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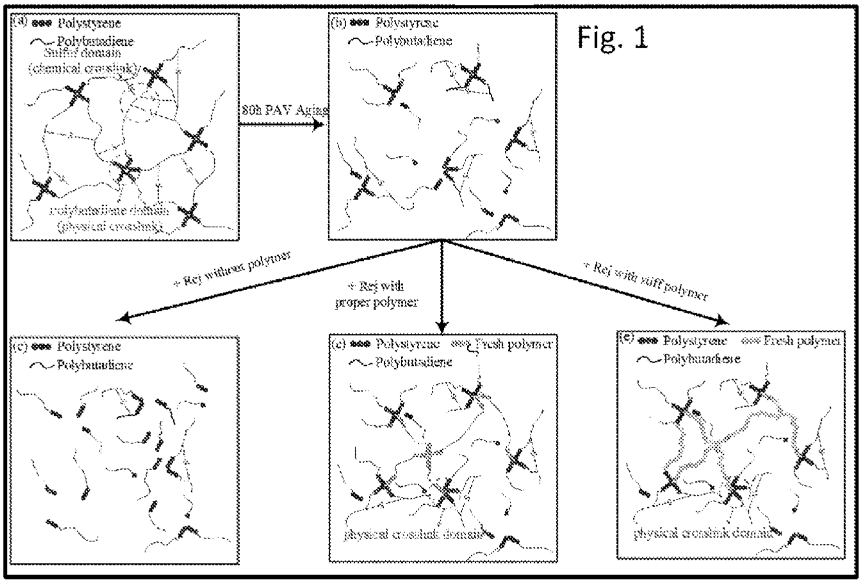

Fig. 1

(57) Abstract: The present invention is in the field of chemical composition referred to as a rejuvenator for recycling of polymer modified asphalt concrete pavement, to a reclaimed polymeric network comprising said rejuvenator, to asphalt comprising reclaimed polymer modified bitumen, to reclaimed asphalt shingles comprising the polymer modified bitumen, to constructions comprising the reclaimed polymeric network, and to a method of applying said rejuvenator.

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Rejuvenator for Recycling of polymer Modified Asphalt Concrete Pavement

FIELD OF THE INVENTION

The present invention is in the field of chemical composition referred to as a rejuvenator for recycling of polymer modified asphalt concrete pavement, to a reclaimed polymeric network comprising said rejuvenator, to asphalt comprising reclaimed polymer modified bitumen, to reclaimed asphalt shingles comprising the polymer modified bitumen, to constructions comprising the reclaimed polymeric network, and to a method of applying said rejuvenator.

BACKGROUND OF THE INVENTION

Asphalt, also known as bitumen is a sticky, black, and highly viscous liquid or semi-solid form of petroleum. It may be found in natural deposits or may be a refined product. Asphalt, as well as polymer modified bitumen (PMB) is often used in road structures. Over time the asphalt/PMB deteriorates and often needs to be replaced as a consequence. It is acknowledged that in the USA asphalt is defined according to ASTM D8-02, and in Europe according to EN 12597. The present invention relates to a mixture of mineral aggregate and a bituminous binder, according to the European definition.

Nowadays, the use of milled or post-processed old asphalt, named reclaimed asphalt pavement (RAP), in newly produced asphaltic materials in plants is a common practice in many countries, offering economic and environmental benefits, such as reduction of material cost, conservation of landfill space and lower demand on natural resources. At the same time, polymer-modified bitumen (PMB) binders have been extensively used worldwide as well for premium (highly trafficked) asphalt pavements. Nevertheless, a large amount of RAP including PMB binders is produced every year. Together with the
continuously increasing demand to incorporate PMB RAP in the asphalt production, the use of rejuvenators for RAP materials modified with polymers is becoming important. High temperatures are used through the recycling process in asphalt plants to improve the activation of aged PMBs and in combination with the complicated mechanism of PMBs aging (i.e., bitumen oxidation and polymer degradation). Therefore special attention is given to developing compatible rejuvenators with the aged PMBs.

Rejuvenators are chemical compositions or compounds designed to restore properties of aged binders to a state at which aged materials could be incorporated in the newly produced asphalt pavements. Examples are organic rejuvenators which can be applied in lower dosages than other. However, these organic rejuvenators are found not suitable to rejuvenate aged PMB. For instance, during shearing and stirring in the production process of PMB binders, styrene-butadiene-styrene (SBS) polymer absorbs the aromatic compounds from the bitumen and polymer swelling occurs. Thus, not suited compounds may lead to agglomeration, segregation and phase separation of the polymeric network in bitumen.

To recover aged binders to their original state, it may be necessary to add a certain amount of polymer modifiers into the rejuvenators. Apart from the SBS polymer that may show improved compatibility with the aged PMB binders, rubber modifiers are also promising as they can improve the low-temperature properties. Especially, the addition of treated rubber modifiers decreases the viscosity of rejuvenators when the terminal blend (TB) modification is followed.

Some background art may be cited. For instance, Martin et al. in “THE EFFECTS OF RECYCLING AGENTS ON ASPHALT MIXTURES WITH HIGH RAS AND RAP BINDER RATIOS”, PHASE I INTERIM REPORT Prepared for National Cooperative Highway Research Program Transportation Research Board of The National Academies, March 2015, recite a comprehensive information search was completed and included a literature review to document aging and recycling of asphalt materials, restoring and characterizing binder rheology with RAs, and improving and characterizing mixture performance with high recycled binder ratios and RAs. A survey of state departments of transportation, contractors, and RA suppliers was also conducted to assess the current state of the practice on the use of RAs in hot-mix asphalt and warm-mix asphalt mixtures containing high percentages of recycled materials. Preliminary laboratory results included findings from testing of binders, mortars, and mixtures from a field project in Texas and supplemental materials to expand an initial knowledge base. All of this information was synthesized and used to develop the Phase II work plan, which is also described in this report. Cong Peiliang et al. in “Investigation on rejuvenation methods of aged SBS modified asphalt binder” (DOI:10.1016/j.fuel.2020.118556), recite SBS modified asphalt binder (SBSMA) is widely used because of its excellent pavement performance. Recycling application for aged SBSMA has drawn increasing attention. In this study, aged SBSMA was rejuvenated with different rejuvenation methods, including the use of rejuvenator (RA), original SBSMA, base asphalt (SK-70) and original SBSMA mixed with SK-70. The conventional performance and rheological behaviour of different rejuvenated SBSMA were investigated. The microscopic changes were analysed by using Gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy and Fluorescence microscopy (FM). Results revealed that RA and original SBSMA have significant effect on the improvement of the physical-rheological and microstructures of aged SBSMA, but SK-70 did not exhibit good rejuvenation effect. The conventional tests showed that the addition of RA greatly improved the low temperature ductility and elastic recovery rate of aged SBSMA. Moreover, it was proved that RA could increase the creep compliance and improve the stress relaxation ability of aged SBSMA according to physical rheological parameters. This result indicated that RA improved the cracking resistance of aged SBSMA at low temperature. Based on the microscopic test results, it was found that RA not only could regulate the internal components of aged SBSMA, but also restore the network structure of aged SBSMA. Furthermore, the SBS polymer content indices and the softening indices are closely correlated with the performances of the rejuvenated SBSMA. From the analysis, it is necessary to rejuvenate the aged SBSMA by softening base asphalt and restoring the network structure of SBS copolymer. Zhao et el. (DOI:10.3390/app8091591) in “Micromechanism of the Dispersion Behaviour of Polymer-Modified Rejuvenators in Aged Asphalt Material”, recite that polymer-modified rejuvenator has a different composition and dispersion behaviour to traditional rejuvenators. The objective of this study was to investigate the micromechanism of polymer-modified rejuvenators on the behaviour of aged asphalt binder. Firstly, gel permeation chromatography (GPC) analysis was conducted to determine the dispersion effectiveness. Secondly, the dispersal behaviour of polymer-modified rejuvenators was studied by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). Rheological, toughness-tenacity, and force–ductility analyses of the rejuvenated asphalt binder were additionally performed. The results indicate that the contacted asphaltenic micelles in aged asphalt binder were dispersed by dispersion agent in the polymer-modified rejuvenator, and that the dispersion ability of the polymer-modified rejuvenator was promoted to the commercial rejuvenator level. Additionally, the polymer-modified rejuvenator was found to improve the rejuvenated asphalt binder’s resistance to deformation, through the formation of polymeric network structures in the asphalt binder. The results may be used to improve the performance of rejuvenated asphalt binder in recycled-pavement engineering. And Wei et al. (DOI:10.1016/J.CONBUILDMAT.2019.117154) recite in “Investigation of rejuvenation and modification of aged asphalt binders by using aromatic oil-SBS polymer blend” that long-term aged base asphalt and SBS modified asphalt binders were rejuvenated and modified simultaneously using a compound rejuvenator containing 77% aromatic oil and 23% SBS polymer. Aromatic oil was used for rejuvenation purpose due to its softening effect while SBS polymer was used for modification purpose because of its potential to form a polymer network. Conventional bitumen tests, dynamic shear rheological (DSR) test and bending beam rheological (BBR) test were conducted to evaluate the rejuvenation and modification effects. Test results indicated that use of the compound rejuvenator enhanced the softening point and ductility for both aged base asphalt and SBS modified asphalt binders. The polymer modification effect of compound rejuvenator was well distinguished by the plateau region of phase angle master curves. Aromatic oil had a strong softening effect on aged asphalt binder which improved the performance at low temperatures, but weakened the performance at high temperatures. The incorporation of

SBS polymer was a good supplement to balance the overall performance of rejuvenated asphalt binders. The compound rejuvenator can be greatly effective for hot recycling of reclaimed asphalt mixture by means of the simultaneous rejuvenation and modification.

The present invention therefore relates to rejuvenator and applications thereof, which solves one or more of the above problems and drawbacks of the prior art, providing reliable results, without jeopardizing functionality and advantages.

SUMMARY OF THE INVENTION

It is an object of the invention to overcome one or more limitations of the prior art. In a first aspect the present invention relates to a rejuvenator for a polymeric network comprising a mixture of 1-25 wt.% of at least one substantially intact polymer, preferably 3-20 wt.%, more preferably 4-15 wt.%, such as 5-11 wt.%, or 25-50 wt.% of at least one substantially intact polymer preferably 30-45 wt.%, more preferably 35-40 wt.%, 15-50 wt.% of at least one aromatic oil, such as a synthetic or natural aromatic oil, preferably 20-45 wt.%, more preferably 25-40 wt.%, such as 30-35 wt.%, 0.3-10 wt.% of at least one first additive, wherein the at least one first additive is preferably selected from terpenes, preferably 0.5-5 wt.%, more preferably 1-4 wt.%, such as 2-3 wt.%, 30-75 wt.% of at least one saturated or unsaturated acidic oil, preferably 35-68 wt.%, more preferably 40-63 wt.%, such as 47-55 wt.%, 0.4-10 wt.% of at least one resin for activating (i.e. improving compatibility between substantially intact polymer and aged polymer in the) polymeric network, preferably 0.5-5 wt.%, more preferably 1-4 wt.%, such as 2-3 wt.%, wherein all weight percentages are based on the total weight of the rejuvenator. The present rejuvenator provides a low degree of segregation, a low degree of separation, a good softening point of the recycled polymeric network, and a good viscosity. The rejuvenator may be considered as a type chemical agent to restore properties of polymeric network and to compensate for the loss of chemical composition during aging, such as the binder in asphalt-like mixtures. The fresh or undamaged polymer, for example crumb rubber, might have been used for a long time, however the polymer network inside is still healthy compared with the polymer network in polymer modified bitumen. It is dissolved in the liquid components of the mixtures, such as the aromatic oil, the first additive, an acidic oil. It is found that at higher temperatures more fresh or undamaged polymer can be added to the mixture. It may be provided as a powder, e.g. with an average particle size of <100 μm, as particles, such as with a size of <5 mm, or a combination thereof (as measured with laser scattering). As mentioned it readily dissolves. The present resin is for activating aged polymer and/or improving the compatibility between polymeric network and bitumen. In a study, a set of rejuvenators was produced and their influence on performance-based properties of PMB binders was investigated. The polymer modified bitumen(PMB) may be considered as a series of special bitumen which contains a polymer, such as SBS. The polymeric network is then a polymer structure in polymer modified bitumen, which is formed by the SBS polymer and can improve the properties of PMB. A set of rheological tests were conducted at low, medium and high temperatures and a ranking method is proposed to evaluate the efficiency of these rejuvenators. A series of rejuvenators were used for the rejuvenator dosage determination as well. Finally, Environmental Scanning Electron Microscopy (E-SEM) was used to visualize the influence of rejuvenators on the micro-structure of the rejuvenated binder. The present rejuvenator was designed on the base of a deep understanding of the aging mechanism of polymer modified bitumen and bitumen colloidal stability theory. The added fresh, substantially intact, polymer component in the invented rejuvenator can assist the reconstruction of the polymeric network and repair the degraded polymers in the aged polymer-modified bitumen. The schematic drawing of the principle of polymer network rebuilt with different types of rejuvenators can be seen in figure 1. An aromatic oil selected to supplement the lost component during aging which is found to enhance the colloidal structure stability of the rejuvenated binder. The proportion of different compositions in the rejuvenator was determined according to bitumen colloidal stability theory and optimized with plenty of tentative tests. Furthermore, several specific components were added in the invented rejuvenator to dissolve the conglomeration of asphaltene and improve its diffusion into aged bitumen, such as an anti-ravelling agent, a warm-mix agent, etc. Compared with several commercial available rejuvenators, the application of the present rejuvenator is more effective in terms of improving the viscoelastic response, cracking resistance, rutting resistance and low-temperature performance of the aged polymer modified bitumen, and the rejuvenation effect is more stable in multi-circle recycling practices. Regarding the rejuvenation mechanism study by using the Differential Scanning Calorimetry (DSC) and Environmental Scanning Electron Microscopy (ESEM) tests, it was found that the present rejuvenator can build up the micro reinforced polymer network inside the rejuvenated bitumen and hence improve the compatibility between fresh and aged polymer modified binder and mechanical performance of the modified RAP. Experimental study of the invented rejuvenator for high-quality recycling of polymer modified asphalt are found.

The present invention is equally applicable to other polymeric networks.

It is found that in particular an SBS-based rejuvenator for PMB binders has showed improved performance at both low and high temperatures after aging, requiring low dosage. Thereto a series of performance-based tests were conducted to establish a performance-based method for rejuvenator selection and dosage optimization. And E-SEM is found a powerful tool to visualize the morphology structures of aged PMB binders before and after incorporating the rejuvenators.

One of these tests is a segregation test. The test method used is "Bitumen and bituminous binders - Determination of storage stability of modified bitumen EN

13399:2010". In an example the PMB is filled in an aluminium tube and stored in the chamber at 163 degrees for 48 hours. Then the top and the bottom part of the PMB samples were collected to conduct softening point test. From the present test results, if the recipe includes the resin, the softening point difference is less than 2 degrees, which meets the standard requirement. If the resin was not included in the recipe, the softening point is larger than 4 degrees, which causes a significant decrease of asphalt performance. The above prior art does not provide test results at all to prove this phenomenon.

The present resin has three main functions, namely to increase the storage stability, such as of the polymer modified bitumen, as described, to decrease the possibility of phase segregation of the rejuvenator containing polymer, and as the rejuvenated PMB is intended for use in the field and will be conducted the second circle of aging. The addition of aromatic oil and resin decreases the risk of phase segregation of recycled PMB during the second aging.

In a second aspect the present invention relates to a reclaimed polymeric network, such as reclaimed modified bitumen, that is obtained directly from an existing polymeric network, such as from an asphalt road, comprising 1-20 wt.% of at least one rejuvenator according to the invention, such as 2-15 wt.%, and rejuvenated aged polymer modified bitumen, wherein the polymer in the modified bitumen is preferably selected from block polymers, such as styrene-butadiene-styrene (SBS) polymer, natural or synthetic latex, such as polychloroprene latex, and reclaimed rubber.

In a third aspect the present invention relates to an asphalt product comprising reclaimed polymer modified bitumen according to the invention, such as asphalt, asphalt shingles, and asphalt waterproofing, or a rejuvenator according to the invention. The rejuvenator may be provided as such, or to the reclaimed asphalt, or may be incorporated in asphalt, such as in capsules, or a combination thereof.

In a fourth aspect the present invention relates to a construction comprising asphalt according to the invention, wherein the construction is selected from a multilayer civil engineering system, such as an asphalt concrete surfacing layer on orthotropic steel deck bridge, a foundation, a wall, a basement, a building, and combinations thereof, and/or wherein the construction comprises at least one of a waterproofing, a top layer, and a deck layer.

In a fifth aspect the present invention relates to a method of applying a mixture comprising a rejuvenator for a polymeric network, the polymeric network comprising intact polymer and aged polymer, according to the invention, wherein the polymeric network is selected from polymer modified bitumen, and modified asphalt comprising a polymer, comprising mixing the rejuvenator and reclaimed asphalt pavement comprising aged polymer modified bitumen into a first mixture, such as during 30 seconds-5 minutes, pre-heating the first mixture to a temperature of 350-433 K(77-160 °C) during a pre-heating period of time, such as during 1-60 minutes, blending the first mixture with aggregate at a temperature of 473-553 K(200-280 °C) and bitumen at a temperature of 423-443 K(150-170 °C)into a second mixture for a second period of time at a temperature of 473-553 K(200-2080 °C), in particular fresh aggregate and fresh bitumen, such as during 1-20 minutes, wherein the second mixture has a temperature of 430-473 K(157-200 °C), maintaining said temperature for at least 1 minute, such as during 2-30 minutes, cooling the mixture, such as to ambient temperature, during a cooling time of 10-60 minutes, and applying the mixture, such as to a road. In a sixth aspect the present invention relates to a use of a rejuvenator for a polymeric network according to the invention for healing the polymeric network, for improving viscoelasticity, enhancing colloidal stability, dissolving asphaltene, improving durability, improving anti-cracking, improving aging resistance, improving compatibility, improving relaxation, increasing maximum stress, or a combination thereof.

Advantages of the present description are detailed throughout the description.

DETAILED DESCRIPTION OF THE INVENTION

In an exemplary embodiment of the present rejuvenator the polymeric network is selected from polymer modified bitumen, modified asphalt comprising a polymer, such as modified asphalt concrete.

In an exemplary embodiment of the present rejuvenator the polymer is selected from co-polymers, preferably comprising a flexible domain, such as from linear copolymers, such as block copolymers, alternating copolymers, periodic copolymers, statistical copolymers, stereo-block copolymers, and gradient copolymers, branched copolymers, and graft copolymers, preferably from ethylene-butyl-acrylate (EBA), styrene-butadiene-styrene (SBS), and natural or synthetic rubber.

In an exemplary embodiment of the present rejuvenator the aromatic oil comprising at least one aromatic moiety has an aromatic content (i.e. molecules with at least one aromatic ring) of > 25%, preferably >30%, more preferably > 40%, even more preferably >50%, such as > 65%.

In an exemplary embodiment of the present rejuvenator the aromatic oil is selected from rubber processing oil, 1-3 vacuum side-stream of crude oil, reduced crude oil, synthetic or natural aromatic oil, mineral oil, and combinations thereof.

In an exemplary embodiment of the present rejuvenator the aromatic oil is adapted to dissolve asphaltene, wherein the aromatic oil may be provided as a liquid comprising 10-65 wt. % solvent.

In an exemplary embodiment of the present rejuvenator the at least one first additive is selected from organic solvents, such as asphaltene solvents, that is solvents for asphaltene, such as monoterpenes ($C_{10}H_{16}$), preferably cyclic- or bicyclic monoterpenes, such as geraniol, terpineol, limonene ($C_{10}H_{16}$; CAS 139-86-3/5989-27-5/5989-54-8), myrcene, linalool, and pinene ($C_{10}H_{16}$; CAS 80-56-8/7785-70-8/7785-26-4/2437-95-8/18172-67-3), sesquiterpenes($C_{15}H_{24}$), such as humulene (CAS 6753-98-6), farnesenes, and farnesol, diterpenes ($C_{20}H_{32}$), such as cafestol, kahweol, cembrene, and taxadiene, triterpenes ($C_{30}H_{48}$), such as squalene.

In an exemplary embodiment of the present rejuvenator the at least one saturated or unsaturated acidic oil, preferably an oil with more than 16 carbons and at least one carboxylic acid, such as more than 20 carbons and at least one carboxylic acid, such as rapeseed oil. Further examples are low viscous vegetable oils, and methyl, ethyl, propyl, and iso-propyl mono esters of such oils, such as a C_{16}, C_{18} vegetable oil. These oils, being vegetable may have having a C_{16} or C_{18} content > 6 %. In an exemplary embodiment of the present rejuvenator the at least one resin is selected from hydrocarbon resins, such as C_4-C_{12} resins, preferably C_5-C_{10} resins, more preferably C_6-C_9 resins, most preferably C_8-C_9 resins. C_5 aliphatic, C_9 aromatic, and DCPD cycloaliphatic resins are most preferred. Hydrocarbon resins are amorphous thermoplastic polymers produced by polymerization of unsaturated hydrocarbons. The feedstock are various by-products of naphtha crackers. These resins have typically a low molecular weight ranging from about 400 to 5000 g/mol. The three main types are C_5 aliphatic, C_9 aromatic, and DCPD cycloaliphatic resins. They are sometimes hydrogenated to reduce discoloration and to improve their heat and UV stability. Aromatic hydrocarbon resins (C_9 Resins) can be made from C_9 aromatic hydrocarbons. Their composition depends on the hydrocarbon feedstock (coal tar, crude oil). The most important base monomers are indene, methylidenes, dicyclopentadiene, styrene, alpha-methyl styrene and various vinyl toluenes. These resins are available in a wide range of softening points. Compared to C_5 resins, they have a much higher melt viscosity, are of darker colour (dark yellow to brown) and have higher softening point ranging from about 100 to 150°C. C_9 resins are very versatile resins that are compatible with many polymers. Hydrogenated C_5/C_9 resins and resin blends are also commercially available. These resins are often colourless and have improved heat and colour stability. Aliphatic hydrocarbon resins (C5 Resins) are made from C5 piperylene and its derivatives. The most important ones are cis/trans 1,3-pentadienes, 2-methyl-2-butene, cyclopentene, cyclopentadiene, and dicyclopentadiene (see below). These monomers are polymerized to oligomeric resins with low to high softening point using Lewis acid catalysts. C5 resins are aliphatic in nature and are, therefore, fully compatible with natural rubber, most olefins (LDPE) and many synthetic elastomers of low polarity. They are available in a wide range of molecular weights (MW) and softening points (solid grades 85 - 115°C and liquid grades 5 - 10°C) and provide outstanding tack. They also have a light yellow to light brown colour and possess excellent heat stability.

In an exemplary embodiment the present asphalt further comprises one or more of particles, coarse aggregate, filler, extender, fibres, oxidants, antioxidants, plastics, anti-stripping agents, and waste material.

The invention will hereafter be further elucidated through the following examples which are exemplary and explanatory of nature and are not intended to be considered limiting of the invention. To the person skilled in the art, it may be clear that many variants, being obvious or not, may be conceivable falling within the scope of protection, defined by the present embodiments.

SUMMARY OF THE FIGURES

Figs. 1-10 show experimental details.

DETAILED DESCRIPTION OF FIGURES

FIGURE 1 Scheme of polymer network of SBS modified bitumen with different rejuvenators. The rubbery supporting network is mainly derived from physical and chemical crosslinking (see FIGURE 1 (a)). The physical crosslinking network is constructed by the polystyrene domain connecting with flexible polybutadiene, which improves elastic response in the high frequency region and brings about higher viscosity compared with base bitumen in the low frequency region. The chemical crosslinking network formed with the help of elemental sulphur, which can form the bonding between sulphur and the polybutadiene chains. As illustrated in FIGURE 1 (b), due to the aging sensitivity of polybutadiene, the flexible and elastic connection parts of the crosslinking network break down, which led to a significant down gradation of rheological properties.

The addition of a rejuvenator containing polymer is a feasible way to compensate for the degradation of the polymer and reconstruct the network. Although the commercial bio-based rejuvenators can significantly decrease the viscosity, it can only dilute and change the distribution of the degraded polymer network, rather than reconstruct the polymer network(see FIGURE 1 (c)). For reconstruction, proper type and content of polymer modifier can be pre-treated to absorb the aromatic and saturate component during fabrication to enhance the quick fusion of rejuvenator and aged binder. After mixing with the aged binder in the RAP at relatively high temperature (135~170 ℃), although chemical crosslinking will not be rebuilt without elemental sulphur, the physical crosslinking is possible to restore after cooling to ambient temperature (FIGURE 1 (d)). And the reconstruction of the polymer network will help to recover the viscoelastic property of the rejuvenated binder. However, it is worth noting that if the polymer selected is too stiff or the polymer content is too high, the degree of crosslinking may become too high, which may lead to a significant increase of stiffness and viscosity (FIGURE 1 (e)). Thus, the key of rejuvenator containing polymer is to find a balance point between decreasing viscosity and recovering polymer network.

Master-curves of complex modulus (figure 2) and phase angle of rejuvenated binders (figure 3).

Figure 4 and 5 Anti-cracking analysis of rejuvenated binders.

Figure 6 Master-curves of complex modulus and figure 7 of phase angle for the rejuvenated binders after a second aging phase (RTFOT+80 hours PAV at 100^{0}C).

Figure 8 Radar chart (a) and rank value (b) of the different rejuvenated binders

Figure 9 Maximum stress of rejuvenated bitumen with different rejuvenator dosage

Figure 10 SEM images of studied binders: (a) original PMB; and aged (b) PMB; (c) PMB +10% Rej B; (d) PMB +20% Rej B; (e) PMB +30% Rej B; (f) PMB +30% Rej F; (g) PMB +30% Rej E; (h) PMB +10% Rej B+50% fresh PMB; (i) PMB +10% Rej E+50% fresh PMB.

Examples

Materials and description

More than 60 types of rejuvenators with different compositions and ratios were prepared in the lab. Four novel rejuvenators are presented here for comparison. Apart from the 4 lab-produced rejuvenators (Rej A to Rej D), rejuvenators E (designed for PMB binders) and F (designed for base binders) were commercially available products (see Table 1). The binder was a commercial SBS-PMB with a softening point of 65.7^{0}C and a penetration of 30 (0.1-mm). To assess the restoring effect of various rejuvenators on this binder after two rejuvenation circles, a special material preparation method was followed. Firstly, the binder was subjected to short-term aging using Rolling Thin Film Oven Test (RTFOT) (EN 12607:2002) and long-term aging with a Pressure Aging Vessel (PAV) (EN14769:2006) for 80 hours, since it is observed this aging condition is similar to the aging of a porous surface layer, such as asphalt, after 10 years of service life. Afterward, the aged binder (AB) was heated at 170 °C and mixed with rejuvenators (10% by weight of AB). In the last step, the rejuvenated bitumen (reB, see Table 1) was again subjected to RTFOT aging and 80 hours PAV to simulate the second rejuvenation cycle.

Table 1 Description of rejuvenators and rejuvenated bitumen binder.

Name	Description
Rejuvenators	
Rej A	EBA-based liquid incl. saturated aromatic component
Rej B	SBS-based liquid incl. saturated aromatic component
Rej C	Rubber-based liquid incl. saturated aromatic component
Rej D S	BS/Rubber-based liquid incl. saturated aromatic component
Rej E	Commercial Bio-based commercial rejuvenator for recycling of polymer modified bitumen
Rej F	Commercial Compound commercial rejuvenator for recycling of base bitumen, including bio-oil, engine oil, and aromatics

Compositions

%	Aromatic Oil	Polymer	Resin	Rapeseed oil	limonene	pinene
A	30-40	4-11%	1-3%	42-63%	1-2%	1-2%
B	25-35	3-10%	2-4%	47-68%	1-2%	1-2%
C	25-30	15-20%	2-4%	42-56%	1-2%	1-2%
D	23-29	15-20%+3-5	2-4%	38-55%	1-2%	1-2%

Rejuvenated Binder

OB Original SBS polymer modified bitumen

AB SBS polymer modified bitumen after ageing

reB-A AB + 10% wt. Rej A

reB-B AB + 10% wt. Rej B

reB-C AB + 10% wt. Rej C

reB-D AB + 10% wt. Rej D

reB-E AB + 10% wt. Rej E

reB-F AB + 10% wt. Rej F

Note: E and F are commercially available products. The Rej-E is a bio-based rejuvenator, and the Rej F is a compound rejuvenator that includes aromatic and bio-oil, being mainly rapeseed oil (Latexfalt B and R20 respectively). Rej E and Rej F were selected as control groups. Rej F is an industrial rejuvenator rich in aromatic fraction (about 50%) and rapeseed oil (also about 50%) and designed based on specific chemo-physical interactions with the polar functionalities introduced in asphaltene-rich domains in an aged multi-phase bitumen system. According to specifications from the producer, the rejuvenator Rej F is specially designed for high RAP asphalt mixes produced at regular asphalt production temperature (160°C). Rej E is a low viscous liquid rejuvenator rich in saturates and contains selected components suitable for the re-compatibilization of the various phases in oxidized bitumen.

With 10% of commercial rejuvenator E, the aged PMB binder recovered to PG-70

Complex modulus and phase angle master-curves

The master-curves of the complex modulus for the rejuvenated binders are presented in Figures 2-3. It can be seen that the aging led to an upward shift of the complex modulus, and the modulus increase at low frequencies is more obvious than at high frequencies. The rejuvenation of the aged binders led to a downward parallel shift of master-curves demonstrating the significant decrease of complex modulus both at high and low frequencies. The complex modulus of the rejuvenated binders did not get as low as the complex modulus of the original binder at high temperatures, but the modulus at the low temperature of the rejuvenated binders was relatively lower compared with the viscoelastic characteristics of the original binder.

From the complex modulus master-curves, reB-B and reB-E had the lowest modulus at low and high frequencies, respectively. As given in Table 1 and Figure 2-3, reB-B was treated with Rej-B, which was an SBS-based rejuvenator including aromatic and saturate compounds. It is found that when the asphaltene content increases during aging, reduction of the aromatic content occurs together with significant degradation of the SBS polymer in SBS-PMB binders. The addition of Rej-B complemented the lost components of the PMB during aging, leading to a significant rejuvenation effect. In the case of reB-E, the mechanism of rejuvenation is totally different compared to Rej-B. The saturate content in bitumen changes little during aging. Hence, the Rej-E plays the so-called “dilution” role by increasing the saturate compounds. The “dilution” effect can reduce the complex modulus effectively, however, it cannot improve the phase angle of the aged binders to the same level. With respect to reB-A, reB-C and reB-D, the rejuvenation effect was not obvious and thus the corresponding Rej-A, Rej-C and Rej-D rejuvenators which were based on EBA, rubber and rubber/SBS, respectively, cannot reduce the modulus effectively both at low and high frequencies. The SBS-based rejuvenator is suitable for upgrading the aged SBS-PMBs.

There is a plateau zone for the phase angle for OB, which is an indicator of the crosslinking network of the SBS polymer. However, the phase angle plateau zone disappeared and the phase angle reduced significantly after aging, indicating a serious deterioration of the SBS polymeric network in bitumen. After rejuvenation, reB-B and reB-F show an increase of the phase angle, indicating that the rejuvenators Rej-B and Rej-F improved the viscous response of the aged binders. The viscous response of binders will assist in minimizing the risk of cracking at medium and low temperatures. The aromatics in both rejuvenators compensate for the loss of aromatics fraction of PMB during aging. Meanwhile, the Rej-B shows a higher rejuvenation efficiency than Rej-F, since the SBS polymer plays a significant role in increasing the viscous response of binders. In terms of reBE, its phase angle is consistent at low frequencies and increases slightly in the high-frequency region, illustrating that the “dilution” effect cannot recover the phase angle effectively.

Regarding reB-A, C and D, the Rej-C and D did not demonstrate much increase of the phase angle and Rej-A even caused a significant decrease of the phase angle at low frequency.

As shown in Figures 4-5, all the curves of aged binders and rejuvenated binders moved towards the lower left side and became more flat, due to the long-term aging. The aged binder (AB) has shown a lower phase angle indicating the loss of viscosity. With regards to the rejuvenated binders, reB-B and reB-F show the same trend as AB and the curves located between the threshold curves (R=2 and R=3), indicating that these two types of rejuvenated binders tend to be viscous. While, reB-C and reB-E show a downward shift, indicating the Rej C and Rej E have an adverse effect on the viscoelasticity. For further anti-cracking analysis of the rejuvenated binders, the Glower-Rowe parameter was calculated and added in Figure 4-5. It is defined as G'/sinδ and measured at 15°C and 0.005 rads-1, which was found to give a good correlation with ductility and cracking resistance. As illustrated in Figure 4-5, the G-R parameter of AB is over the threshold value(G-R=450), indicating that the aged PMB binders had a high risk of cracking without rejuvenation. With the addition of rejuvenators, GR parameters of reB-B, reB-E and reB-F are below 180 kPa, implying there is no cracking risk.

The aging stability of already rejuvenated binders has a significant impact on the potential reusability of RAP binders, so the rejuvenated binders are also subjected to a second aging cycle. To simulate the aging during service on the road, the rejuvenated bitumen was again aged in RTFOT and after that 80 hours of PAV aging. For a clear comparison of the viscoelastic properties before and after aging, the master-curves of rejuvenated binder and aged binder are plotted in Figures 6-7. As it is observed in Figures 6-7, the change in viscoelastic properties of aged SBS modified binder after the second aging cycle (AB) is similar to the change from OB to AB. The complex modulus curve shifts upwards and the phase angle master-curve shifts downwards, indicating that the AB aged becomes stiffer and more elastic. The reB-B, reB-E and reB-F binders have shown a significant rejuvenation effect, reduction in complex modulus and an increase in phase angle. However, after the second aging cycle, the complex modulus of aged reB-E aged, reB-F and AB binders are almost the same indicating that the rejuvenation effect disappears during the second aging phase. For the phase angle, the master-curves of reB-E and reB-F are even lower, indicating that the rejuvenation has an adverse effect, resulting in a higher elastic response. On the contrary, the rejuvenation effect of rejuvenator B is very significant. The complex modulus and phase angle difference between reB-B aged and AB aged are even larger than of reB-B and AB, indicating that the Rej-B can reduce the influence of a second aging phase to a certain extent.

To develop a tool for practice to choose the most suitable rejuvenators for aged PMB binders, a simple ranking method was introduced based on the seven tests discussed earlier. Firstly, the studied materials are ranked for each test. The highest-ranked materials obtain a ranking value (RV) of 6, and the last one is ranked with 1 RV. Then, by summing up the RV for each binder, the total rank value (TRV) is given for this material. The RV and TRV of the rejuvenated bitumen are plotted in a radar chart. The RV results can be seen in Figure 8, and it shows contrasting values between ageing stability and the medium/low-temperature performance-based properties Figure 8. For example, reB-E has shown advantages in fatigue and low-temperature properties but drawbacks in aging stability. However, reB-B has shown the highest TRV and either rank first or second in most of the performance-based properties, indicating that Rej-B can keep the balance on both sides and probably is a very efficient rejuvenator in all aspects. In this case, the added SBS polymer played a very important role in compensating the loss of SBS polymer, and at the same time, the degradation of SBS can reduce the aging of the base asphalt.

The determination of rejuvenator dosage in the recycling of RAP is a practical concern. The traditional method is to determine the rejuvenator dosage according to rejuvenated bitumen's penetration and softening point values. In this research, it is found that a series of performance-based tests can also be used to determine the rejuvenator dosage in recycling. For example, the relaxation tests were performed at 0 °C, with 1% shear strain (in 0.1 seconds) at the beginning and followed by 100 seconds of relaxation time. As illustrated in Figure 9, the maximum stress at 0.1s showed an exponential relationship with the rejuvenator dosage added to the aged PMB. An exponential fitted curve can be established between the maximum stress and rejuvenator dosage. As the maximum stress of original PMB has been tested, the rejuvenator dosage to recover rejuvenated binder's maximum stress to its original state can be calculated according to the exponential fitted curve.

A promising technique for observing asphalt microstructure is the E-SEM. The electron beam emitted by the E-SEM displaces the lighter binder molecules, revealing a microstructure, which has been shown to correspond to the resins and possibly a part of the asphaltenes fraction of the binder. As illustrated in Figure 10, the morphology of bitumen is mainly influenced by the aging state, rejuvenator dosage, rejuvenator type and addition of fresh bitumen. From the comparison of (a) and (b), the "worm structure" tend to be smaller, denser and coarser during the aging process. As shown in (c), the addition of 10% Rej B led the "worm structure" relatively larger and smoother, which is similar to that of original PMB. In the comparison of (c), (d) and (e), the increase of rejuvenator dosage led the "worm structure" to be larger and thicker. When rejuvenator dosage is the same (30%), the significant difference in (e), (f) and (g) indicates that the rejuvenator type also influences the "worm structure". Furthermore, when the rejuvenated binder was mixed with the fresh PMB, the morphology is not homogeneous, indicating the inhomogeneity of the miscibility state between fresh and aged PMB.

Exemplary method

1 Blend rejuvenator with RAP and get mixture 1

2 Heat the mixture 1 to 350-433 K(77-160 °C)

3 Heat the fresh aggregate to 200~280 °C; heat the fresh bitumen to 150~180 °C. The fresh bitumen can be base bitumen or polymer modified bitumen

4 Blend mixture 1 with heated fresh aggregate and heated bitumen to get mixture 2. The temperature of mixture 2 is usually 430-453 K(157-180 °C)

5 Pave mixture 2 on the road at 430-453 K(157-180 °C) and compact mixture 2 with a roller compactor.

6 Wait until the mixture 2 cool to the ambient temperature and open traffic.

CLAIMS

1. Rejuvenator for a polymeric network comprising intact polymer and aged polymer, wherein the polymeric network is selected from polymer modified bitumen, and modified asphalt comprising a polymer, comprising a mixture of

1-25 wt.% or 25-50 wt.% of at least one substantially intact polymer, preferably 3-20 wt.%, more preferably 4-15 wt.%, such as 5-11 wt.%, or preferably 30-45 wt.%, more preferably 35-40 wt.%,

15-50 wt.% of at least one aromatic oil, wherein the aromatic oil is selected from rubber processing oil, vacuum third residual from crude oil, reduced crude oil, synthetic or natural aromatic oil, mineral oil, and combinations thereof, ,

0.3-10 wt.% of at least one first additives, wherein the at least one first additive is selected from organic solvents, such as from terpenes, preferably 0.5-5 wt.%, more preferably 1-4 wt.%, such as 2-3 wt.%,

30-75 wt.% of at least one saturated or unsaturated acidic oil, wherein the at least one saturated or unsaturated acidic oil is an oil with more than 16 carbons and at least one carboxylic acid, preferably 35-68 wt.%, more preferably 40-63 wt.%, such as 47-55 wt.%,

0.4-10 wt.% of at least one resin for improving compatibility between substantially intact polymer and aged polymer in the network polymeric network, preferably 0.5-5 wt.%, more preferably 1-4 wt.%, such as 2-3 wt.%, wherein the at least one resin is selected from hydrocarbon resins,

wherein all weight percentages are based on the total weight of the rejuvenator.

2. Rejuvenator for a polymeric network according to claim 1, wherein the polymeric network is modified asphalt concrete.

3. Rejuvenator for a polymeric network according to any of claims 1-2, wherein the at least one substantially intact polymer is selected from co-polymers, preferably comprising a flexible domain, such as from linear copolymers, such as block copolymers, alternating copolymers, periodic copolymers, statistical copolymers, stereo-block copolymers, and gradient copolymers, branched copolymers, and graft copolymers, preferably from ethylene-butyl-acrylate (EBA), styrene-butadiene-styrene (SBS), and natural or synthetic rubber.

4. Rejuvenator for a polymeric network according to any of claims 1-3, wherein the aromatic oil comprising at least one aromatic moiety has an aromatic content of > 25%, preferably >30%, more preferably > 40%, even more preferably >50%, such as > 65%.

5. Rejuvenator for a polymeric network according to any of claims 1-4, comprising 20-45 wt.%, 25-40 wt.%, aromatic oil, such as 30-35 wt.% aromatic oil .

6. Rejuvenator for a polymeric network according to any of claims 1-5, wherein the aromatic oil is adapted to dissolve asphaltene, wherein the aromatic oil may be provided

as a liquid comprising 10-65 wt. % solvent.

7. Rejuvenator for a polymeric network according to any of claims 1-6, wherein the at least one first additive is selected from asphaltene solvents, such as monoterpenes ($C_{10}H_{16}$), preferably cyclic- or bicyclic monoterpenes, such as geraniol, terpineol, limonene, myrcene, linalool, and pinene, sesquiterpenes($C_{15}H_{24}$), such as humulene, farnesenes, and farnesol, diterpenes ($C_{20}H_{32}$), such as cafestol, kahweol, cembrene, and taxadiene, and from triterpenes ($C_{30}H_{48}$), such as squalene.

8. Rejuvenator for a polymeric network according to any of claims 1-7, wherein the at least one saturated or unsaturated acidic oil is an oil with more than 20 carbons and at least one carboxylic acid, such as rapeseed oil.

9. Rejuvenator for a polymeric network according to any of claims 3-8, wherein the at least one resin is selected from C_4-C_{12} resins, preferably C_5-C_{10} resins, more preferably C_6-C_9 resins.

10. Reclaimed polymeric network, in particular reclaimed modified bitumen, comprising 1-20 wt.% of at least one rejuvenator according to any of claims 1-9, such as 2-15 wt.%, and rejuvenated aged polymer modified bitumen, wherein the polymer in the modified bitumen is selected from block polymers, such as styrene-butadiene-styrene (SBS) polymer, natural or synthetic latex, such as polychloroprene latex, and reclaimed rubber.

11. Asphalt product comprising reclaimed polymer modified bitumen according to claim 10, or a rejuvenator according to any of claims 1-9.

12. Asphalt according to claim 11, further comprising one or more of particles, coarse aggregate, filler, extender, fibres, oxidants, anti-oxidants, plastics, anti-stripping agents, and waste material.

13. Construction comprising asphalt according to any of claims 11-12, wherein the construction is selected from a multilayer civil engineering system, such as an asphalt concrete surfacing layer on orthotropic steel deck bridge, a foundation, a wall, a basement, a building, and combinations thereof, and/or
wherein the construction comprises at least one of a waterproofing, a top layer, and a deck layer.

14. Method of applying a rejuvenator mixture for a polymeric network, the polymeric network comprising intact polymer and aged polymer, according to any of claims 1-9, wherein the polymeric network is selected from polymer modified bitumen, and modified asphalt comprising a polymer, comprising mixing the rejuvenator and reclaimed asphalt pavement comprising aged polymer modified bitumen into a first mixture, such as during 30 seconds-5 minutes, pre-heating the first mixture to a temperature of 350-433 K(77-160 °C) during a pre-heating period of time, such as during 1-60 minutes, blending the first mixture with aggregate at a temperature of 473-553 K(200-280 °C) and bitumen at a temperature of 423-443 K(150-170 °C)into a second mixture for a second period of time

at a temperature of 473-553 K(200-2080 °C), in particular fresh aggregate and fresh bitumen, such as during 1-20 minutes, wherein the second mixture has a temperature of 430-473 K(157-200 °C), maintaining said temperature for at least 1 minute, such as during 2-30 minutes, cooling the mixture, such as to ambient temperature, during a cooling time of 10-60 minutes, and applying the mixture, such as to a road.15. Use of a rejuvenator for a polymeric network according to any of claims 1-9, wherein the polymeric network is selected from polymer modified bitumen, modified asphalt comprising a polymer, wherein the rejuvenator is applied for healing the polymeric network, for improving viscoelasticity, enhancing colloidal stability, dissolving asphaltene, improving durability, improving anti-cracking, improving aging resistance, improving compatibility, improving relaxation, increasing maximum stress, or a combination thereof.

1/6

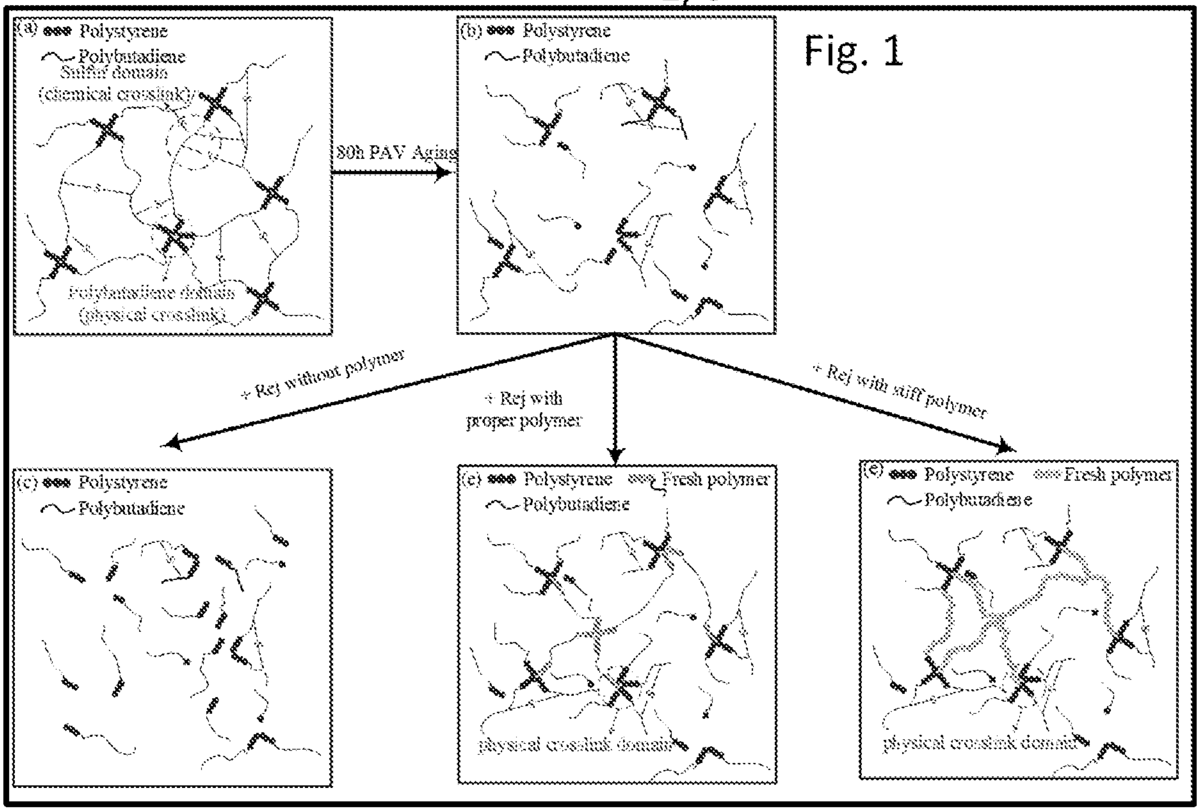

(a) Polystyrene
Polybutadiene
Sulfur domain
(chemical crosslink)
Polybutadiene domain
(physical crosslink)
80h PAV Aging
(b) Polystyrene
Polybutadiene
+ Rej without polymer
+ Rej with
proper polymer
+ Rej with stiff polymer
(c) Polystyrene
Polybutadiene
(e) Polystyrene
Fresh polymer
Polybutadiene
physical crosslink domain
(e) Polystyrene
Fresh polymer
Polybutadiene
physical crosslink domain

Fig. 1

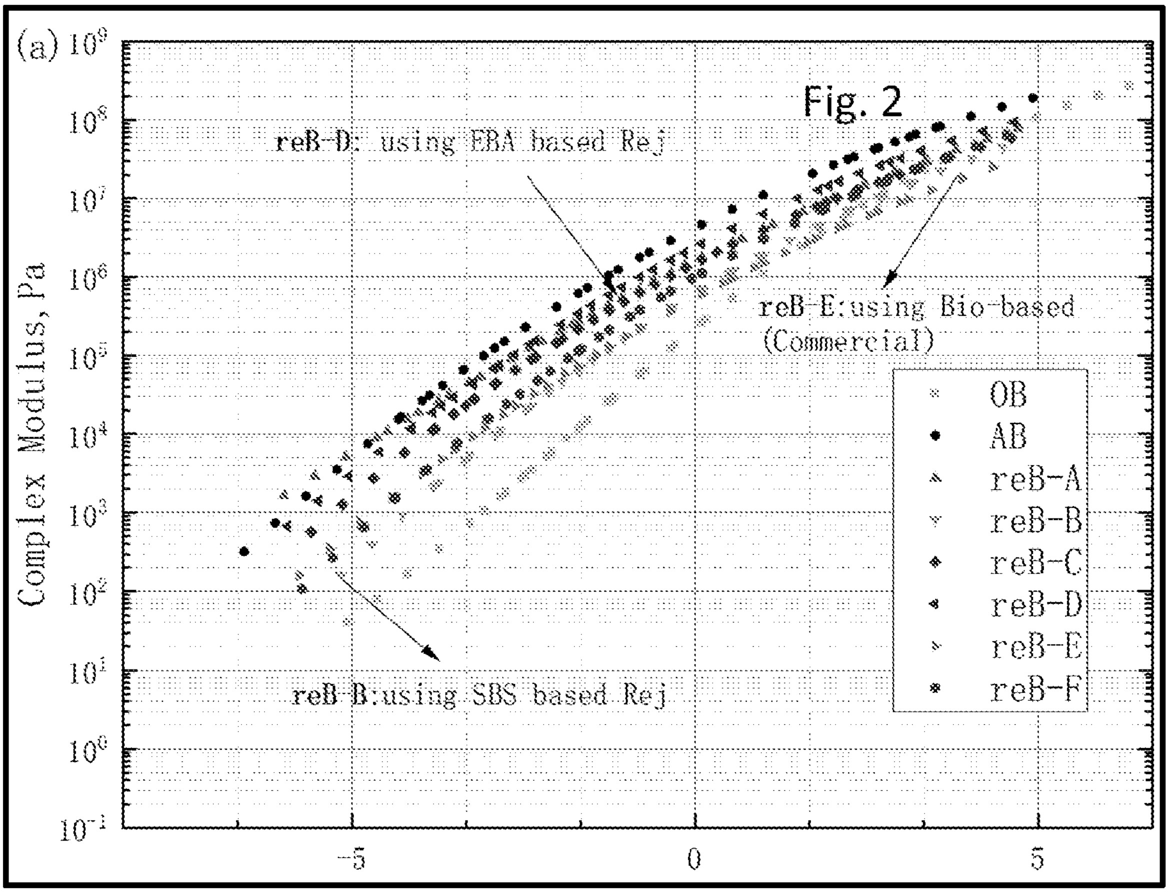

(a)
Complex Modulus, Pa
reB-D: using EBA based Rej
reB-E:using Bio-based
(Commercial)
reB-B:using SBS based Rej
OB
AB
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F
-5
0
5

Fig. 2

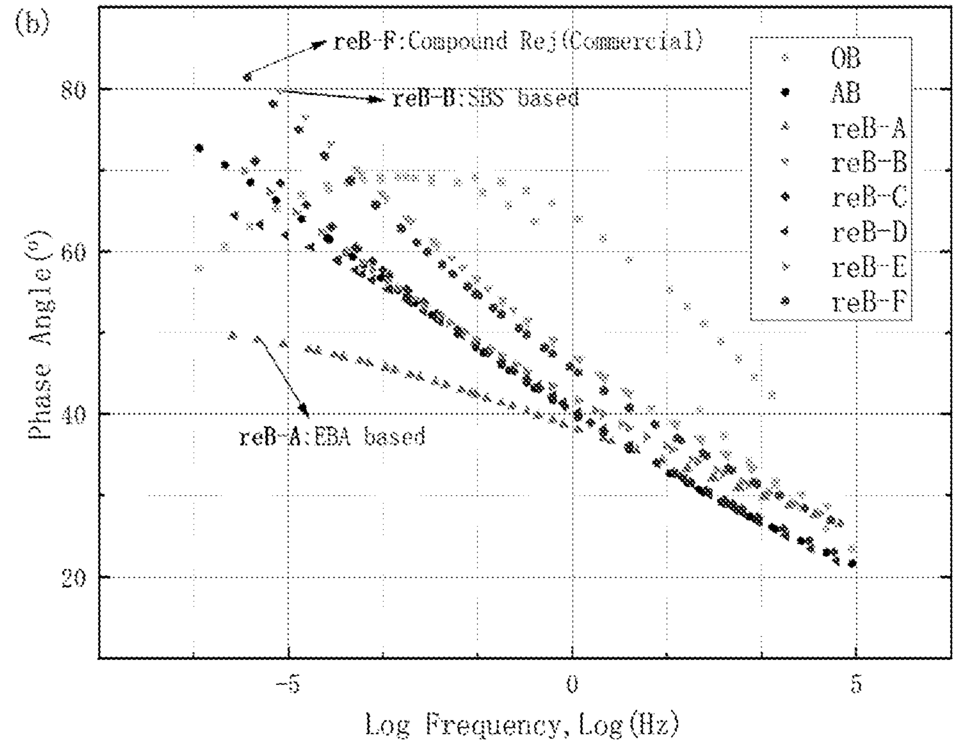

(b)
reB-F:Compound Rej(Commercial)
reB-B:SBS based
reB-A:EBA based
OB
AB
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F
Phase Angle (°)
Log Frequency, Log(Hz)
80
60
40
20
-5
0
5

Fig. 3

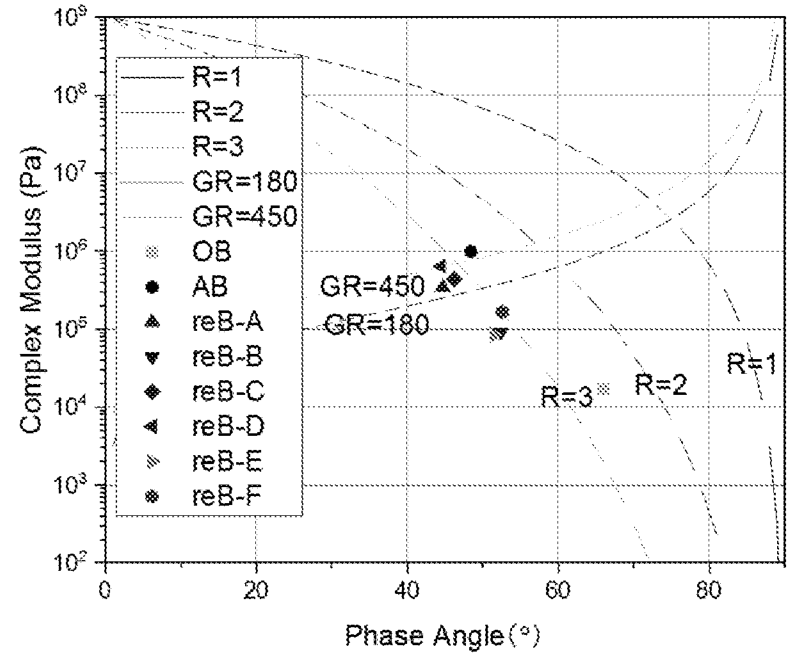

R=1
R=2
R=3
GR=180
GR=450
OB
AB
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F
GR=450
GR=180
R=3
R=2
R=1
Complex Modulus (Pa)
Phase Angle (°)
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
0
20
40
60
80

Fig. 4

Fig. 5

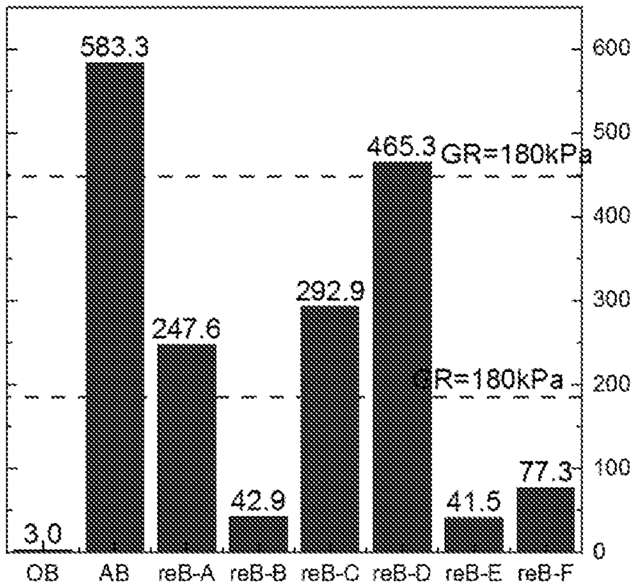
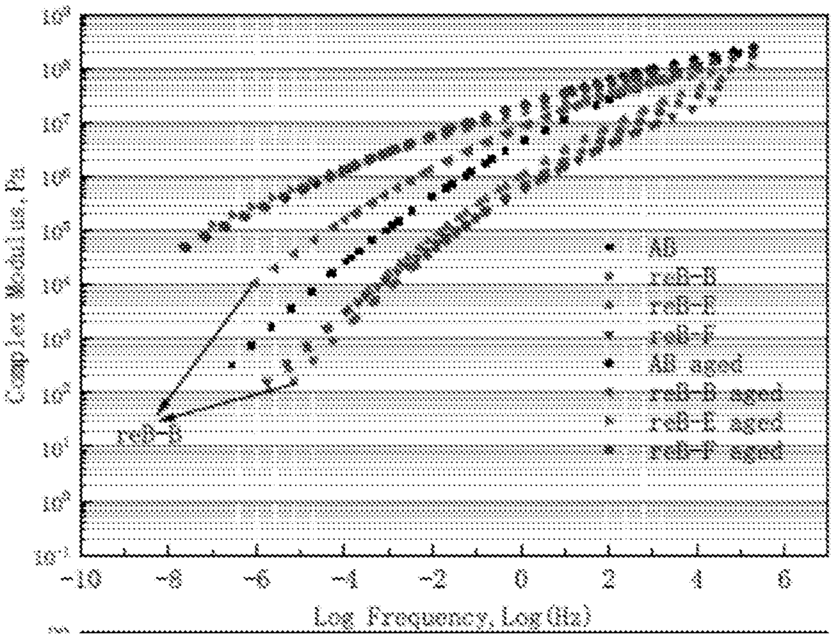

583.3
465.3
GR=180kPa
292.9
247.6
GR=180kPa
42.9
41.5
77.3
3.0
OB
AB
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F
Glover-Rowe Parameter (Pa)
0
100
200
300
400
500
600

Fig. 6


Complex Modulus, Pa
Log Frequency, Log (Hz)
AB
reB-B
reB-E
reB-F
AB aged
reB-B aged
reB-E aged
reB-F aged
reB-B
-10
-8
-6
-4
-2
0
2
4
6

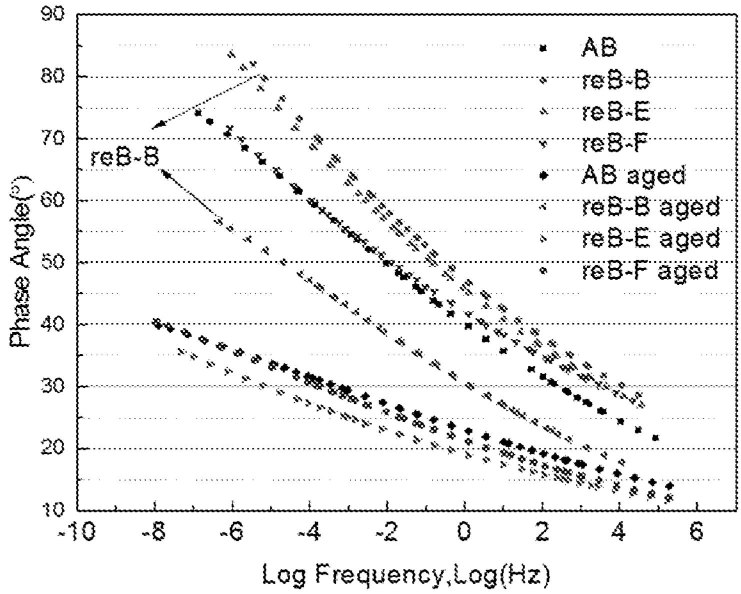

90
80
70
60
50
40
30
20
10
-10
-8
-6
-4
-2
0
2
4
6
Phase Angle(°)
Log Frequency,Log(Hz)
AB
reB-B
reB-E
reB-F
AB aged
reB-B aged
reB-E aged
reB-F aged
reB-B

Fig. 7

Fig. 8

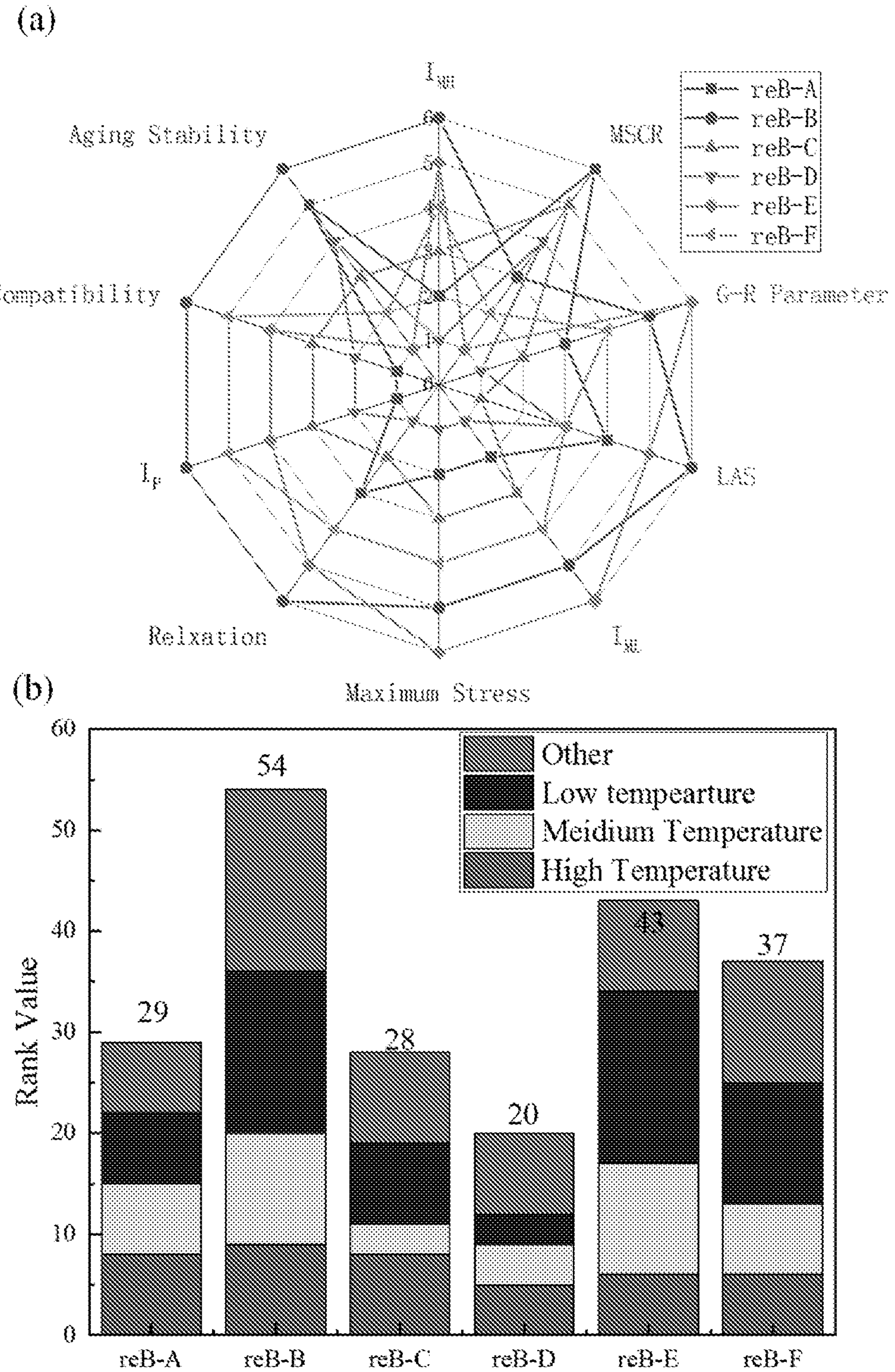

(a)
I_{WH}
MSCR
G-R Parameter
LAS
I_{WL}
Maximum Stress
Relxation
I_F
Compatibility
Aging Stability
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F
(b)
Rank Value
Other
Low tempearture
Meidium Temperature
High Temperature
29
54
28
20
43
37
reB-A
reB-B
reB-C
reB-D
reB-E
reB-F

Fig. 9

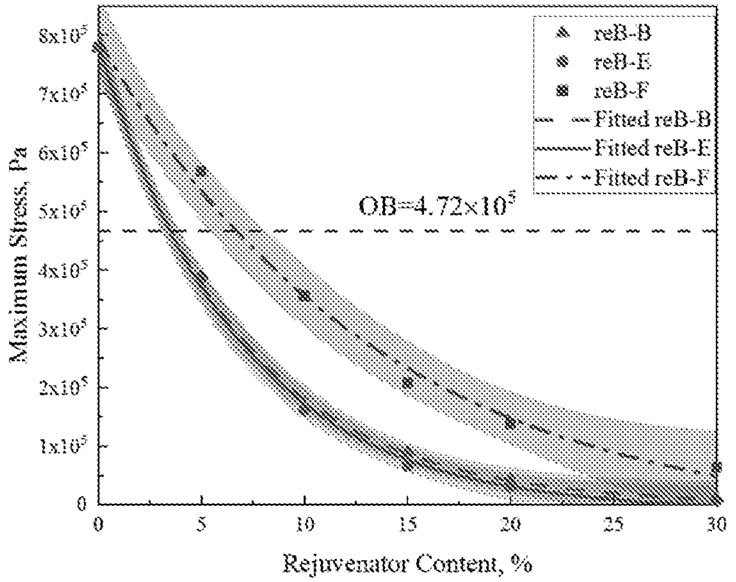
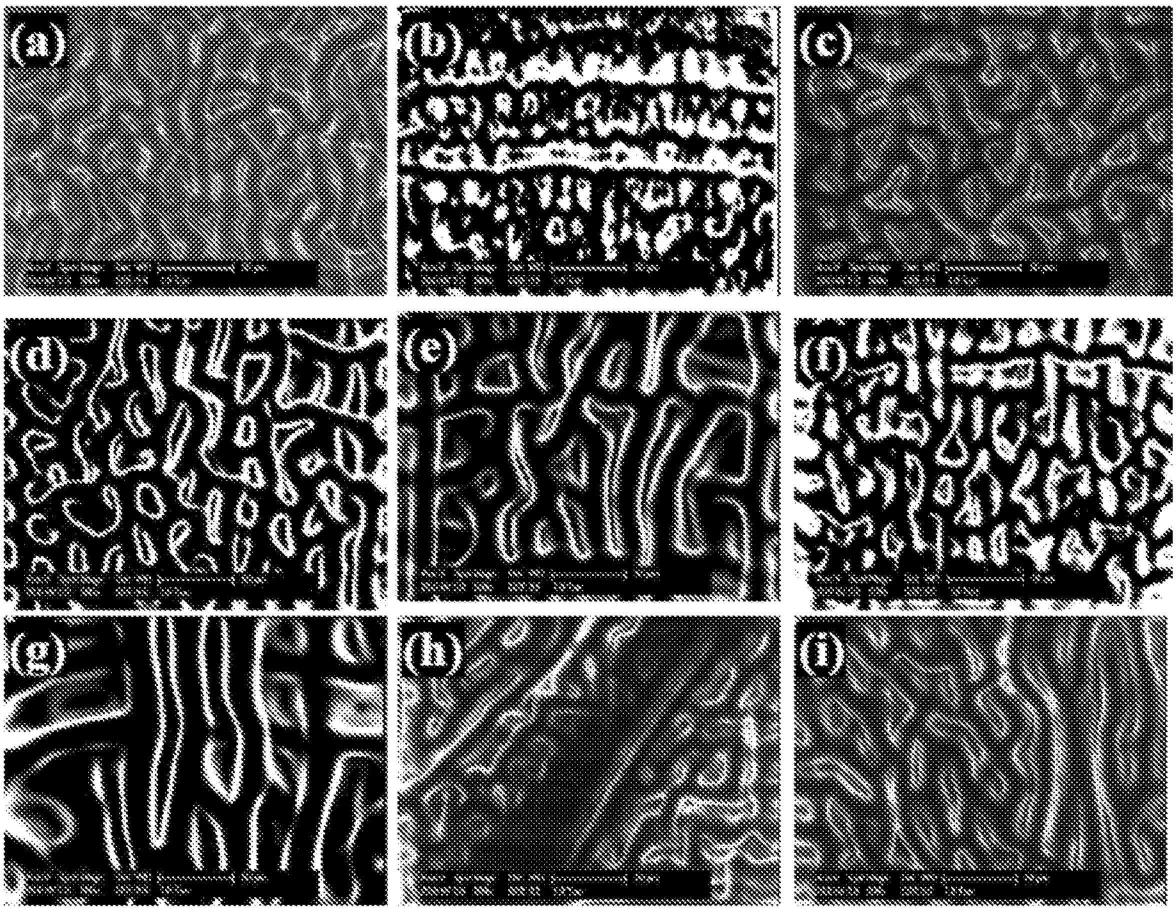

reB-B
reB-E
reB-F
Fitted reB-B
Fitted reB-E
Fitted reB-F
OB=4.72×10^5
Maximum Stress, Pa
Rejuvenator Content, %
0
5
10
15
20
25
30
8x10^5
7x10^5
6x10^5
5x10^5
4x10^5
3x10^5
2x10^5
1x10^5

Fig. 10


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2021/050354

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L91/00 C08L95/00 C08L93/00 C08L53/02 C08K5/01
C04B26/26 E01C7/18 E01C11/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08K C09J E01C C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	Amy Epps Martin ET AL: "THE EFFECTS OF RECYCLING AGENTS ON ASPHALT MIXTURES WITH HIGH RAS AND RAP BINDER RATIOS (Project N? 9-58)", , 1 March 2015 (2015-03-01), XP055356566, Retrieved from the Internet: URL:http://onlinepubs.trb.org/onlinepubs/nchrp/docs/NCHRP09-58_PhI_InterimReport.pdf [retrieved on 2017-03-20] paragraph [02.1]; figure 2.1 the whole document -----	1-15

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 2021	06/09/2021

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	olde Scheper, Bernd

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	PANOS APOSTOLIDIS ET AL: "Synthesis of Asphalt Binder Aging and the State of the Art of Antiaging Technologies", TRANSPORTATION RESEARCH RECORD., vol. 2633, no. 1, 1 January 2017 (2017-01-01), pages 147-153, XP055526871, US ISSN: 0361-1981, DOI: 10.3141/2633-17 the whole document -----	1-15
T	CONG PEILIANG ET AL: "Investigation on rejuvenation methods of aged SBS modified asphalt binder", FUEL, IPC SIENCE AND TECHNOLOGY PRESS , GUILDFORD, GB, vol. 279, 6 July 2020 (2020-07-06), XP086241441, ISSN: 0016-2361, DOI: 10.1016/J.FUEL.2020.118556 [retrieved on 2020-07-06] page 2 the whole document -----	1-15
T	LI JIAN ET AL: "New Additive for Use in Hot In-Place Recycling to Improve Performance of Reclaimed Asphalt Pavement Mix", TRANSPORTATION RESEARCH RECORD., vol. 2445, no. 1, 1 January 2014 (2014-01-01), pages 39-46, XP055773798, US ISSN: 0361-1981, DOI: 10.3141/2445-05 the whole document -----	1-15
T	MOUILLET ET AL: "Infrared microscopy investigation of oxidation and phase evolution in bitumen modified with polymers", FUEL, IPC SIENCE AND TECHNOLOGY PRESS , GUILDFORD, GB, vol. 87, no. 7, 22 February 2008 (2008-02-22), pages 1270-1280, XP022495863, ISSN: 0016-2361, DOI: 10.1016/J.FUEL.2007.06.029 the whole document ----- -/--	1-15

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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