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(54) Title: MODIFIED ASPHALTS AND METHODS FOR PRODUCING THE SAME

(57) Abstract: Modified asphalts and methods for producing the same are disclosed. The modified asphalts can include asphalt having a T5 boiling point of 400 °C or more, an olefin compound, and an acid promoter. The modified asphalt can include at least a portion of the olefin compound chemically grafted to at least a portion of the asphalt. The method can include exposing the asphalt, olefin compound, and acid promoter to a temperature of about 160 °C or more.

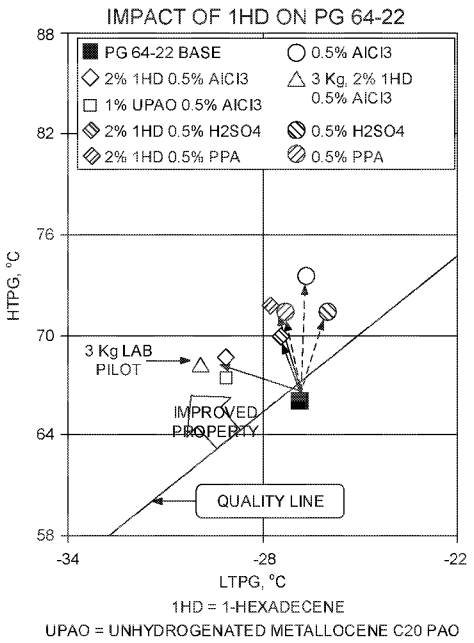


FIG. 1.

WO 2020/131311 A1

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MODIFIED ASPHALTS AND METHODS FOR PRODUCING THE SAME

FIELD

[0001] Modified asphalts and methods for producing the same are provided.

BACKGROUND

[0002] Asphalt, a material derived from the distillation residue of crude petroleum, can be utilized as a binder for stone aggregate in pavement construction. In certain conventional systems, the asphalt may be blended with various components, such as one or more polymers, to produce an asphalt binder for use in pavement construction that has a reduced tendency to creep and rut in warmer weather and/or can minimize cracking of the pavement in colder weather. Certain conventional high performance asphalt binders are known that may be suited for road surfaces with high load, stress, and deformation such as highways, bridges, and runways. However, the production of such conventional high performance asphalt binders can be resource intensive and may require complex formulations and/or manufacturing processes. It would be desirable to produce modified asphalts, e.g., high performance asphalt binders, in a less resource intensive manner and/or with a reduced manufacturing or formulation complexity that exhibit suitable storage stability.

[0003] Chinese Patent No. 102181299 describes the conversion of petroleum pitch to mesophase pitch at increased temperature and pressure. The conversion utilizes small C_2-C_4 olefins including ethylene, propylene, and 1-butene, and a Friedel-Crafts catalyst including HF, sulfuric acid, and boron trifluoride. The conversion is performed at elevated pressure which requires complex engineering in a manufacturing facility.

[0004] PCT Application Publication No. WO1999/002776 describes bitumen-polymer compositions that include the use of styrene-butadiene-styrene (SBS) and a sulfur coupling agent. The sulfur coupling agent can cross-link the butadiene backbone of SBS to create cross-linked SBS in the composition. However, the formation of these bitumen-polymer compositions with the cross-linked SBS requires an elevation in the paving temperature and results in increased H_2S emissions.

[0005] US Patent No. 6,743,838 describes polyepoxy-polymer-linked asphalt having enhanced properties. The polyepoxy-polymer-linked asphalt is made by reacting a glycidyl-functionalized ethylene copolymer with reactive asphalt. However, the method of manufacturing this polyepoxy-polymer-linked asphalt is rather complex, as the polyepoxy-polymer-linked asphalt has a propensity to gel if the cross-linking/grafting reaction is not controlled.

SUMMARY

[0006] In one aspect, a method for modifying an asphalt is provided. The method can include exposing an asphalt having a T5 boiling point of 400 °C or more to: 1) 0.2 wt. % to 5 wt. % of an

olefin compound having a molecular weight of 0.2 kDa to 110 kDa; and 2) 0.1 wt. % to 2 wt. % of an acid promoter to form a modified asphalt.

[0007] In another aspect, an asphalt composition is provided. The asphalt composition can include an asphalt having an initial or T5 boiling point of 400 °C or more; 0.2 wt. % to 5 wt. % of an olefin compound having a molecular weight between 50 kDa and 110 kDa; and 0.1 wt. % to 2 wt. % of an acid promoter selected from $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, zeolites, or a combination thereof. The asphalt composition can be formed at a temperature of 160 °C to 230 °C. Additionally, the asphalt composition can have a high temperature performance grade of 58 °C or more and a low temperature performance grade of -34 °C to -16 °C.

BRIEF DESCRIPTION OF THE FIGURES

[0008] FIG. 1 depicts a SUPERPAVE™ matrix grid showing the performance grade of various modified asphalts.

[0009] FIG. 2 depicts a bar graph of storage stability test results for various modified asphalts.

[0010] FIG. 3 depicts another bar graph of storage stability test results for various modified asphalts.

[0011] FIG. 4 depicts a graph of the multi-stress creep recovery test results for various modified asphalts.

[0012] FIG. 5 depicts another graph of the multi-stress creep recovery test results for various modified asphalts.

DETAILED DESCRIPTION

Overview

[0013] In various aspects, modified asphalts and methods for producing the same are provided. In aspects, the modified asphalts can include an asphalt that has been modified by the chemical grafting of an olefin compound facilitated by an acid promoter.

[0014] Asphalt is a viscoelastic semi-solid bituminous material derived from the distillation residue of crude petroleum. Asphalt may be obtained from a variety of sources including straight run vacuum residue, mixtures of vacuum residue with diluents such as vacuum tower wash oil, paraffin distillate, aromatic and naphthenic oils and mixtures thereof, oxidized vacuum residues or oxidized mixtures of vacuum residues and diluent oils and the like. Other asphalt materials may include coal tar pitch, rock asphalt and naturally occurring asphalt.

[0015] Because asphalt is hydrophobic and has good adhesive and weathering characteristics, it may be used as a binder or cement for stone or rock aggregate in pavement construction (conventionally about 5 weight % of the mixture). If, because of the nature of the crude oil distilled,

the asphalt is too soft at ambient temperature, a harder product may be manufactured, for example, by increasing the vacuum distillation tower temperature, by extraction of the lighter components with liquid propane or other solvents, or by oxidizing by air blowing at an elevated temperature. However, in most cases, these manufacturing processes can produce asphalts that are too brittle at low temperature, and result in excessive cracking in cold weather. As discussed above, another way of stiffening soft asphalt with less detrimental impact on its low temperature properties and so as to extend its useful temperature range is by blending with suitable polymers. Polymers can reduce the tendency of an asphalt pavement to creep and rut in warm weather by increasing its high temperature viscoelastic stiffness and at the same time permit the use of softer grades of asphalt to minimize cracking in cold weather. Thus, conventionally, polymers have been blended with asphalt which permit the use of, in some instances, softer grades of asphalt to reduce cracking in cold weather without risking excessive softening leading to undesirable deformation/rutting in hot, summer weather. Unfortunately, many of such asphalt-polymer blends are not storage stable.

[0016] For example, a polymer such as polyethylene has been added to asphalt to produce asphalts which exhibit an increased resistance to creep or deformation. In addition, polyethylene modified asphalts should also have good compatibility between the asphalt and polyethylene, and be stable at high temperatures during storage and asphalt plant operation for ease of handling and application. Compatibility between the polyethylene and asphalt is important to ensure that the engineering properties of both the asphalt and polyethylene are transferred to the finished product and to provide good long term performance. However, most polyethylene modified asphalts require either continuous mixing or the addition of various additives to avoid phase incompatibility which require continuous high shear mixing to obtain physical dispersion of a polyolefin in bitumen, and/or the addition of one or more dispersants to a polyethylene modified asphalt to avoid phase separation.

[0017] The addition of block copolymer such as styrene-butadiene-styrene (SBS) has been used to modify asphalt for additional applications, such as roofing sheets, adhesives and coatings. In certain systems, such a modified asphalt may exhibit a higher elasticity and greater range of plasticity than straight-run asphalts. In certain other systems, SBS-modified asphalts have resulted in improved adhesiveness, strength and deformation resistance, and can be useful as a pavement structure for roadways which experience heavy repetitive loads.

[0018] In various systems, asphalt can be made by distillation under vacuum to a cut temperature yielding, typically, a resid with particular penetration at 25°C and viscosity at 100 °C. Once it meets the specific penetration and viscosity ranges the asphalt may be routed to a rundown tank where it can be held for certification testing against all specifications. Once it meets the

specifications the tank of asphalt can be certified and sealed until shipped to the customer with no new asphalt production added. Prior to delivery such asphalt can be stored in the refinery at industry typical temperatures depending on the hardness or stiffness of the asphalt. Reference is made to a best practices publication issued by the Asphalt Paving Environmental Council comprising The Asphalt Institute, the National Asphalt Paving Association and the State Asphalt Pavement Associations entitled "Best Management Practices to Minimize Emissions During HMA Construction", EC 101 04/00. This publication contains a table insert of "Typical Asphalt Binder Temperatures". The highest stiffness, lowest penetration asphalt listed, designated as PG 82-22 has a recommended hot mix asphalt (HMA) plant asphalt storage tank temperature range of 157 to 168 °C and a recommended HMA plant mixing temperature of 143 to 171 °C when mixing the fluid asphalt with the aggregate to adequately cover all of the aggregate surface area. In order to accommodate this industry practice the asphalt manufacturer strives to deliver to the HMA plant at an industry accepted 176 °C maximum. This requires that the asphalt manufacturer heat the asphalt at the lowest possible temperature to guarantee delivery to these temperature limits. This practice of minimizing emissions translates to mixing and blending vacuum resid asphalt and enhanced asphalts to the lowest, feasible temperature ranges. In addition to generating emissions, storage of asphalt at higher temperatures can lead to product hardening during storage and difficult handling and unloading at the HMA plant. Therefore, industry practice is to store asphalt and asphalt based products at the lowest, feasible temperature as soon as possible following manufacture.

[0019] It is not always practical to keep an asphalt-polymer blend continuously homogenized before mixing the blend with aggregates: consequently, storage stability is desirable to keep the blend from separating under storage conditions. Various methods have been suggested for making polymer modified asphaltic compositions that are sufficiently storage stable and that also have the visco-elastic properties in the ranges required for a particular application. In most of cases, this results in products for which the softening point property is strongly affected by the nature of the virgin asphalt.

[0020] Various components have been added to asphalts and polymer modified asphalts to improve their physical properties such as storage stability and viscoelastic properties, including one or more of the polymers mentioned above, as well as ethylvinyl acetate (EVA), polyphosphoric acid (PPA), and reactive elastomeric terpolymers. However, such conventional manufacturing of binder formulations can be complex and/or resource intensive.

[0021] The resource intensive and/or complex manufacturing processes required for certain conventional asphalt binders is evident in the conventional asphalt binders that utilize a chemically

reactive and/or cross-linked polymer to enhance specific performance properties, e.g., elastic properties, of an asphalt binder. In one example, such a cross-liked polymer can be a cross-linked SBS, where the butadiene backbone is cross-linked via the addition of a vulcanization agent, e.g., sulfur. However, such a modified asphalt binder may require elevated paving temperatures and result in increased H_2S emissions.

[0022] Other conventional modified asphalts can include the use of reactive elastomeric terpolymers. The reactive elastomeric terpolymers can include functional glycidyl functional groups in the polymer backbone, which may react with other polymer chains and/or asphaltene or resin constituents in the asphalt. However, such a modified asphalt can have an increased propensity to gel if the cross-linking or grafting reaction under certain conditions, resulting in a complex manufacturing process.

[0023] The modified asphalts and methods of producing the same disclosed herein can provide modified asphalts with improved performance properties that can be manufactured in a less complex manner. For instance, the modified asphalts described herein can be manufactured at ambient pressure and can be manufactured in several manners, such as bulk methods, high shear mixing, or low shear mixing. Further, in aspects, the asphalt can be modified by the addition of an olefin compound and an acid promoter, which can facilitate the chemical grafting of the olefin onto the asphalt. In such an aspect, after the chemical grafting is performed the acid promoter can stay in the modified asphalt, as there is no requirement to remove it from the modified asphalt product. Additionally, in certain aspects, the modified asphalt described herein can exhibit improved performance properties over prior asphalt-polymer products. For instance, in certain aspects, the modified asphalts described herein can exhibit improved multi-stress creep recovery and/or improved storage stability.

[0024] In this discussion, unless otherwise specified, a "T5 boiling point" refers to a temperature at which 5 wt. % of the feed, effluent, product, stream, or composition of interest will boil. One suitable method for measuring boiling points of crude oils or heavy feeds is ASTM test method D7169.

Modified Asphalt Compositions – Asphalt Component

[0025] In various aspects, the modified asphalt compositions disclosed herein can include an asphalt, one or more olefin compounds, and an acid promoter. In certain aspects, the asphalt is viscoelastic semi-solid bituminous material derived from the distillation residue of crude petroleum. In one or more aspects, the asphalt can be a product of atmospheric and/or vacuum distillation of crude petroleum.

[0026] In aspects, the asphalt can exhibit a T5 boiling point of about 400 °C or more, such as up to 550 °C or more, about 450 °C or more, such as up to 550 °C or more, or about 500 °C or more, such as up to 550 °C or more.

[0027] One way of characterizing an asphalt composition is by using SUPERPAVE™ criteria. SUPERPAVE™ criteria (as described in the 1996 edition of the American Association of State Highway and Transportation Officials (AASHTO) Provisional Standards Book and 2018 revised edition) can be used to define the Maximum and Minimum Pavement service temperature conditions under which the binder must perform. SUPERPAVE™ is a trademark of the Strategic Highway Research Program (SHRP) and is the term used for new binder specifications as per AASHTO MP-1 standard. Maximum Pavement Temperature (or "application" or "service" temperature) is the temperature at which the asphalt binder will resist rutting (also called Rutting Temperature). Minimum Pavement Temperature is the temperature at which the binder will resist cracking. Low temperature properties of asphalt binders can be measured by Bending Beam Rheometer (BBR). According to SUPERPAVE™ criteria, the temperature at which a maximum creep stiffness (S) of 300 MPa at 60s loading time is reached, is the Limiting Stiffness Temperature (LST). Minimum Pavement Temperature at which the binder will resist cracking (also called Cracking Temperature) is equal to LST-10°C.

[0028] The SUPERPAVE™ binder specifications for asphalt paving binder performance establishes the high temperature and low temperature stiffness properties of an asphalt. The nomenclature is PG XX-YY which stands for Performance Grade at high temperatures (HT), XX, and at low temperatures (LT), -YY degrees C, wherein -YY means a temperature of minus YY degrees C. Asphalt must resist high summer temperature deformation at temperatures of XX degrees C and low winter temperature cracking at temperatures of -YY degrees C. An example popular grade in Canada is PG 58-28. Each grade of higher or lower temperature differs by 6°C in both HT and LT. This was established because the stiffness of asphalt doubles about every 6°C. One can plot the performance of asphalt on a SUPERPAVE™ matrix grid. The vertical axis represents increasing high PG temperature stiffness and the horizontal axis represents decreasing low temperature stiffness towards the left, which can be seen in FIG. 1 and is discussed further below.

[0029] In some aspects, the asphalt used for producing the modified asphalts described herein can have a performance grade at high temperature of 58 °C or more, or 52 °C or more, or 46 °C or more, or 40 °C or more; or from about 40 °C to about 58 °C, or from about 46 °C to about 58 °C. In the same or alternative aspects, the asphalt used for producing the modified asphalts described herein can have a performance grade at low temperature of about -16 °C or less, about -22 °C or

less, about -28 °C or less, or about -34 °C or less; or from about -34 °C to about -22 °C, or from about -34 °C to about -16 °C.

Modified Asphalt Compositions – Olefin Compound Component

[0030] In certain aspects, the modified asphalts described herein can include an asphalt modified by an additive or polymer, e.g., an olefin compound. In various aspects, the olefin compound can have a molecular weight of about 0.2 kDa or more, about 2.0 kDa or more, or about 50 kDa or more. In aspects, the olefin compound can have a molecular weight of about 200 kDa or less, about 150 kDa or less, or about 110 kDa or less. In various aspects, the olefin compound can have a molecular weight of about 0.2 kDa to about 110 kDa, about 2.0 kDa to about 110 kDa, or about 50 kDa to about 110 kDa.

[0031] In various aspects, the olefin compound can include any compound having at least one site of chemical unsaturation. In one aspect, the olefin compound can include a polymer comprising ethylene monomers, a polymer comprising propylene monomers, or a combination thereof. A wide variety of polymers comprising propylene monomers, ethylene monomers, ethylene-propylene co-polymers, or a combination thereof are known, and one such specific example that is useful in the modified asphalts described herein includes, but is not limited to, the VISTAMAXX™ performance polymers from ExxonMobil. In aspects, the olefin compound can include an ethylene propylene diene terpolymer. A wide variety of ethylene propylene diene terpolymers are known and example ethylene propylene diene terpolymers that are useful in the present modified asphalts include, but are not limited to, the VISTALON™ EPDM rubbers from ExxonMobil. In various aspects, the olefin compound can include one or more vinyl terminated polymers. In one aspect, the vinyl terminated polymer can include an atactic polypropylene having one or more vinyl/vinylidiene terminal double bonds. A wide variety of vinyl terminated polymers are available including, but not limited to, those described in U.S. Patent Nos.: 8,283,428, 8,093,336, 6,444,773, 8,372,930, 7,279,536, 6,117,962, 6,147,180, 8,283,428, and 9,255,168.

[0032] In certain aspects, the olefin compound can include linear or branched olefin compounds having about 12 carbon atoms or more, about 14 carbon atoms or more, about 16 carbon atoms or more, or about 20 carbon atoms or more. In aspects, the olefin compound can include linear or branched olefin compounds of any size, as long as such compounds have more than 4 carbon atoms. In aspects, small olefin compounds, e.g., olefin compounds having four carbon atoms or less, are too small to provide any improved properties to the modified asphalt.

[0033] In certain aspects, the olefin compound can be present in the modified asphalt in a concentration of about 0.5 wt. % or more, about 0.75 wt. % or more, or about 1.0 wt. % or more. In the same or alternative aspects, the olefin compound can be present in the modified asphalt in a

concentration of about 7.0 wt. % or less, about 5.0 wt. % or less, or about 3.0 wt. % or less. In certain aspects, the olefin compound can be present in the modified asphalt in a concentration of about 0.5 wt. % to about 7.0 wt. %, about 0.75 wt. % to about 5.0 wt. %, or about 1.0 wt. % to about 3.0 wt. %.

Modified Asphalt Compositions – Acid Promoter

[0034] As noted above, the modified asphalts described herein can include an acid promoter. In aspects, the acid promoter can catalyze the chemical grafting of the olefin compound onto the asphalt. In aspects, the acid promoter can be a Lewis acid or a Bronsted acid. A non-limiting list of acid promoters that can be used to produce the modified asphalts described herein includes $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, solid acids, such as zeolites, and combinations thereof. In one aspect, the acid promoter can be any convenient Friedel-Crafts catalyst, such as $AlCl_3$, that in appropriate conditions can catalyze the alkylation of an aromatic component of the asphalt, for example. In certain aspects, the strength of the Lewis acid utilized can directly correlate to increased performance of the modified asphalt, e.g., improved performance grade at high and/or low temperatures, increased storage stability, or improved delayed elastic response. For instance, utilizing the acid promoter $AlCl_3$ (a stronger Lewis acid than H_2SO_4) in manufacturing a modified asphalt described herein may result in enhanced performance grade or storage stability compared to a modified asphalt that was made with the use of H_2SO_4.

[0035] In certain aspects, the acid promoter can be present in the modified asphalt in a concentration of about 0.1 wt. % or more, about 0.25 wt. % or more, or about 0.3 wt. % or more. In the same or alternative aspects, the acid promoter can be present in the modified asphalt in a concentration of about 0.9 wt. % or less, about 0.75 wt. % or less, or about 0.5 wt. % or less. In certain aspects, the acid promoter can be present in the modified asphalt in a concentration of about 0.1 wt. % to about 0.9 wt. %, about 0.25 wt. % to about 0.75 wt. %, or about 0.25 wt. % to about 0.5 wt. %.

Modified Asphalt Compositions – Properties

[0036] In various aspects, the modified asphalts described herein can exhibit one or more improved properties. For instance, in certain aspects, the modified asphalts described herein can exhibit a Penetration at 25 °C of about 30 decimillimeters (dmm) (1 dmm = 0.1 mm) to about 110 dmm, or about 40 dmm to about 100 dmm, as determined according to test method EN 1426. In the same or alternative aspects, the modified asphalts described herein can exhibit a Penetration at 25 °C, 100 g test for 5 s, of about 20 dmm to about 110 dmm, or about 30 dmm to about 100 dmm, as determined according to Chinese test method T0604.

[0037] In certain aspects, the modified asphalts described herein can exhibit a Softening Point of about 50 °C or more, about 55 °C or more, about 60 °C or more, or about 65 °C or more, as determined according to test method EN 1427. In the same or alternative aspects, the modified asphalts described herein can exhibit a R & B Softening Point of about 50 °C or more, about 55 °C or more, or about 60 °C or more, as determined according to Chinese test method T0606.

[0038] In one or more aspects, the modified asphalts described herein can exhibit a storage stability of about 0.8 to about 1.2, or about 0.9 to about 1.1 as determined according to ASTM test method D7173 and described further below in the Examples.

[0039] In various aspects, the modified asphalts described herein can exhibit an improved delayed elastic response. For instance, in certain aspects, the modified asphalts described herein may exhibit a non-recoverable creep compliance at 64 °C, of about 1 kPa^{-1} or less, or about 0.5 kPa^{-1} or less, as determined according to the American Association of State Highway and Transportation Officials test method AASHTO M-332. In the same or alternative aspects, the modified asphalts described herein may exhibit an average Multi-Stress Creep Recovery at 3.2 kPa and 64 °C of about 35 % or more, about 40 % or more, about 50 % or more, or about 60 % or more, as determined according to the American Association of State Highway and Transportation Officials test method AASHTO M-332.

Modified Asphalt Compositions – Method of Manufacturing

[0040] As discussed above, the modified asphalt described herein, in aspects, can include the grafting of an olefin compound onto asphalt by the use of an acid promoter. In aspects, generally the asphalt is mixed with one or more olefin components and one or more acid promoters in the presence of heat to, in part, facilitate the chemical grafting of the olefin to the asphalt.

[0041] In various aspects, the specific blending technology can be chosen based on the nature of the additives, facilities available, and the desired performance properties. Further, in such aspects, the temperature and/or duration of mixing can be adjusted to achieve desired additive dispersion and enhanced property development. In certain aspects, the asphalt, olefin compound, acid promoter, or a combination thereof can be heated to any temperature above ambient temperature, e.g., 25 °C, and that is below the temperature at which the asphalt, olefin compound, and/or acid promoter would thermally decompose. In certain aspects, the asphalt, olefin compound, acid promoter, or a combination thereof may be heated to a temperature of about 120 °C or more, about 140 °C of more, or about 150 °C or more. In the same or alternative aspects, the asphalt, olefin compound, acid promoter, or a combination thereof may be heated to a temperature of about 120 °C to about 250 °C, about 120 °C to about 230 °C, or about 140 °C to about 230 °C.

[0042] In aspects, the modified asphalt can be made in a number of manners. For instance, one example method of manufacturing can include the preparation of a stock solution of asphalt, olefin compound, and acid promoter, which can be thereafter blended into a bulk amount of asphalt. In such an aspect, the olefin compound can be in liquid form prior to formation of the stock solution. Another example method can include the high shear blending of the asphalt and a solid olefin component, and after a period of time, adding the acid promoter. In yet another example method of manufacturing the modified asphalt can include low shear blending of asphalt and liquid polymer followed by the addition of an acid promoter. Specific examples of these methods are provided in the below Examples.

[0043] In certain aspects, the modified asphalt described herein can be further physically blended or compounded with other asphalt-modifying components, e.g., after the manufacture of the modified asphalts described above. In such an aspect, the modified asphalt can be compounded with one or more polymers, such as a polymer comprising ethylene monomers, a polymer comprising propylene monomers, ethylene-propylene co-polymer, ethylene-propylene diene terpolymer, vinyl terminated polymer, styrene-butadiene-styrene (SBS), or a combination thereof. In such an aspect, the modified asphalt can be compounded with additional asphalt-modifying components using any convenient compounding techniques.

Examples – Manufacturing Modified Asphalt with a Stock Solution

[0044] A stock solution was prepared in the following manner. A three neck round bottom flask containing a stir bar was charged with asphalt (40 g, of a commercially available asphalt having a SUPERPAVE™ rating of PG 64-22) and heated to 160 °C with mixing. Once the asphalt reaches 160 °C the olefin (40 mL, 1-hexadecene ("1HD") or a commercially available unhydrogenated metallocene C20-poly-α-olefin ("uPAO")) was charged into the flask, and the acid promoter (2 g, $AlCl_3$) was added slowly. After addition of the acid promoter, the mixture was heated to 190 °C for 15 minutes to disperse the promoter and subsequently cooled to 160 °C. After 4 hours, the heat was removed and the stock solution was discharged into a receiver for storage and subsequent blending.

[0045] The blend was prepared in the following manner. 200 g, 16.7 wt. %, of the above stock solution was blended into a bulk amount of asphalt (1 kg, 83.3 wt. %) under low shear for 1 hour at 160 °C. After 1 hour, the heat was removed and the volatiles were separated under vacuum distillation or solvent stripping conditions. The bottoms material was collected for storage and subsequent testing.

Examples – Manufacturing Modified Asphalt with High Shear Conditions

[0046] 350 g of asphalt (commercially available asphalt having a SUPERPAVE™ rating of PG 64-22) was added into a container and heated to 190 °C with high shear mixing. Solid polymer (11 g) was slowly added at high shear and continue blending after addition for 1 hour. The polymer was either the uPAO mentioned above or a commercially available ethylene-propylene co-polymer (having 16 wt. % ethylene content, a flexural modulus, 1% secant, of about 14.4 Mpa measured according to ASTM test method D790, and a Tear Strength, die C, of about 33.3 kN/m measured according to ASTM test method D624 ("EPC"), or an atatic polypropylene having vinyl/vinylidiene terminal double bonds and having a molecular weight of 2kDa, 59 kDa, 75 kDa, or 123 kDa ("VTM")). The blend is removed from high shear and is continued blending at low shear for 20 hours at 160 °C. After 20 hours, the acid promoter is added (0.9 g, $AlCl_3$). The blend was warmed to 190 °C for 15 minutes to disperse the promoter and subsequently cooled to 160 °C. After 4 hours the heat was removed and the blend was stored for subsequent testing.

Examples – Manufacturing Modified Asphalt with Low Shear Conditions

[0047] 350 g of asphalt (commercially available asphalt having a SUPERPAVE™ rating of PG 64-22) was added into a container and heated to 160 °C with low shear. Liquid polymer (11 g) was added slowly at low shear and continued to blend after addition for 1 hour, followed by addition of the acid promoter (0.9 g, $AlCl_3$). The blend was warmed to 190 °C for 15 minutes to disperse the acid promoter and subsequently cooled to 160 °C. After 4 hours the heat was removed and the blend was stored for subsequent testing.

Examples –Modified Asphalts with Improved Performance Grade

[0048] FIG. 1 shows a SUPERPAVE™ matrix grid of modified asphalts that were made as described in any of the above manufacturing examples and tested for low temperature and high temperature grade performance according to the AASHTO MP-1 standard mentioned above. Particularly, the asphalt was modified with 1 wt. % or 2 wt. % 1HD and 0.5 wt. % acid promoter (either $AlCl_3$, H_2SO_4, or polyphosphoric acid ("PPA")). As can be seen in FIG. 1, an improvement in the low temperature quality was observed (improvement over the base quality line for unmodified asphalt) for the asphalt modified with 2 wt. % 1HD and 0.5 wt. % $AlCl_3$, and for the asphalt modified with 1 wt. % uPAO and 0.5 wt. % $AlCl_3$. These modifications, i.e., the chemical grafting of 1HD or uPAO to the asphalt in the present of $AlCl_3$ improved the performance grade of the asphalt from a PG 64-22 grade to a PG 64-28 grade.

[0049] Further, as can be seen in FIG. 1, of the three acid promoters that were evaluated ($AlCl_3$, H_2SO_4, and PPA), $AlCl_3$ was best at improving the low temperature performance grade, while H_2SO_4 had an effectiveness of improving the low temperature performance grade between that of $AlCl_3$ and PPA. This ranked order ability of the promoter to improve the low temperature asphalt

properties ($AlCl_3$ > H_2SO_4 > PPA) correlates to the promoter's relative Lewis acidity. Improvements in performance grade quality were also observed with other asphalts.

Examples –Modified Asphalt with Improved Storage Stability

[0050] In this Example, the storage stability of various modified asphalts were tested. The storage stability was tested according to ASTM test method D7173. Generally the modified asphalts were placed in a container and exposed to 163 °C for 48 hours, and then thereafter the top and bottom portions of the samples were separately tested for any separation by performing dynamic shear rheometer (DSRo) measurements according to ASTM test method D7175. In this stability test, a DSRo Top/DSRo Bottom ratio between about 0.9 and about 1.1 can be considered the stable zone.

[0051] FIG. 2 depicts the storage stability test results for asphalts modified with 3 wt. % EPC alone, or modified asphalt with 3 wt. % EPC in the presence of 0.5 wt. % acid promoter (either $AlCl_3$, H_2SO_4, and PPA), and an asphalt modified with 2 wt. % EPC and 0.5 wt. % $AlCl_3$. Particularly, FIG. 2 depicts a bar graph showing the above-described asphalts modified with EPC, with the bar representing the DSRo Top/DSRo Bottom ratio. In particular, the asphalts that were modified with 2 wt. % or 3 wt. % EPC and 0.5 wt. % $AlCl_3$ showed improved storage stability compared to asphalt modified with 3 wt. % EPC with or without 0.5 wt. %, H_2SO_4, or PPA. Thus, this example shows that the EPC polymer itself does not impart storage stability to the asphalt. Further, this Example demonstrates the increased efficacy of the $AlCl_3$ promoter compared to the other promoters tested.

[0052] FIG. 3 depicts the storage stability test results for asphalts modified with 3 wt. % VTM of varying molecular weights (2 kDa, 59 kDa, 75 kDa, and 123 kDa) in the presence and absence of 0.5 wt. % $AlCl_3$. As can be seen in FIG. 3, the storage stability decreased with increasing molecular weight of the VTM. The storage stable modified asphalts were obtained with the 2 kDa, 59 kDa, and 75 kDa VTM-modified asphalts.

Examples –Modified Asphalt with Improved Multi-Stress Creep Recovery (MSCR) Properties

[0053] In this Example the Multi-Stress Creep Recovery (MSCR) of various modified asphalts were tested. The MSCR was tested according to the AASHTO M-332 test standard. The MSCR is a performance test for high performance asphalts that provides measures of delayed elastic response (Average % Recovery) and rutting resistance (Non-Recoverable Creep Compliance). These parameters are calculated based on the measured response of an asphalt sample to repeated stress (0.1 kPa or 3.2 kPa 1 sec) and recovery (9 sec) cycles under the test conditions.

[0054] FIG. 4 depicts the MSCR test results for asphalts modified with various amounts of EPC. FIG. 4 also depicts a benchmark asphalt blended with 2 wt. % SBS and 0.5 wt. % PPA. As

can be seen in FIG. 4, the 2 wt. % and 3 wt. % EPC grafted blends matched or exceeded the MSCR properties of the SBS benchmark blend generated for this experiment. Particularly, FIG. 4 illustrates the improvement in delayed elastic response and rutting resistance for asphalts modified with EPC and $AlCl_3$.

[0055] FIG. 5 depicts the MSCR test results for asphalts modified with 3 wt. % VTM of varying molecular weights (2 kDa, 59 kDa, and 75 kDa). FIG. 5 also depicts a benchmark asphalt blended with 2 wt. % SBS and 0.5 wt. % PPA. FIG. 5 illustrates the improvement in delayed elastic response and rutting resistance for asphalts modified with VTM and $AlCl_3$. Further, as can be seen in FIG. 5, the asphalts modified with the 59 kDa or the 75 kDa VTM exceeded the MSCR properties of the SBS benchmark blend.

Additional Embodiments

[0056] Embodiment 1. A method for modifying an asphalt, comprising: exposing an asphalt having a T5 boiling point of 400 °C or more to: 1) 0.2 wt. % to 5 wt. % of an olefin compound having a molecular weight of 0.2 kDa to 110 kDa; and 2) 0.1 wt. % to 2 wt. % of an acid promoter to form a modified asphalt.

[0057] Embodiment 2. The method of embodiment 1, wherein the exposing occurs at atmospheric pressure.

[0058] Embodiment 3. The method of embodiment 1 or 2, wherein the acid promoter comprises $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, zeolites, or a combination thereof.

[0059] Embodiment 4. The method of any of embodiments 1-3, wherein the olefin compound comprises a polymer comprising ethylene monomers, a polymer comprising propylene monomers, an ethylene-propylene co-polymer, an ethylene propylene diene terpolymer, one or more vinyl-terminated polymers, or a combination thereof.

[0060] Embodiment 5. The method of any of embodiments 1-4, wherein the asphalt comprises a high temperature performance grade of 58 °C or more and/or a low temperature performance grade of -34 °C to -22 °C.

[0061] Embodiment 6. The method of any of embodiments 1-4, wherein the modified asphalt comprises a high temperature performance grade of 64 °C or more and/or a low temperature performance grade of -34 °C to -16 °C.

[0062] Embodiment 7. The method of any of embodiments 1-6, wherein the exposing results in at least a portion of the olefin compound being covalently attached to at least a portion of the asphalt to form a grafted asphalt.

[0063] Embodiment 8. The method of any of embodiments 1-7, wherein the modified asphalt comprises a storage stability of about 0.8 to about 1.2 as determined according to the Storage Stability ASTM test method 7173, a Softening Point of about 50 °C or more, as determined according to test method EN 1427 a Penetration at 25 °C of about 30 dmm to about 110 dmm (or about 40 dmm to about 100 dmm), as determined according to test method EN 1426, or a combination thereof.

[0064] Embodiment 9. The method of any of embodiments 1-8, further comprising compounding the modified asphalt with a polymer comprising ethylene monomers, a polymer comprising propylene monomers, an ethylene-propylene co-polymer, an ethylene-propylene diene terpolymer, a vinyl terminated polymer, styrene-butadiene-styrene (SBS), or a combination thereof.

[0065] Embodiment 10. An asphalt composition comprising: an asphalt having an initial or T5 boiling point of 400 °C or more; 0.2 wt. % to 5 wt. % of an olefin compound having a molecular weight between 50 kDa and 110 kDa; and 0.1 wt. % to 2 wt. % of an acid promoter selected from $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, zeolites, or a combination thereof, wherein the asphalt composition is formed at a temperature of 160 °C to 230 °C , the asphalt composition having a high temperature performance grade of 58 °C or more and a low temperature performance grade of -34 °C to -16 °C.

[0066] Embodiment 11. The asphalt composition of embodiment 10, wherein the asphalt composition has a high temperature performance grade of 64 °C or more and a low temperature performance grade of -34 °C to -22 °C.

[0067] Embodiment 12. The asphalt composition of embodiments 10 or 11, wherein the acid promoter comprises $AlCl_3$.

[0068] Embodiment 13. The asphalt composition of any of embodiments 10-12, wherein the olefin compound comprises a polymer comprising ethylene monomers, a polymer comprising propylene monomers, an ethylene-propylene co-polymer, an ethylene-propylene diene terpolymer, one or more vinyl-terminated polymers, or a combination thereof.

[0069] Embodiment 14. The asphalt composition of any of embodiments 10-13, wherein the asphalt composition comprises a storage stability of about 0.8 to about 1.2 as determined according to the Storage Stability ASTM test method 7173, a Softening Point of about 50 °C or more, as determined according to test method EN 1427, a Penetration at 25 °C of about 3 mm to about 11 mm, as determined according to test method EN 1426, or a combination thereof.

[0070] Although the present invention has been described in terms of specific embodiments, it is not so limited. Suitable alterations/modifications for operation under specific conditions should

be apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations/modifications as fall within the true spirit/scope of the invention.

CLAIMS:

1. A method for modifying an asphalt, comprising:

exposing an asphalt having a T5 boiling point of 400°C or more to: 1) 0.2 wt. % to 5 wt. % of an olefin compound having a molecular weight of 0.2 kDa to 110 kDa; and 2) 0.1 wt. % to 2 wt. % of an acid promoter to form a modified asphalt.

2. The method of claim 1, wherein the exposing occurs at atmospheric pressure.

3. The method of claim 1, wherein the acid promoter comprises $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, zeolites, or a combination thereof.

4. The method of claim 1, wherein the acid promoter comprises $AlCl_3$.

5. The method of claim 1, wherein the olefin compound comprises a polymer comprising ethylene monomers, a polymer comprising propylene monomers, or a combination thereof.

6. The method of claim 1, wherein the olefin compound comprises an ethylene-propylene co-polymer, an ethylene propylene diene terpolymer, or combination thereof.

7. The method of claim 1, wherein the olefin compound comprises one or more vinyl-terminated polymers.

8. The method of claim 1, wherein the asphalt comprises a high temperature performance grade of 58 °C or more.

9. The method of claim 1, wherein the asphalt comprises a low temperature performance grade of -34 °C to -22 °C.

10. The method of claim 1, wherein the exposing results in at least a portion of the olefin compound being covalently attached to at least a portion of the asphalt to form a grafted asphalt.

11. The method of claim 1, wherein the modified asphalt comprises a storage stability of about 0.8 to about 1.2 as determined according to the Storage Stability ASTM test method 7173.

12. The method of claim 1, wherein the modified asphalt comprises a Softening Point of about 50 °C or more, as determined according to test method EN 1427.

13. The method of claim 1, wherein the modified asphalt comprises a Penetration at 25 °C of about 30 dmm to about 110 dmm, as determined according to test method EN 1426.

14. The method of claim 1, further comprising compounding the modified asphalt with a polymer comprising ethylene monomers, a polymer comprising propylene monomers, an ethylene-propylene co-polymer, an ethylene-propylene diene terpolymer, a vinyl terminated polymer, styrene-butadiene-styrene (SBS), or a combination thereof.

15. An asphalt composition comprising:

an asphalt having an initial or T5 boiling point of 400°C or more;

0.2 wt. % to 5 wt. % of an olefin compound having a molecular weight between 50 kDa and 110 kDa; and

0.1 wt. % to 2 wt. % of an acid promoter selected from $AlCl_3$, H_2SO_4, polyphosphoric acid, BCl_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, zeolites, or a combination thereof,

wherein the asphalt composition is formed at a temperature of 160 °C to 230 °C , the asphalt composition having a high temperature performance grade of 58 °C or more and a low temperature performance grade of -34 °C to -16 °C.

16. The asphalt composition of claim 15, wherein the asphalt composition has a high temperature performance grade of 64 °C or more and a low temperature performance grade of -34 °C to -22 °C.

17. The asphalt composition of claim 15, wherein the acid promoter comprises $AlCl_3$.

18. The asphalt composition of claim 15, wherein the olefin compound comprises a polymer comprising ethylene monomers, a polymer comprising propylene monomers, or a combination thereof.

19. The asphalt composition of claim 15, wherein the olefin compound comprises an ethylene-propylene co-polymer, an ethylene-propylene diene terpolymer, or combination thereof.

20. The asphalt composition of claim 15, wherein the olefin compound comprises one or more vinyl-terminated polymers.

21. The asphalt composition of claim 15, wherein the asphalt composition comprises a storage stability of about 0.8 to about 1.2 as determined according to the Storage Stability ASTM test method 7173.

22. The asphalt composition of claim 15, wherein the asphalt composition comprises a Softening Point of about 50 °C or more, as determined according to test method EN 1427.

23. The asphalt composition of claim 15, wherein the asphalt composition comprises a Penetration at 25 °C of about 30 dmm to about 110 dmm, as determined according to test method EN 1426.

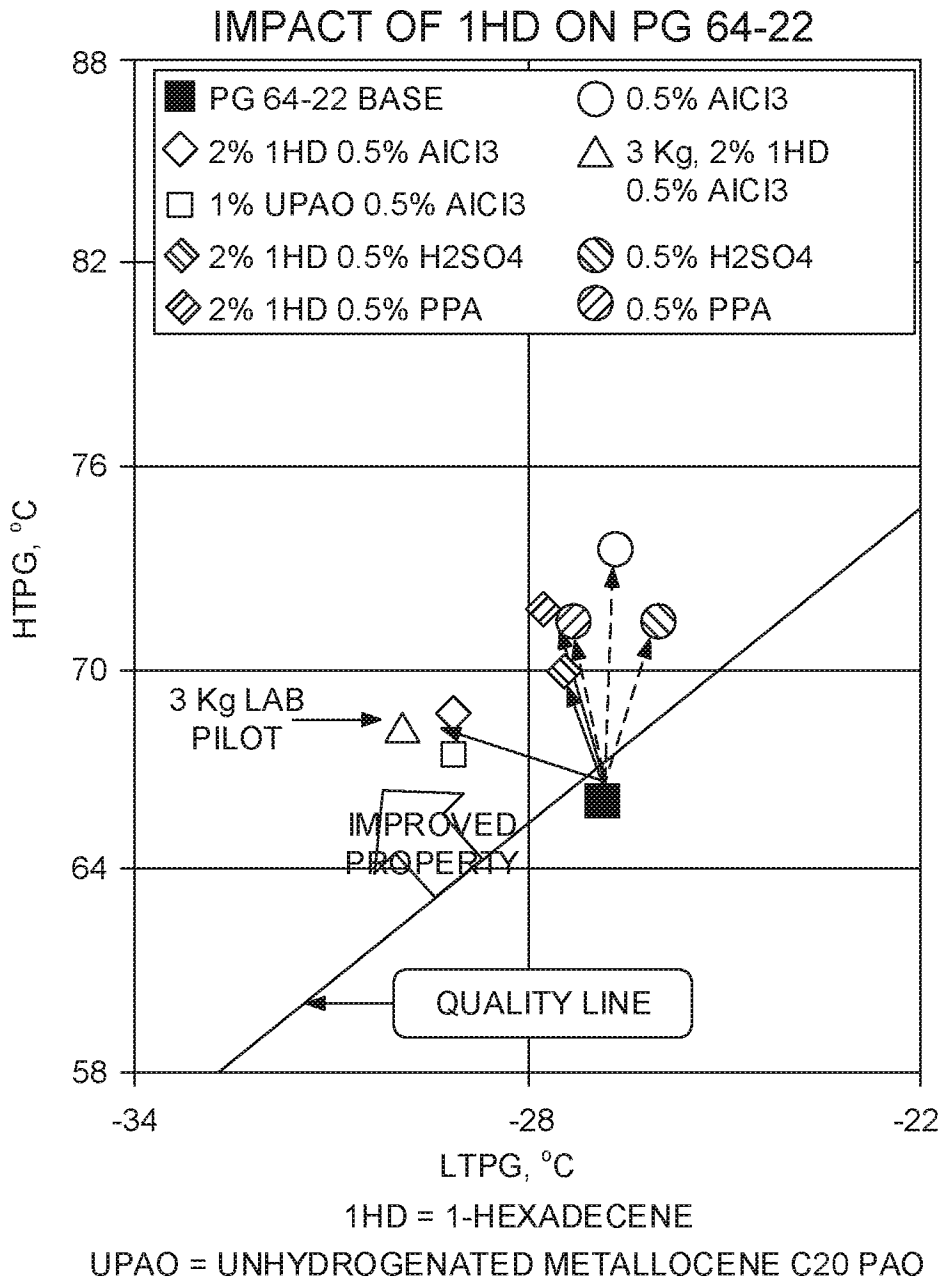

IMPACT OF 1HD ON PG 64-22
PG 64-22 BASE
0.5% AlCl3
2% 1HD 0.5% AlCl3
3 Kg, 2% 1HD 0.5% AlCl3
1% UPAO 0.5% AlCl3
2% 1HD 0.5% H2SO4
0.5% H2SO4
2% 1HD 0.5% PPA
0.5% PPA
88
82
76
70
64
58
HTPG, °C
3 Kg LAB PILOT
IMPROVED PROPERTY
QUALITY LINE
-34
-28
-22
LTPG, °C
1HD = 1-HEXADECENE
UPAO = UNHYDROGENATED METALLOCENE C20 PAO

FIG. 1.

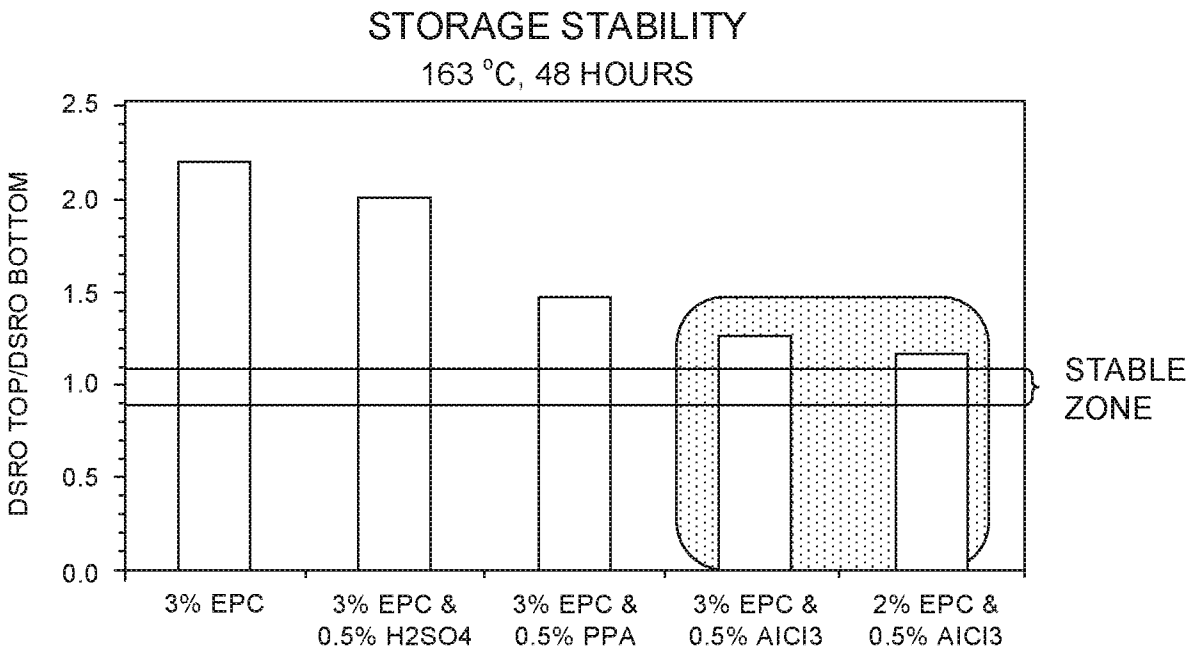

STORAGE STABILITY
163 °C, 48 HOURS
DSRO TOP/DSRO BOTTOM
2.5
2.0
1.5
1.0
0.5
0.0
STABLE ZONE
3% EPC
3% EPC & 0.5% H2SO4
3% EPC & 0.5% PPA
3% EPC & 0.5% AICI3
2% EPC & 0.5% AICI3

FIG. 2.

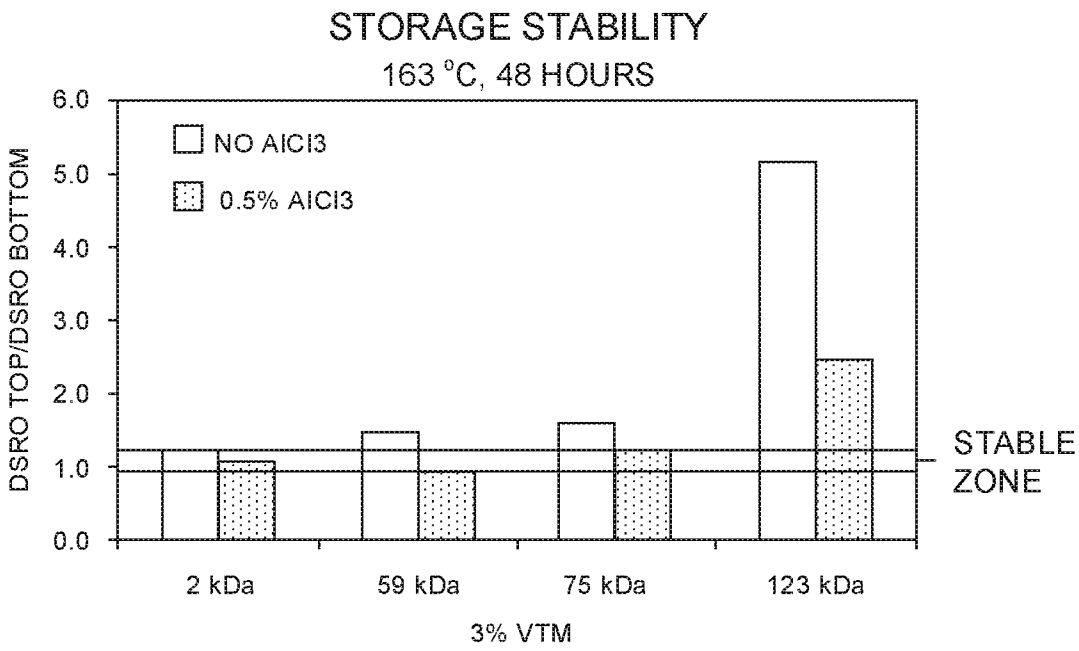

STORAGE STABILITY
163 °C, 48 HOURS
DSRO TOP/DSRO BOTTOM
6.0
5.0
4.0
3.0
2.0
1.0
0.0
NO AICI3
0.5% AICI3
STABLE ZONE
2 kDa
59 kDa
75 kDa
123 kDa
3% VTM

FIG. 3.

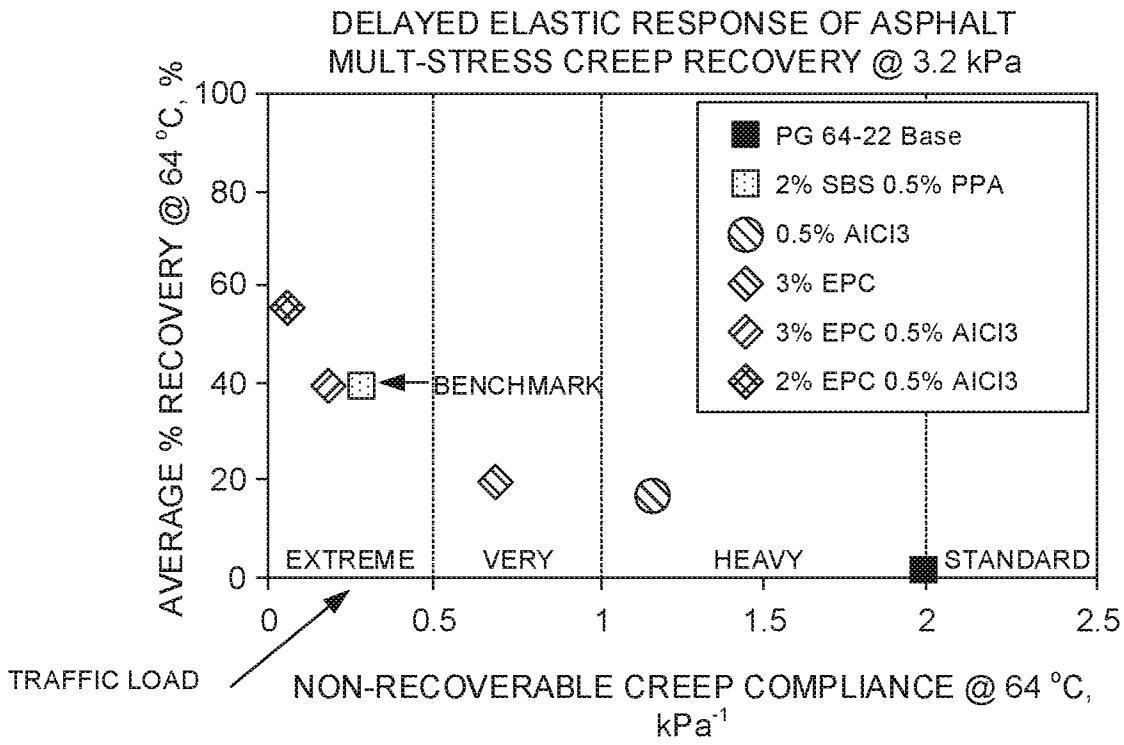

DELAYED ELASTIC RESPONSE OF ASPHALT
MULT-STRESS CREEP RECOVERY @ 3.2 kPa
AVERAGE % RECOVERY @ 64 °C, %
100
80
60
40
20
0
PG 64-22 Base
2% SBS 0.5% PPA
0.5% AlCl3
3% EPC
3% EPC 0.5% AlCl3
2% EPC 0.5% AlCl3
BENCHMARK
EXTREME
VERY
HEAVY
STANDARD
0
0.5
1
1.5
2
2.5
TRAFFIC LOAD
NON-RECOVERABLE CREEP COMPLIANCE @ 64 °C,
kPa-1

FIG. 4.

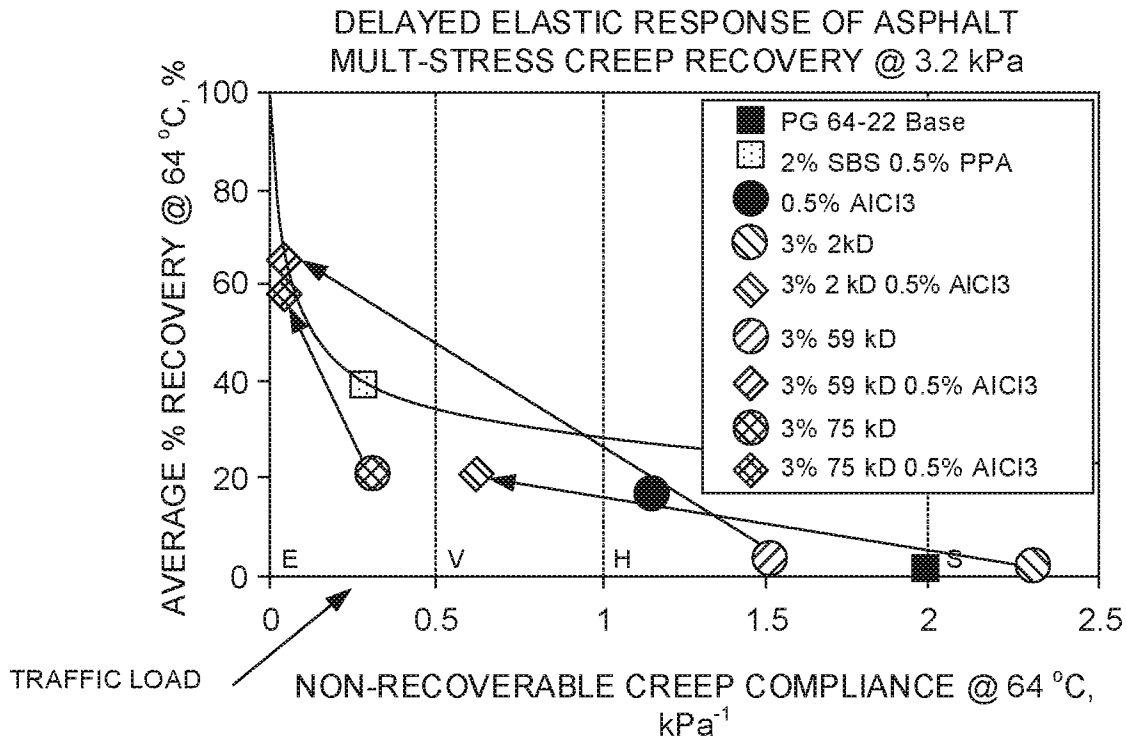

DELAYED ELASTIC RESPONSE OF ASPHALT
MULT-STRESS CREEP RECOVERY @ 3.2 kPa
AVERAGE % RECOVERY @ 64 °C, %
100
80
60
40
20
0
PG 64-22 Base
2% SBS 0.5% PPA
0.5% AlCl3
3% 2kD
3% 2 kD 0.5% AlCl3
3% 59 kD
3% 59 kD 0.5% AlCl3
3% 75 kD
3% 75 kD 0.5% AlCl3
E
V
H
S
0
0.5
1
1.5
2
2.5
TRAFFIC LOAD
NON-RECOVERABLE CREEP COMPLIANCE @ 64 °C,
kPa-1

FIG. 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/063010

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L95/00 C08L23/00 C08L23/04 C08L23/10 C08K3/16
C08K5/55 C08K3/30 C08K3/32 C08K5/01
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)
C08K C08L

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	Anonymous: "SECTION 916 BITUMINOUS MATERIALS; AASTHO M320-10, Table 1", , 31 August 2012 (2012-08-31), pages 1-11, XP055292352, Retrieved from the Internet: URL:ftp://ftp.dot.state.fl.us/lts/CO/Specifications/SpecBook/2013Book/916-2013.pdf [retrieved on 2016-08-01] abstract	1-23

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

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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
6 February 2020	25/02/2020

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/063010

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 239 the whole document	1-23

Y	GIOVANNI POLACCO ET AL: "A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility", ADVANCES IN COLLOID AND INTERFACE SCIENCE, vol. 224, 1 October 2015 (2015-10-01), pages 72-112, XP055422164, NL ISSN: 0001-8686, DOI: 10.1016/j.cis.2015.07.010 paragraph [3.6.1] - paragraph [3.6.2] the whole document	1-23

X	KR 1999 0079717 A (SK CORP [KR]) 5 November 1999 (1999-11-05)	1-23
Y	the whole document	1-23

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/063010

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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Y	example 4 the whole document	1-23

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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