Developing test methods for the determination of the performance and damage to asphalt of bio-sourced asphalt release agents (ARAs) and bitumen removers (BRs)

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RÉSUMÉ. L'objectif de cette étude est le développement de méthodes d'essais pour caractériser la performance des anti-adhérents (AA) pour asphalte, et leur innocuité vis-à-vis de l'asphalte sur chantier. L'essai de performance développé, appelé « asphalt slide test », fournit deux indicateurs : la masse résiduelle de bitume sur support acier et le temps de glissance. Cet essai a montré la capacité d'AA bio-sourcés à réduire l'adhésion entre l'asphalte et la surface de l'acier (représentative d'outils ou de lit de camions…). L'essai d'innocuité mis en œuvre consiste à mesurer l'endommagement de l'asphalte par l'AA, par des essais CBR et de fendage de l'asphalte et de dégradation du bitume par immersion. Pour l'innocuité, les essais de traction par fendage sur asphalte ont donné des résultats plus cohérents que les essais CBR.

ABSTRACT. The objective of this study is to develop testing methods of asphalt release agent (ARA) performance and the degree to which they may damage the asphalt. The testing of ARA performance demonstrated their ability to reduce the adhesion between the asphalt and the surface of steel (asphalt tools, truck beds…) by the asphalt slide test, which provided two indicators for quantifying performance. The testing of the their damage to asphalt consisted of the measurement of the degree to which the compacted asphalt is damaged by the ARA including CBR resistance, indirect-tensile strength and bitumen degradation testing, the latter also serving as a test to find the most effective bitumen remover (BR). For asphalt degradation, the indirect tensile strength test provided more consistent results than CBR resistance.

MOTS-CLÉS : anti-adhérent, débituminant, essais sur asphalte, agent bio-sourcé, construction des routes.

KEY WORDS: asphalt release agents (ARA), bitumen removers, asphalt mix testing, bio-sourced agent, road construction.

1. Introduction

The most important component of an asphalt mixture is bitumen, which through adhesion keeps the aggregates together and the asphalt mix cohesive. These same adhesion properties can make it very difficult to clean surface of equipment that has been used to work or transport asphalt mixtures intended for road construction. In the case of the truck beds used for transporting the asphalt mix for example, the adhesion prevents the mixture from smoothly sliding out of the bed as the truck attempts to discharge its load [CRU 08, SCA 07]. In such cases, workers must spend time and effort to manually coax the residual mixture out of the truck bed, while exposing themselves to volatile organic compounds (VOCs) from the mixture [TAN 08]. This issue is even more significant for polymer modified mixtures (PMA), which tend to be more adherent than conventional asphalt mix [LAV 03].

Asphalt release agents (ARAs) are used for spraying surfaces that come into contact with the mixture during the road construction process, such as truck beds, pavers, finishers, tools and various other (usually metal but sometimes plastic) items. The reduction in bitumen adherence is based on the interaction of the bitumen, the ARA and the surface the ARA is applied to [BYM 09, TAN 06]. As opposed to bitumen removers (BRs), asphalt release agents are not intended to break down the bitumen, but rather to protect the equipment used to produce and place the mixture from bitumen residue. Therefore, it is important that asphalt release agents do not cause significant damage to the asphalt pavement when coming into contact with it. BRs on the other hand, are used to clean materials that come into contact with asphalt mix and function best by dissolving the bitumen as efficiently as possible [MIK 14].

Tang [TAN 05, TAN 06, TAN 08] has classified ARAs into three categories according to their chemical composition: petroleum based [SCA 07], fatty-oil based [ART 12, BAL 93, BYM 09, CHE 01, DAV 05, DIT 02, KIN 00, KOD 97, KUL 00, LOC 99, OLS 99, ZAN 03] and non-oil based formulations [DeL 94, ESC 11b, MAR 00, MAH 03, MAR 78, SAL 99, ZAK 13].

Petroleum-based ARAs and BRs, such as diesel fuel, have been used for years as they are inexpensive, available on most construction sites and adhere to most surfaces due to their low viscosity. They function by softening the bitumen on the surface, that is, reducing its viscosity, cohesiveness, and thereby the adherence to the surface [DeL 96, SCA 07]. Petroleum products such as diesel fuel however, are skin irritants and emit volatile compounds harmful to human health, while also causing environmental problems in the area around the construction site by leaching into the soil and groundwater [TAN 08]. Petroleum based ARAs are flammable, and when they come into contact with the new asphalt pavement in high concentrations on the asphalt truck bed or by an accidental spill, may cause damage to the bitumen leading to soft spots that reduce the structural integrity of the roadway [BAL 93, TAN 05, TAN 06]. The deterioration effect is exacerbated with increasing heat, light and time of contact with the bitumen [ACT 13, KOD 97, MAR 78].

Due to their high volatility, there is also the issue of them evaporating during particularly long voyages, leading to a loss in functionality [MAH 03]. For this reason, the U.S. Department of Transportation as well as many state departments have restricted the use of diesel fuel as an asphalt release agent as part of the Oil Pollution Act of 1980, defining ARAs as "biodegradable while not posing a health risk to workers or an impact on the environment" [ACT 13, ZAK 13]. This has necessitated the development of alternative biodegradable ARAs and BRs.

Alternative ARAs include bio-sourced fatty-oil based agents. They can be composed of lecithin dispersed in an ether [KOD 97, OLS 99], tall oil [KUL 00] fatty acids diluted in water [KIN 00], glycerol [ART 12, DIT 02, LOC 99, ZAN 03], soybean, cottonseed, canola, peanut, sunflower and palm oils, [BAL 93, DAV 05]. Other biodegradable agents can be organic, inorganic or a mixture of both. These agents can be composed of water based mixtures with polycycloaliphatic amines, polyalkalene glycols [SAL 99], polysiloxane in emulsion [MAR 00, MAH 03, ZAK 13], water-based solutions of magnesium or calcium chloride [DeL 94] and organic esters [ESC 11b] among others.

All of the above agents are claimed to be biodegradable and to work as a surfactant by reducing the interfacial tension between bitumen and the contact surface as well as the friction, forming a separating layer or substrate that does not damage the asphalt mix. However, this has been shown to not always be the case. There has also been damage to asphalt mix observed from the use of certain bio-sourced ARAs such as ester (C18) based formulations. [ESC 11A] mixed diesel fuel and a vegetable-based ARA with bitumen and compared their changes in penetration (ASTM D5-EN 1426) and softening point (ASTM D36-EN 1427). It was found that the penetration is significantly higher with the diesel mix while the softening point was lower. These were strong indications of the diesel and the vegetable-based agent deteriorating the bitumen in a similar manner.

Alternative biodegradable ARAs and BRs have often been found to be less effective than diesel [BYM 09, MAH 03, TAN 08], although this has begun to change in recent years [SCA 07]. The agents may have less power to damage the bitumen than petroleum-based ARAs, but will stay in contact with the asphalt mix for a longer time due to their higher evaporation temperatures [ESC 11b, ZAK 13]. Additionally, bio-sourced chemicals can also possess an unpleasant odor, attracting insects such as flies and therefore presenting a nuisance and even health hazard to the surrounding area [LOC 99].

The American Association of State Highway and Transportation Officials (AASHTO) National Transportation Product Evaluation Program (NTPEP) for asphalt release agents [NTP 14] has two tests for evaluating ARA performance and one for damage to the asphalt. However, their results are pass/fail and the tests are subjective in their implementation. There are many US departments of transportation that have similar rating systems. There are no known tests or testing programs for BRs.

Asphalt release agents are widely used to protect tools and truck beds from the residue of bitumen; however, the study of their performance or of the damage that they can cause to the asphalt mix has been minimal due to the fact that ARA manufacturers – in the cases where they have testing for their products before filing patents or putting the products on the market – do not publish the results of these studies [TAN 08]. Studies or patents on BRs appear to not exist, most likely due to the fact that BRs function simply as bitumen solvents and thus, need to meet fewer performance criteria than ARAs. The only information available on most ARAs and BRs are generally material safety data sheets (MSDS), which do not present the full compositions of the products.

The only peer reviewed articles [TAN 05, TAN 06] on ARAs test them only for the chemicals that can be harmful to worker health (VOCs), which although very important but not a main objective of this study. Some preliminary work has been done on ARAs by [ESC 11A, NIV 11, RAN 10], although with little in the way of tangible results.

The purpose of this paper is to present the testing methods of ARA and BR performance and the degree to which ARAs may damage the asphalt mix. The objectives of the test development are to provide testing that (i) reflects as much as possible the on-site conditions, (ii) can differentiate between various ARAs, (iii) can provide new insight into the interaction of ARAs, BRs and asphalt mix and (iv) that are relatively simple and cost effective to implement. The testing of ARA performance was done by the asphalt slide test. The testing of the damage to asphalt by the ARAs consisted of CBR resistance, indirect-tensile strength and bitumen degradation testing. The bitumen degradation test is also intended as a means of determining the most effective BR. The products tested included diesel fuel, 3 bio-sourced ARAs and 3 bio-sourced BRs. The validity and limits of the test developed are also discussed.

2. Materials and methods

2.1. Materials

2.1.1. Bitumen

The bitumen used for testing and in the asphalt mix was Total 35/50 as classified by NF EN 12591, indicating a penetration (NF EN 1426) value of between 3.5 and 5.0 mm.

2.1.2. Asphalt mix

The asphalt mixes (BBSG 0-10 classe 3 by NF EN 13108-1) were manufactured in accordance with NF EN 12697-35+A1 with Total 35/50 bitumen and limestone/silica aggregates. The aggregates consisted of coarse aggregates, fine aggregates and limestone filler that were graded in accordance with NF EN 13108-2.

2.1.3. Commercial Asphalt Release Agents

The asphalt release agents tested consisted of 3 bio-based ARAs available on the French market. Additionally, diesel fuel, a petroleum product historically used as an ARA and BR in the past was also tested. Although this product is no longer permitted for use as an ARA or BR on construction sites, it was nevertheless tested as a reference. Additionally, 3 vegetal-based BRs were used as products that are known to cause damage to asphalt mix in order to test ARA damage to asphalt. Technical information for these products is shown in Table 1. The density of the bio-based products was around 0.89kg/L, slightly higher than the density for diesel. The viscosity at 40°C is 5-14mm^2/s for the bio-based products while being much lower at 3 mm^2/s for diesel. It is possible for lower viscosity product to penetrate into the mixture further, possibly resulting in a higher degree of damage. The evaporation point of the bio-based ARAs is much higher than for the diesel, on one hand being less volatile and nauseating, but on the other hand, staying in contact with the asphalt for a longer time, possibly causing more damage.

Table 1. *Technical and physical information for commercially available ARAs and BRs.*

Product	Origin	Density @ 20˚C (kg/L)	Evaporation point (˚C)	Kinematic viscosity @ 40˚C (mm^2/s)
Diesel fuel	Petroleum	0.82-0.86	60	3
ARA 1	Bio-based	0.88	250	11
ARA 2		0.89 (@25°C)	250	14
ARA 3		0.86-0.90	350	12.5
BR 1		0.88	170	10-11
BR 2		0.895 (@25°C)	250	10.5
BR 3		0.89 (@25°C)	250	5

2.2. ARA Performance

The objective of ARA performance testing is to measure the ability of the ARA to reduce the adherence of bitumen to tools and machinery for road construction (generally metal surfaces). The challenge in this testing is to develop a qualitative analysis that best represents the conditions in the field and that is as cost and time effective as possible to implement.

2.2.1. ARA Performance Evaluation Apparatus

The ARA Performance Evaluation Apparatus (ARA-PEA) is a device developed by LR Vision of Castanet-Tolosan and LMDC of Toulouse for evaluating the performance of ARAs in reducing the adhesion between bitumen and construction materials as decribed in [MIK 14]. The device consists of an interchangeable plate (usually steel) that can be adjusted to an incline from 0-70°. The principle of the device is that when an ARA is applied to the plate, sliding asphalt mix or bitumen from the top of the plate can allow us to observe the performance of the ARA as the asphalt mix slides or bitumen flows down the incline. In order to facilitate this, a heating mechanism is installed beneath the plate that is capable of heating it to over 200°C.

2.2.2. Asphalt Slide Test

The mixture slide test is part of AASHTO program for asphalt release agents (NTPEP, 2014). The test developed in this study follows some of the same principles as the AASHTO one, while adding the ability to quantify ARA performance. The purpose of the test is the performance of an ARA on a scaled version of an asphalt truck bed using the ARA-PEA.

The test involves spraying an ARA over an area of 21x40cm on a steel plate resting horizontally. This is followed by placing 1000±10g of hot asphalt mix (150±10°C) on the surface of the plate, so that is spread out as evenly as possible. The plate is maintained horizontal and a sheet of wax paper is placed on top of the mixture to prevent sticking, followed by a wooden board (21x40cm, 883g). On top of the board, a load of 20 kg is placed creating a distributed pressure on the mixture of 2,5kPa. This simulates the transportation of the mixture where there is a pressure on the asphalt mix in contact with the truck bed from the mixture mass resting on top. The plate rests horizontally for a certain period of time (0.5-1h), after which it is placed on the ARA-PEA and immediately inclined at a certain angle (0-70°), simulating the discharge of the asphalt mix from the truck. It is also possible to heat the plate from below when it rests on the device. With the application of an ARA, the mixture falls off the plate, and from this action, the following data can be taken for judging the performance of the ARA:

-The mass of asphalt residue left on the plate (by a balance precise to 0,01g);

-The area of asphalt residue left on the plate (by image analysis);

-The time that it takes the mixture to slide down after the plate is inclined (through a chronometer precise to 1s).

2.3. ARA Effects on Asphalt Mix

2.3.1. Asphalt Mix Compaction

The type of compaction method significantly influences the mechanical properties of mixture, especially the granular skeleton [BAH 13]. Two types of asphalt mix compaction methods were considered in this study: by proctor and by compression.

The first method is similar to the French NF P 18-127 standard for compacting the mixture, as well as the method used in [NIV 11, RAN 10]. The mixture (1000±10g) was heated to 160±10°C and placed in a Ø100mm mould (NF EN 13297-30). The mixture was then proctor compacted by 2 series of 25 drops, cleaning the proctor head of bitumen and turning the mould 45° horizontally between the series. The mould was removed and placed to cool to less than 40°C so as to allow the compacted mixture to harden. The samples produced were short cylindrical samples (pills) Ø100mm with a height of 62±2mm, always higher on the outer perimeter (by about 3mm) than at the center of the specimen because of a non-uniform compaction (edge effect of the mould wall) of the sample.

The second method of compaction is by compression and is based on the compaction method from the French NF P 98 251-1, adapted for use with Ø100mm moulds (NF EN 13297-30). The mixture (1000±10g) was heated so that it was at 160±10°C before compaction and placed in the mould (pre-heated to 150±10°C). The mixture was compacted by a piston pressed (pre-heated to 150±10°C) on the mixture through a compressor and maintained for a certain period of time at a constant pressure. While the standard provides a pressure of 11.94MPa for 5min as the time the pressure was maintained on the sample, as it was found that these specifications were not necessary or practical for this test. A pressure of 2.5MPa for 3min was found to be adequate to attain a 4-8% voids content (6.9% as determined by NF EN 12697-6) and thereby, be in accordance with NF P 98-150-1 for this mixture. The samples produced were pills Ø100mm with a height of 62±2mm, with a plain surface on either side.

2.3.2. Measuring the Resistance to Loading of Asphalt Mix in Contact with ARAs

The degradation of the asphalt mix by the ARA from CBR or indirect tensile loading is taken as the reduction in resistance (RR%). The reduction of resistance represents the difference between the maximum resistance in tensile strength (S_{ARA}) of the samples treated with an ARA and the control (S_C) samples as described in Eq.[1].

$$RR\% = 100\% \text{ x } (S_C - S_{ARA})/ S_C \quad [1]$$

The ARA is applied to the center of the flat surface on top of the sample by a graduated burette. This is done either just before compaction or after compaction of the asphalt mix, representing in the field contact during production on pre-compacted mixture or accidental spills on compacted mixture, respectively. It was determined from preliminary testing that a dosage of above 5mL was too damaging to the samples for the purposes of our testing. Dosages of 5, 2 and 1±0.2mL were tested in order to determine the optimum. The samples were allowed to rest for 7 days before they were subject to testing in order for the ARA to have time to interact with the asphalt mix., due to the continued effects of the ARA from 0-7 days found by [RAN 10].

To test the degradation of the sample by the ARA, the samples were subjected to loading by California Bearing Ratio (CBR) piston as attempted in [NIV 11, RAN 10] at 1.27mm/min.

An alternative to CBR loading was investigated in resistance by indirect tensile strength (ITS), which places the cylindrical sample on its tangential side and proceeds to load it from the top uniaxially creating tension forces in the middle of the sample. ITS is preferred as direct tension is very time consuming to implement [HUB 95, PAR 03, SIL 03]. This method has been developed with cyclic loading at different temperatures to determine an indirect tensile stiffness modulus (ITSM) [DIB 13, CAR 03, CHE 08, GRA 01, NEV 05, NGU 13, PAR 13, PAR 03], although this may not be necessary for our purposes. Simple ITS testing has been investigated [ANA 72, DAV 11, KAT 13, TRA 09], which will be the kind used in this case. Standards for ITS on asphalt mix include NF EN 12697-34, AASHTO T322 and ASTM D 4867, the latter in which the samples are submerged in water to test the effects of moisture on the asphalt mix. The aforementioned testing has used a defined loading strip (contact area between testing apparatus and sample), and in [DAV 11], it was determined that maximum ratio of tension to compression strength is attained with a flat loading surface. The loading rate is set at 1.27mm/min. The tensile strength S_t [KAT 13] can be derived from the maximum rupture force P, the thickness of the sample t, and the diameter of the sample d, as shown in Eq.[2].

$$S_t = 2P/\pi dt \quad [2]$$

2.3.3. Bitumen Degradation Testing

A test for the degradation of asphalt mix by ARAs exists in (NTPEP, 2014), although it is rather subjective. A quantitative test was attempted on asphalt mix by [ESC 11A] but not really developed. The degradation of bitumen directly by the ARA is determined by the Bitumen Degradation Test (BDT). The samples were prepared by pouring 10±1g of hot bitumen, heated at 160±5°C for 2h, into circular silicon moulds. This produces “cone with flat top” shaped samples with the dimensions: Ø37±0.5mm top, Ø31±0.5mm bottom, h= 10±0.5mm. The samples are left to cool for 8±4h after which they are demoulded, and weighed to the nearest 0.01g. The samples are placed into 150mL graduated glass beakers of known mass, and the product is poured in so that the bitumen sample is submerged in it completely (approximately 18g of product, depending on its density). The sample is left for 24h at a temperature of 20±1°C, after which, the product is drained out, with the bitumen sample now sticking to the bottom of the beaker. The sides of the beaker above the bitumen sample are wiped with a cloth and the remains of the samples are weighed to the nearest 0.01g. The bitumen degradation (BD%) is taken as the difference between the mass of the bitumen sample before (BB) and after (BA) the test as shown in Eq.[3].

$$BD\% = 100\% \times (BB-BA)/BB \qquad [3]$$

3. Results

3.1. ARA Performance

3.1.1. Asphalt Slide Test

A number of parameters were used in developing the test in order to find the ones that can lead to the most indicative results. For test No. 1, the ARA was applied at 20±1mL/m^2 and the plate was not heated during the test. The asphalt did not move from the plate when inclined, requiring the top of the mixture to be pushed lightly before the start of the sliding, even at the maximum possible inclination of 70°. The light pushing did not appear to move the control sample.

For test No. 2, the ARA was applied at 20±1mL/m^2 and the plate was heated to around 70°C before ARA application and was heated during the inclination part of the test at 70°C. This time, the mixture slid after inclination, indicating the necessity of heating the plate before the mixture slides. A cooling time of 30min was found to be adequate for the mixture to develop some adherence to the plate as there was a certain delay between when the plate was inclined and when the mixture slid, allowing for the measuring of time to the beginning of the slide after the inclination as a performance characteristic for the ARAs. An angle of inclination of 45° was found adequate for the sliding as well.

For test No. 3, the ARA was applied at 25±1mL/m^2 the cooling time was set at 30min and the angle of inclination at 45°. The plate was not heated before the asphalt mix was applied; however, the ARA-PEA was heated at varied temperatures in order to determine an optimum for the test. It was found that for a temperature of 60°C at inclination, the samples with ARAs slid, but the control samples did not. A temperature of 60°C was therefore set for the plate at inclination.

For test No. 4, the test was conducted with diesel, ARA 1 and ARA 2. While the test with these parameters was shown to be repeatable in terms of residual bitumen (σ of 0.11-0.87g/m^2), the variability of the time to start of slide was found to be elevated (σ of 0-60s). As source of this could have been the inconsistency with the contact between the mixture, the agent and the plate over the plate area. The application of the ARA by spraying as well as the asphalt mix can leave some parts of the plate with thicker layers of ARA than others. This confirmed by the low time to beginning of slide for diesel, which corresponds to diesel having the most even coverage on the plate visually.

For the final test, performed with three trials for each sample, it was decided to increase the quantity of the asphalt mix to 1200±10g and the quantity of the ARA to 65mL/m^2 in order to reduce the variability from lack of coverage of the plate. The test was conducted with diesel, ARA 1, ARA 2 and BR 2 (BR 2 had obtained a result in the BDT that suggested that it was safe enough to use as an ARA). The photos of the plates after the test are shown in Figure 1 and the results of the test in terms of residual mass and time to beginning of slide are shown in Table 2. The variation in residual mass was about the same (σ of 0.11-0.87g/m^2), despite an increase in residual mass in general due to the higher dosage of ARA and asphalt mix. The variation in time to beginning of slide was reduced as well (σ of 4.11-13.41s), as it would with the reduction of retention time, but remains significantly higher than the variation in residual mass.

FIGURE 1 *Images of plates after Asphalt Slide Test final (mixture mass: 1200+-10g, ARA: 65 mL/m2, cooling time: 30mn, heating of plate: 60°C, inclination angle of plate: 45°)*

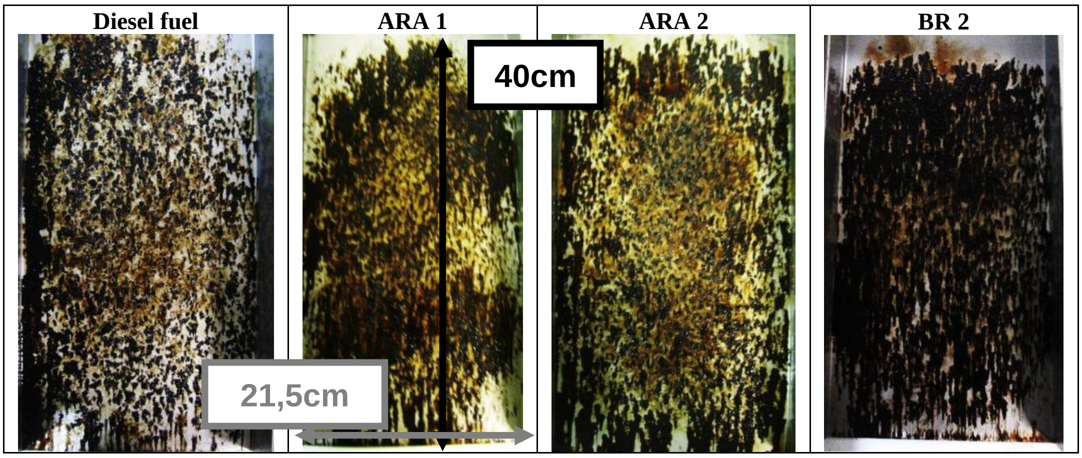

TABLE 2 *Results for Asphalt Slide Test final (asphalt mass: 1200+-10g, ARA: 65 mL/m2, cooling time: 30 min, heating of plate: 60°C, inclination angle of plate: 45°)*

Product	Residual mass (g/m^2)	Time to beginning of slide (s)
Diesel fuel	8.92	8.0
STDDEV σ	*0.21*	*4.1*
ARA 1	7.12	5.2
STDDEV σ	*0.55*	*4.5*
ARA 2	8.20	9.9
STDDEV σ	*0.82*	*13.4*
BR 2	8.92	12.7
STDDEV σ	*0.63*	*9.9*

3.2. ARA Effects on Asphalt Mix

3.2.1. Asphalt Mix Degradation by ARAs

In evaluating the tests for the degradation of asphalt mix by ARAs, there were several considerations. These included the state of the moulds, the resistance of the asphalt mix to CBR/Indirect Tensile loading and the distribution of the ARA inside the sample. All of the samples for CBR loading were made with proctor compaction and had a 5mL dosage of ARA, determined by a series of preliminary testing. The resistance to CBR loading of the control samples manufactured 10 days apart, shows a significant difference in both the shape of the resistance (kN) vs. displacement (mm) curve and the maximum resistance with a coefficient of variability (CVAR% = σ_{std}/avg) of 22% for the 6 samples.

Although asphalt mix is known to exhibit some variability, the variability in this case was overly significant for our purposes. Another set of tests was conducted to determine if the source of the error was the asphalt mix, taking extra precautions to keep the asphalt mix homogenous. The second set of control samples also had a high CVAR% of 13%. In addition to this, some ARAs appear to actually increase the resistance of the asphalt mix relative to the control samples. leaching of the bitumen onto the moulds was found after demoulding as was observed in [ESC 11b] as well as the tendency of the ARAs to move to the sides of the samples due to the center of the samples having a higher density through proctor compaction process, that is, away from the part of the sample tested by CBR. All of these factors indicated that the test methods needed to be changed.

For ITS Trial No. 1, samples were compacted by compression and the ARA quantity was 5±0.2mL applied immediately after compaction at a mixture temperature of around 130ºC. The CVAR% for the ITS control samples (all made on different days) was 5%, lower than for the CBR samples. It is shown that all of the RR% values are above 50%, indicating that the quantity of ARA could be reduced.

For ITS Trial No. 2, the samples were compacted by compression and the ARA quantity was 2±0.2mL applied immediately before compaction at around 150±10ºC. The application of the ARA after compaction represented an ARA accidentally spilled on the compacted asphalt pavement, or from a roller. While this is a potential source of degradation by ARAs; it may not represent the most severe case, which is more likely be the interaction of the asphalt mix and the ARA applied to the truck bed, an interaction that occurs before compaction. All of the RR% values were above 50%, indicating that the ARA quantity is rather elevated. However there is a clear difference between the ARA resistance values and that for the BR. Additionally, the leaching of bitumen on the moulds was almost negligible, indicating that nearly the entire quantity of the ARA stays in the sample. The variability in the results was lower as well with CVAR% of 1-3%.

For the final test, with three trials for each agent, it was decided to lower the ARA quantity to 1±0.2mL while keeping the rest of the parameters from Trial No. 2 the same. It was found that the RR% values were less than 50% for all of the three products tested, while there is an even larger discrimination between the ARA RR% values (21.8-32.2%) and those for the BR (43.1%).

3.2.2. Bitumen Degradation by ARAs

The BDT was performed at 24h (contact time between product and bitumen) for all of the samples (3 trials for each) shown in Table 1 and at 7d (single trial) for ARA 1, ARA 2 and BR 1. As shown in Table 3, the mass of all of the bitumen samples were reduced in this test, with the reduction being increased further for the samples submerged for 7 days. In general, the BD% for the ARA samples was far lower than for the BR, with the exception of ARA 3, which appeared to cause high degradation (53.63%) while BR 2 had a relatively low degradation (32.73%) relative to the other BRs.

Table 3 *Bitumen Degradation Test results*

Product	% Bitumen degradation	
	after 1 day	after 7 days
Diesel fuel	67.10	-
CVAR%	*6%*	
ARA 1	28.95	69.42
CVAR%	*4%*	-
ARA 2	21.39	75.84
CVAR%	*5%*	-
ARA 3	53.63	-
CVAR%	*1%*	
BR 1	53.73	95.30
CVAR%	*2%*	-
BR 2	32.73	-
CVAR%	-	
BR 3	51.87	-
CVAR%	*11%*	

4. Discussion

4.1. Validity and limits of ARA performance test methods

The Asphalt Slide Test was tested with ARAs using five different sets of parameters. The ARA-PEA (ARA Performance Evaluation Apparatus) provides a good platform for this test. While the pre-heating of the plate is not necessary, the heating of the plate during inclination is needed for the mixture to slide down by itself. A cooling time of 30min appears to be adequate to allow for the mixture – subject to a 2.5kPa load simulating the mixture mass in the truck – to adhere to the plate. Practical situations would vary significantly from load to load depending on the transportation distance and outdoor temperature. The 30min is applied as being both i) within range of a normal transportation times for hot mix asphalt [NAP 11] and ii) is not excessively long so that the testing can be conducted in a timely fashion. A mixture quantity of 1.2kg and an ARA quantity of 65mL/m2. Our objective was to have a complete covering of the plate by the ARA, and a higher dosage was needed to ensure this.

There were two types of results observed during the testing:

1. Time the mixture was retained on the plate after inclination;

2. Mass of residue retained on the plate after the mixture slides down.

The parameters are quantitative results that can be used to compare the performance of various ARAs. For the residual mass, the variability is quite low; while it is quite significant for the retention time; even at higher dosages of ARA.

It terms of field applications, the residual mass would correspond either: i) to the mass of residual bitumen that would need to be cleaned off the surface of the truck bed, with higher mass increasing required workload or ii) a significant mass of ARA remains on the truck bed and can be left for the next asphalt mix load, increasing time between ARA application and reducing the required quantity of product. From the observation of residual bitumen on the plates after testing, we can hypothesize that it is the former and that less residual mass may be preferred. However, it should be noted that during our study, exclusively diesel fuel and ester based formulations were tested; agents that were found to have degraded the bitumen to a certain degree. We should not exclude the possibility that there are ARAs that function as a substrate and that do not degrade the bitumen, such as those described in [BYM 09, CHE 03, DAV 05, DIT 02, KIN 00, KOD 97, KUL 00, KUL 00, LOC 99, MAR 00, MAH 03, OLS 99, SAL 99, ZAK 13]. For if there was only ARA left on the plate, it would be to an advantage to have a higher residual mass.

The retention time for the asphalt mix has a high variability, and taking into account all of the variables that could involve themselves in the process, it is not difficult to see why. For one, it can be difficult to ensure that the agent is applied evenly over the surface of the plate. While we can apply the agent at a controlled mass, this does not ensure equal distribution of the agent all along the surface of the plate. While care was taken to distribute the agent as evenly as possible, this was limited by the scope of our eyes and the capability of our sprayers. The ARA's also have varied viscosities, with the agents with lower viscosity, such as diesel; spreading more easily on the plate. As another parameter of performance, it may be useful to measure how easily the mixture spreads on the plate. Other factors of variability include the way the mixture is applied, mixture temperature at contact with plate and ambient temperature.

4.2. Validity and limits of ARA degradation test methods

The evaluation of asphalt mix degradation by ARAs involved testing two different methods of loading resistance with two different methods of compaction. The samples tested with CBR loading and proctor compaction did not provide results that were repeatable. Even though samples manufactured at the same time had similar resistance values, both control samples and samples with ARA addition did not correlate if they were made on different days. Additionally, many of the samples where ARAs were used, showed similar or higher resistance to CBR loading than the control samples.

It was clear that the ARAs had caused the leaching of bitumen from the observation of moulds after the samples were demoulded as in [ESC 11b]. However, this effect was not understood from the results of CBR loading. It was interesting to note that from the photos of the insides of the asphalt mix samples after testing; the ARAs appeared to move towards the sides the samples. On the other hand, the CBR loading tested the middle 50mm diameter of the sample, which would mean less of the ARA-asphalt mix interaction areas in the asphalt mix, would be subject to the test.

ITS was evaluated as an alternative to the CBR. As opposed to solely loading the inner diameter of the sample, ITS subjects the entire mid-section to loading. The maximum resistance from the ITS corresponded to a vertical crack formed in the middle of samples. The tensile resistance is observed at the beginning of the loading, before the formation of the crack corresponding to the maximum resistance of the sample.

After the formation of the crack, the resistance to loading is essentially the resistance in compression of the two halves of the original sample. While both the tensile and compression properties are observed before the formation of the crack, the tensile resistance of the samples depends more on the properties of the bitumen (the part of the asphalt mix affected by ARA degradation, as the aggregates would be inert), which are found in the sample loading before maximum resistance is reached. By comparison, the resistance to CBR loading depends more on the arrangement and the mechanical properties of the aggregate skeleton than for ITS. This is also why ITS is far more common for asphalt mix than compression or CBR type of testing [DIB 13, PAR 13].

Compaction by compressor was used as an alternative to proctor compaction in order to obtain a more evenly distributed density in the sample. The voids content, for a compression pressure of 2.5MPa for 3min, was determined to be 6.9% in accordance with NF P 98-150-1 for this mixture. With this method, the CVAR% for resistance to loading for the control samples was much smaller than with the CBR-proctor samples.

For an ARA quantity of 5mL applied after compaction, the results in loss of resistance for diesel, the ARAs and the BRs were all over 50%. Additionally, there was significant leaching of the asphalt mix by the ARA onto the moulds, indicating that the dosage had to be lowered. There was however, a significant difference in loss of resistance for ITS between the ARA 2 and BR 2, indicating that the test is able to distinguish between products that are meant to degrade bitumen and those that are not.

The application of the ARA after compaction was generally performed at around 130°C. This situation represented an ARA accidentally spilled on the compacted asphalt mix, or from a roller. While this is a potential source of degradation by ARAs; it may not represent the most severe case, which could be the interaction of the asphalt mix and the ARA applied to the truck bed, an interaction that occurs before compaction.

For the second ITS test, the ARA was applied at 2mL before compaction of the sample, allowing it to be applied at around 160ºC, which is generally the peak temperature in mixture fabrication, and can be assumed to increase the dynamics of the ARA-bitumen interaction as well. After the fabrication, the moulds did not show much bitumen leaching by the ARA, indicating that almost all of the ARA stayed in the sample. This is important because too much bitumen leaching could vary the quantities of ARA that act on the mixture, sample to sample. The loss of resistance was still over 50% for all of the applied products.

For the finalized ITS test, the ARA was applied at 1mL before compaction and showed RR% values of below 50%. Additionally, there was higher distinction between the values for the two ARAs and BR 1, indicating a test that can differentiate ARA products in terms of their tendency to degrade asphalt mix.

For further development of the test, the difference of adding the ARA before and after compaction should be considered as two relevant tests with this method, although before compaction seems like a more relevant condition of application in the development of ARAs. Furthermore, a higher loading rate as used in AASHTO T322, which is more common for softer materials such as asphalt mix. The temperature control of the test should also be considered as asphalt mix performance is very dependent on temperature change [HIH 14, LES 14], as was also observed in this study. The defining of a loading strip width could also help to reduce variability. Preparation of the cylindrical sample such as flatting the rounded contact surface [DAV 11], pre-cutting a fracture plane or setting up a semicircular bend test, where a fracture plane is cut into a semicircular specimen [WAG 05], could help the tensile forces to be more pronounced in the results.

The bitumen degradation test is able to differentiate the degradation from ARAs and BRs on bitumen and is a repeatable test that is relatively simple to implement. Samples were submerged for both 1 and 7 days, and the 7 day samples showed that the bitumen continued to degrade after 24h from exposure to the product. Despite this, due to the severity of the conditions of the BDT, a 1 day test is more just for evaluating the performance of BRs because faster degradation is required.

5. Conclusions

The conclusions in developing test methods for the determination of the performance and damage to asphalt of bio-sourced ARAs are as follows:

- The asphalt slide test provides two indicators of ARA performance including mass of asphalt residue (residual mass) and time for mixture to begin sliding after inclination (retention time). The residual mass for the AST has less variability and likely a more significant indicator of performance than the retention time;
- For the AST, heating under the plate is needed for the mixture to begin sliding on the ARA-PEA;
- The testing of asphalt mix degradation by ARAs with the CBR-loading does not produce reproducible or coherent results;
- The testing of asphalt mix degradation by ARAs with ITS produces reproducible results and is able to differentiate the damage from ARAs and BRs;
- A dosage of 1mL provides results that enable discriminate agents that are intended to degrade asphalt mix and those that are not;
- Compaction of the asphalt mix by compression as opposed to proctor produces a more consistent sample in terms of density distribution;
- The bitumen degradation test at 1 day is able to differentiate the damage from ARAs and BRs on bitumen with low variability, proving this to be a simple and efficient test for bitumen degradation from ARAs and BRs.

Acknowlegments

The authors would like to thank FUI (French Designated Inter-Ministry Fund), Région Midi-Pyrénées (France) and OSEO, which funded the AGRIBTP research project, (www.agribtp.fr) and USIRF for their financial support as well as Malet (France) and Kemerid (France, www.kemerid.com) for their technical support.

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