crystallographic anisotropy [26,27]. The charged aggregate surface attracts and orients bitumen polar molecules. Indeed, mineral rocks used for asphalt concrete can be of an acidic type, whose surfaces have a tendency to become negatively charged, or of a basic type, whose surfaces are prone to become positively charged. Acidic aggregates include those with high silica contents (quartz-based granites), while basic aggregates include mostly carbonates (calcite-based limestones). An irregular aggregate surface on the microscale level could hamper the spreading phenomenon. In most cases, a damp mineral surface will tend to repel an untreated binder, thereby thwarting its adhesive action. Since bitumen has much less affinity for the aggregate surface than water, the addition of APs confers to the binder the ability to remove water from aggregate surfaces, thus promoting active adhesion, which will be better defined in the next section.

3. Survey of Types of Adhesion Promoters Currently Used in the Asphalt Industry and Their Functions

The chemical affinity between bitumen and aggregate can be favored by the addition of trace amounts of organic additives, which modify the interface properties of both the aggregate surface and bitumen. These compounds are known as adhesion promoters. The goal is to maximize the chemical-physical interaction between bitumen and mineral surface. The topic regarding the of adhesion promoters designed for road paving industry is strictly connected to the WMA technology, which is characterized by working temperatures (110–140 °C) lower than the traditional hot mixing [5]. Under those conditions, it is likely that bitumen comes in contact with aggregates with residual moisture, which in the long term is considered to favor undesirable stripping phenomena, which was previously described in the Introduction. Therefore, there is a technological need for the addition of organic compounds to bitumen to increase its coating efficiency onto the stones and promote a better bitumen adhesion. A successful adhesion promoter will be able to impair the intermolecular interactions between residual water and polar aggregate surface and consequently lower the contact energy between the bituminous apolar liquid phase and the solid mineral phase.

In some technical reports, these organic additives are widely classified according to the following two categories, namely, Passive Adhesion Promoters (PAPs) and Active Adhesion Promoters (AAPs) [28]. The main difference refers to the ability of the former, also called anti-strip additives (ASAs), to maintain a strong adhesive bond between binder and dry aggregate surface and to prevent stripping under wet condition once bond formation is achieved, while the latter promote bonding between bitumen and aggregate surface, even if there is residual water present on the surface of the aggregate.

Therefore, the last property is less restrictive than the passive adhesion because with AAPs even wet aggregate surface may be coated. The latter class of compounds are basically emulsifier surface active agents whose first application was reported in the literature in the sixties by Mathews [29]. They form oriented monolayers at the interface between the apolar bitumen and the aggregate polar surface and act by decreasing the surface tension of bitumen. While the head groups bind strongly to the aggregate surface, the hydrocarbon tails of the molecules are compatible with the binder. AAPs thus act as a bridge between the bitumen and the mineral surface and displace water at the interface (see Figure 2). In some of the patented formulations, the chemical additive contains a surfactant, which acts as lubricant and works at the microscopic interface between the polar mineral aggregate and hydrophobic bitumen [30].

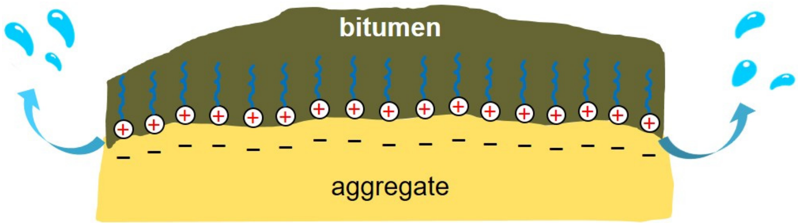

Figure 2. Active adhesion is ensured by the favorable orientation of positively charged surface-active molecules by decreasing the contact angle between bitumen and the negatively charged aggregate interface, allowing the water displacement, and maximizing the surface coating.

Amines, poly-amines, and amido-amine adhesion promoters (AMAPs) represent one of the most common classes of organic additives, which are basic compounds [31]. The supposed anti-stripping mechanism is supported by the nitrogen electron lone pair, which reacts with acidic silica surfaces, hence enhancing adhesion. Another explanation is linked to the capacity of Lewis bases to capture protons from acidic groups of bituminous polar components, leaving the acids negatively charged. The formation of quaternary ammonium ions ($R–NH_3^+$) provides an electrostatic favorable interaction with the aggregate surface, leading to adhesion enhancement. The optimum adhesion power is the result of a compromise between the length of the apolar hydrocarbon chain and the number of amine polar groups. The best performance can be reached with 14–18 carbon chains, linked to one or even two amine groups, with at least one primary amine group. Recently, a type of AMAP has appeared on the market with the tradename Rediset® WMX from Akzo Nobel, Amsterdam, the Netherlands [32]. This material, formulated in combination with a non-foaming non-ionic additive, contains a fatty polyamine structure with a long chain aliphatic hydrocarbon, which is able to promote both active and passive adhesion [33]. It is a combination of surfactants and organic additives in which the surfactants improve the wetting of the aggregate surfaces with binder by active adhesion, and the other components reduce the binder viscosity [34]. Cecabase® from Ceca Arkema Group, La Garenne-Colombes, France, is another powerful chemical additive, which has been found to improve coating of the aggregate particles, workability, and compaction [30]. It is formulated as a combination of emulsification agents, surfactants, polymers, and AP additives [35]. Several investigators reported that addition of Cecabase® to bitumen has no noticeable effects on the rheological properties of asphalt binder but improves workability at low mixing temperature, which is a desirable condition for WMA design [36].

Other compounds such as naphthenates, metal salts of organic acids obtained from the alkali washes of petroleum fractions, have also been demonstrated to play the role of adhesion promoters [37]. It has been presumed that iron naphthenate operates as an ASA by migrating to the aggregate-asphalt interface (while the asphalt is still hot) and forming a water-resistant complex [38].

Another group of APs is represented by organosilanes-based adhesion promoters (OSAPs) $R_1Si(OR)_3$ possessing a hydrocarbon chain with affinity for bitumen and a polar silane end group with affinity for inorganic surface [39,40]. Oliviero Rossi et al. [40] have recently shown that the addition of OSAPs can improve the bitumen wettability towards mineral stones at concentrations as low as 0.01 wt. % (Figure 3).

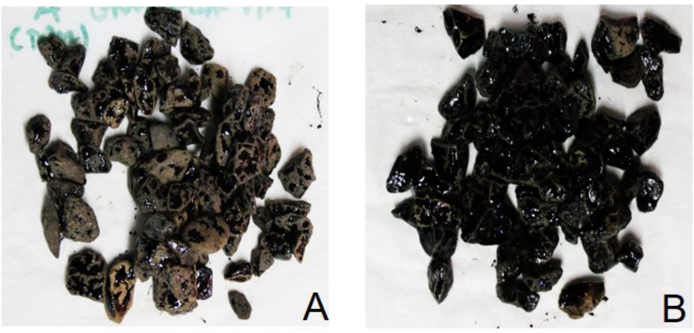

Figure 3. Surface aggregate areas covered with (**A**) untreated bitumen and (**B**) pre-blended bitumen with organosilanes-based adhesion promoters (OSAPs) to a final concentration of 0.01 wt. %. Reproduced with permission from [40], Elsevier, 2016.

Moreover, the adhesive performance of the modified binder has been quantitatively determined by contact angle testing and found to be in excellent agreement with the conventional empirical boiling test [40]. The latter method, ASTM D3625, is a standardized procedure for evaluating the moisture sensitivity of an asphalt-aggregate mixture [41]. Briefly, a certain amount of aggregate sample covered with bitumen is immersed in boiling water for 10 min. Then, the mixture is allowed to cool while the stripped asphalt is skimmed away. The water is drained, and the wet mixture is placed on a paper towel and allowed to dry. Visual rating is conducted to assess the level of stripping. The contact angle approach through the goniometer and the Wilhelmy plate methods is another powerful technique that is able to evaluate the effects of surfactant-based additive on the surface free energy of a modified binder. The technique is reviewed elsewhere, for example, in [35]. Polymer materials have also been found to be efficient as anti-stripping additives. Bagampadde et al. [42] showed that Styrene Butadiene Styrene (SBS) copolymer significantly enhanced moisture resistance of slag aggregates in harsh desert environments. Moreover, bitumen modified with SBS in conjunction with polyphosphoric acid (PPA) positively affected wettability performance and increased binder stability during long-time storage at elevated temperatures [43–46]. For example, PPA added to bitumen in a few wt. % is responsible for a stiffening effect due to several chemical mechanisms detailed in [44,47,48], which overall would promote an increase of the effective volume of asphaltenes, thus enhancing the rigidity of bitumen. The hardening effect played by PPA has also been compared to bitumen containing different commercial types of waxes [49].

An interesting comparison between AMAPs, OSAPs, and SBS has recently been reported by Taylor et al. [50] who have followed a fracture mechanics approach to quantify the adhesion between the modified bitumens and the aggregates in selected asphalt mixtures. The best result was achieved for modification with OSAPs, confirming that the addition of organosilane-based AP is a useful method to bridge the interface between the organic bitumen and the inorganic mineral aggregate, especially for the silica-rich granites. A class of compounds that contain both basic (ammine) and acid (phosphate) polar residues can be represented by natural phospholipids such as, for example, phosphatidyl choline, phosphatidyl inositol, phosphatidyl ethanolamine, and phosphatidic acid [51].

They can be efficiently dissolved in hydrocarbons due to their significant lipophilic properties [52,53]. Motivated by the increasing need to seek environmental friendly low cost and non-toxic additives, a systematic investigation on the potential effects played by commercial Food Grade Phospholipids (FGPs) as APs for bitumen have recently been undertaken [54]. In particular, hot bitumen pre-blended with small amounts of FGPs added as a commercial liquid mixture has been made suitable to improve the percentage of bitumen coating retained after boiling and consequently decrease the contact angle between binder and tested stone. Similar results have been obtained for bitumens modified with slightly higher amounts of FGPs added as solid powdered form.

4. Effects of Adhesion Promoters on the Mechanical Performances of Modified Bitumen

Bitumen is a viscoelastic liquid that exhibits Newtonian flow behavior at high temperatures (typically above 60 °C), viscoelastic behavior at intermediate temperatures (typically between -20 and 60 °C), and glassy, brittle behavior at low temperatures (typically below -20 °C). Specifically, according to Lesueur et al. [55,56], two regimes can be identified for the temperature dependence of bitumen rheology, namely, a Newtonian-viscoelastic flow transition occurring above room temperature attributed to the solid phase (asphaltene) and a viscoelastic-elastic glass transition showing up in the low temperature regime due to the vitrification of liquid phase (maltene). The addition of organic compounds able to stabilize/destabilize the dynamics of the complex bituminous colloidal microstructure would give rise to either a hardening or softening effect on the correspondent modified bitumen. For practical cases where it is desirable or required that the addition of APs does not significantly alter the mechanical properties of bitumen [36], OSAP has been made useful for fulfilling this requirement. Indeed, the transition temperature from a viscoelastic to a viscous regime was found to be independent of the addition of organosilane surfactant, which was able to act as a strong and efficient AP [39,40]. An organic compound endowed with a dual-property, viz. adhesion promoter and rheological modifier, would be appealing in most of the applications of the bitumen industry. To the best of our knowledge, FGPs added at a few percentages to bitumen represent, at the moment, the unique class of organic additives that fulfill the double requirement. As it has recently been documented in [54], the Newtonian-viscoelastic flow transition determined by time cure rheological tests can be shifted to temperatures higher than 64 °C, correspondent to virgin bitumen, upon addition of FGPs provided either as solid powder or as liquid dispersion. In the former case, a maximum increment of $\Delta t_{\max}$ = 17 °C has been detected for the softening temperature measured for the correspondent modified bitumen, while, in the latter, an even higher $\Delta t_{\max}$ = 25 °C has been obtained in the presence of 6 wt. % of additives (see Figure 4).

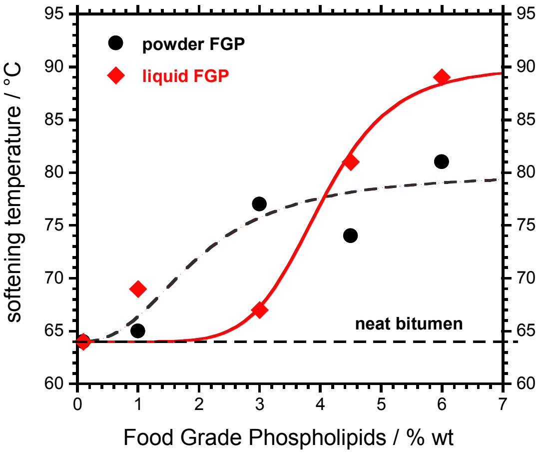

Figure 4. Softening temperature as a function of Food Grade Phospholipid (FGP) content in hot bitumen. FGP added as solid powder (circles) or as liquid dispersion (rhombus). Reproduced with permission from [54], Elsevier, 2017.

Those differences have been ascribed to the different miscibility properties manifested by both liquid and solid forms of food grade additives, once mixed to the binder.

5. Conclusions and Suggested Future Research

In the industry of road construction, the current challenge is to develop more ecological products while maintaining asphalt mixture performance and durability. In this context, the use of more sustainable technologies for asphalt production aims to reduce the working temperature, save energy, and guarantee the safety of specialized personnel. To overcome the loss of adhesion quality between bitumen and aggregate caused by the demanding reduction of the manufacturing temperature it is therefore crucial to seek and test new organic additives that are able to improve the adhesive properties of bitumen at working conditions of warm mix asphalt technology. One of the ways in which the adhesion between bitumen and mineral stones can be improved is by the use of adhesion promoters (APs). Therefore, to meet the demanding need for an environmentally friendly and economically attractive asphalt paving material, novel APs will be increasingly used in the near future. The effect of using more and more powerful APs will yield economic benefits with important environmental impacts such as reducing production and paving temperatures, decreased fuel or energy consumption (with consequential decreased costs), reduced emissions and odors from plants, reduced smoke and, thus, consternation from the public, and improved working conditions at the paving site. The market offers a large number of different chemical varieties of adhesion promoters. The range of organic compounds available includes fatty amines, poly-amines and amido-amine derivatives, organosilanes, food grade emulsifiers, and modified polymers, which can be tailor-made for a specific application. However, since only phenomenological models that are capable of capturing a rough physico-chemical picture of the complex colloidal dispersion underlying the bitumen microstructure are currently available in the established literature, it is evident that a complete prevision of mechanism of action provided by APs is far from being achieved.

Although this review identifies some of the more important physical and chemical properties of APs that play a critical role on the bond between bitumen and aggregate, it also draws attention to the numerous variables and parameters that influence bonding and the paucity of research data concerning their effect on bonding. Indeed, many points remain unclear and should trigger further research addressed to identify the principal intermolecular interactions brought by APs, interpreted in the framework of colloidal model of bitumen. In this context, it would be worth testing the adhesion properties of selected classes of APs added to a model bitumen, namely, a colloidal mixture of known composition in asphaltene and maltene representative of the most common bituminous materials. It would be equally critical to optimize the physico-chemical parameters governing the stability of polar interactions between APs and aggregate surfaces in order to maximize the bitumen wettability. Therefore, in the absence of predictive models, selected adhesion promoters must be chosen experimentally to ensure good quality bond to the aggregate particle–binder interface and tested against several external control parameters such as, for example, salinity and temperature excursion.

Last, but not least, although tests and techniques which quantify these physical and chemical properties exist, they are often complicated and/or necessitate expensive equipment. Development of reproducible tests such as, for example, the measurement of contact angle, to predict the aggregate performance (in regard to water susceptibility) could provide for challenging future research work.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

APs	adhesion promoters
ASAs	anti-strip additives
AAPs	active adhesion promoters
AMAPs	amine-based adhesion promoters
FGPs	food grade phospholipids
HMA	hot-mix asphalt
OSAPs	organosilane-based adhesion promoters
PAPs	passive adhesion promoters
PPA	polyphosphoric acid
SBS	styrene butadiene styrene
WMA	warm-mix asphalt

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