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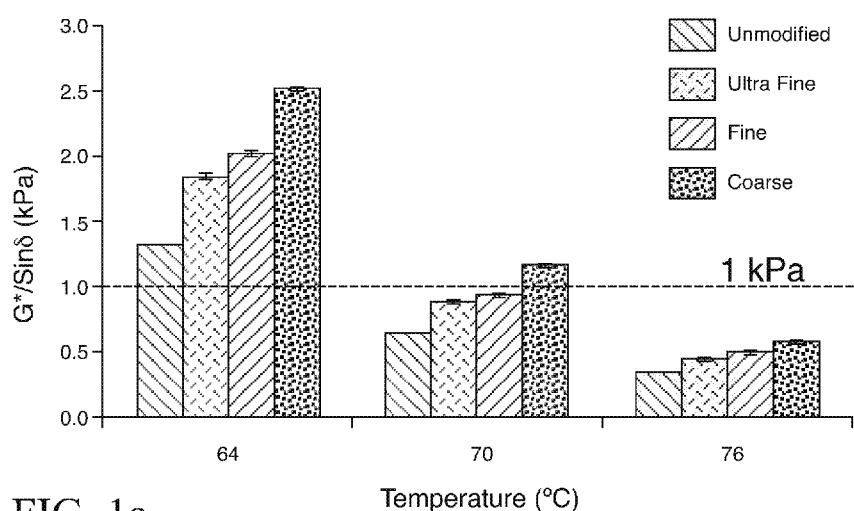


FIG. 1a

(57) Abstract: Disclosed are asphalt compositions that include a polymeric aromatic product of an aromatic isocyanate manufacturing process, as well as pavements produced using such compositions. The asphalt pavements produced from these asphalt compositions can have increased high temperature rutting resistance. Also disclosed are methods for making these asphalt compositions that include a polymeric aromatic product of an aromatic isocyanate manufacturing process.

PAVING GRADE ASPHALT COMPOSITIONS AND METHODS FOR THEIR MANUFACTURE

FIELD

[0001] The present specification relates generally to paving grade asphalt compositions that, in at least some cases, can provide asphalt pavements with increased high temperature rutting resistance.

BACKGROUND

[0002] Asphalt compositions for pavement are known. These compositions include aggregates coated with a hydrocarbon binder. The hydrocarbon binder typically is based on bitumen. The performance capability of the binder, and hence the resulting pavement, is often described by the SUPERPAVE™ criteria (as described by Standard AASHTO M320-17) which defines the bitumen binder relative to a maximum temperature and a minimum temperature at which the binder's mechanical performance properties remain acceptable. A binder rating Performance Grade ("PG") 64-22, for example, means that the highest temperature the pavement can withstand, for the 7 hottest consecutive days, is 64°C and the lowest temperature the pavement can withstand, for the coldest day, is -22°C. The high temperature limit, such as 64°C, corresponds to the temperature at which minimal resistance to irreversible deformation of the pavement has been reached, which is sometimes referred to with respect to the rutting resistance of the pavement. The low temperature limit, such as -22°C, represents the temperature at which the resistance to thermal shrinkage-induced stress is reached, and thus cracking occurs. Further information regarding the SUPERPAVE™ binder specifications can be found, for example, and without limitation, in United States Patent No. 7,150,785 B2 at col. 5, line 46 to col. 6, line 58, the cited portion of which being incorporated herein by reference.

[0003] As will be appreciated, therefore, asphalt binders with different ratings may be desirable for use in pavements in different geographical regions or climatic conditions and it can be desirable to increase the rating of a particular asphalt binder. It is typically advantageous to increase the asphalt binder stiffness and elasticity at high temperature to guard against permanent pavement deformation. In addition, particularly at low temperatures, asphalt binders that are able to relax induced thermal or mechanical stresses and maintain lower levels of stress are thereby less prone to cracking.

[0004] It is not uncommon to add a polymer modifier to an asphalt binder. Recycled tire rubber, for example, can be added to an asphalt composition to improve its high temperature performance. A difficulty with this, however, is that of storage stability. When asphalt binders modified with particulate additives, such as recycled tire rubber, are stored in asphalt tanks, the particulates are very susceptible to settling to the bottom of the storage tanks or floating to the top of the storage tanks. This results in high material variability and practical challenges for asphalt producers. Rubber also can lead to a sticky asphalt mixture which is difficult to process.

[0005] As a result, it would be desirable to provide asphalt compositions that can, for example, have improved high temperature performance and that use an additive that is less prone to storage stability problems than, for example, the commonly used recycled tire rubber.

[0006] Toluene diisocyanate ("TDI") is an important product for the manufacture of polyurethanes. It is manufactured by phosgenation of diamines followed by distillation to recover solvents and the diisocyanate(s). This distillation process results in a high molecular weight residue of the TDI (often referred to as "TDI residue") that is typically discarded as waste. Since TDI is manufactured in large quantities, such disposal can be expensive and otherwise undesirable.

[0007] As a result, it would also be desirable to identify uses of certain types of TDI residue. In particular, since certain types of TDI residue are the product of a highly controlled, highly repeatable and reproducible process; are based on highly consistent raw materials; and are themselves very consistent over time in their composition and physical and chemical characteristics, it would be desirable to identify applications that would benefit from use of such a material as a raw material to produce another product.

[0008] The inventions described herein were made in view of the foregoing.

SUMMARY OF THE INVENTION

[0009] In certain respects, the present specification is directed to asphalt compositions. These asphalt compositions comprise an aggregate coated with a coating comprising: (a) a paving grade asphalt binder, and (b) an organic particulate, wherein the organic particulate has a particle size of no more than 200 micrometers and comprises: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0010] In other respects, the present specification is directed to methods of increasing the high temperature rutting resistance of asphalt pavement, comprising coating aggregate with an asphalt composition comprising an organic particulate dispersed in a paving grade asphalt binder, wherein the organic particulate has a particle size of no more than 200 micrometers and comprises: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0011] In yet other respects, the present specification is directed to asphalt pavements comprising an aggregate coated with an asphalt composition comprising a paving grade asphalt binder having an organic particulate dispersed therein, wherein the organic particulate has a particle size of no more than 200 micrometers and comprises: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0012] The present specification is also directed to, among other things, related methods for making such asphalt compositions and pavements.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Various features and characteristics of the inventions described in this specification may be better understood by reference to the accompanying figures, in which:

[0014] Figures 1a and 1b illustrate the results of high temperature PG grading of Flint Hills ("FH") 64-22 graded asphalt binders prepared as described by Example 1;

[0015] Figure 2 illustrates the results of $G^*/\sin\delta$ measurements for the Val 58-22 and FH 64-22 graded asphalt binders tested as described by Example 1;

[0016] Figure 3 illustrates the intermediate temperature testing results with and without Coarse particle modification (4% by weight, based on total binder weight) of FH 64-22 binders tested as described by Example 1; and

[0017] Figure 4 illustrates the results of $G^*/\sin\delta$ measurements for the asphalt binders tested as described by Example 2.

DETAILED DESCRIPTION

[0018] Various embodiments are described and illustrated in this specification to provide an overall understanding of the structure, function, properties, and use of the disclosed inventions. It is understood that the various embodiments described and illustrated in this specification are non-limiting and non-exhaustive. Thus, the invention is not limited by the description of the various non-limiting and non-exhaustive embodiments disclosed in this specification. The features and characteristics described in connection with various embodiments may be combined with the features and characteristics of other embodiments. Such modifications and variations are intended to be included within the scope of this specification. As such, the claims may be amended to recite any features or characteristics expressly or inherently described in, or otherwise expressly or inherently supported by, this specification. Further, Applicant(s) reserve the right to amend the claims to affirmatively disclaim features or characteristics that may be present in the prior art. Therefore, any such amendments comply with the requirements of 35 U.S.C. § 112 and 35 U.S.C. § 132(a). The various embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described herein.

[0019] Any patent, publication, or other disclosure material identified herein is incorporated by reference into this specification in its entirety unless otherwise indicated, but only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material expressly set forth in this specification. As such, and to the extent necessary, the express disclosure as set forth in this specification supersedes any conflicting material incorporated by reference herein. Any material, or portion thereof, that is said to be incorporated by reference into this specification, but which conflicts with existing definitions, statements, or other disclosure material set forth herein, is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material. Applicant(s) reserves the right to amend this specification to expressly recite any subject matter, or portion thereof, incorporated by reference herein.

[0020] In this specification, other than where otherwise indicated, all numerical parameters are to be understood as being prefaced and modified in all instances by the term "about", in which the numerical parameters possess the inherent variability characteristic of the underlying measurement techniques used to determine the numerical value of the parameter. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter described in the present

description should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0021] Also, any numerical range recited in this specification is intended to include all sub-ranges of the same numerical precision subsumed within the recited range. For example, a range of "1.0 to 10.0" is intended to include all sub-ranges between (and including) the recited minimum value of 1.0 and the recited maximum value of 10.0, that is, having a minimum value equal to or greater than 1.0 and a maximum value equal to or less than 10.0, such as, for example, 2.4 to 7.6. Any maximum numerical limitation recited in this specification is intended to include all lower numerical limitations subsumed therein and any minimum numerical limitation recited in this specification is intended to include all higher numerical limitations subsumed therein. Accordingly, Applicant(s) reserves the right to amend this specification, including the claims, to expressly recite any sub-range subsumed within the ranges expressly recited herein. All such ranges are intended to be inherently described in this specification such that amending to expressly recite any such sub-ranges would comply with the requirements of 35 U.S.C. § 112 and 35 U.S.C. § 132(a).

[0022] The grammatical articles "one", "a", "an", and "the", as used in this specification, are intended to include "at least one" or "one or more", unless otherwise indicated. Thus, the articles are used in this specification to refer to one or more than one (i.e., to "at least one") of the grammatical objects of the article. By way of example, "a component" means one or more components, and thus, possibly, more than one component is contemplated and may be employed or used in an implementation of the described embodiments. Further, the use of a singular noun includes the plural, and the use of a plural noun includes the singular, unless the context of the usage requires otherwise.

[0023] As indicated, certain embodiments of the inventions described in this specification are directed to asphalt compositions.

[0024] Such asphalt compositions comprise an aggregate. As will be appreciated, aggregate is typically produced from rock, including hard rocks, such as granite and/or soft rocks, such as sandstone, that have been processed by, for example, crushing and screening, to produce aggregates having a desired particle size and angularity.

[0025] In asphalt compositions for pavement applications, such as those of the present specification, the aggregate is typically coated with a paving grade asphalt binder. Various grades of asphalt can be used in the asphalt compositions of the present disclosure, typically; however, the asphalt binder is a paving grade asphalt binder. As a result, in certain embodiments, the asphalt compositions of the present specification comprise an

asphalt binder having a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-16, PG 70-22, PG 76-22, or PG 70-28, when graded according to Standard AASHTO M 320-17.

In some of these embodiments, the asphalt compositions of the present specification comprise an asphalt binder having a performance grade rating of PG 64-22, when graded according to Standard AASHTO M 320-17.

[0026] As will be appreciated, "asphalt", which may also be referred to herein interchangeably with "bitumen", is a dark brown to black, semi-solid or viscous mixture of paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulfur, nitrogen, and oxygen, and includes those which occur naturally and industrially, such as a residue in the refining of crude oil, including residues from atmospheric distillation, vacuum distillation, and solvent deasphalting units. Asphalt can be derived from a cut in petroleum distillation after naphtha, gasoline, kerosene and other fractions have been removed from crude oil.

[0027] In certain embodiments, the asphalt binder is present in the asphalt composition in an amount of up to 99.99% by weight, such as up to 99.9% by weight, up to 99% by weight, up to 98% by weight, or, in some cases, up to 97% by weight and/or at least 80% by weight, such as at least 90% by weight, at least 92% by weight, at least 94% by weight, or, in some cases, at least 95% by weight, based on the total combined weight of the asphalt binder and the organic particulates in the asphalt composition.

[0028] As earlier indicated, the asphalt compositions of the present disclosure comprise an asphalt binder that comprises an organic particulate comprising: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups (and sometimes a content of isocyanate groups); and (ii) a high-boiling hydrocarbon. As used herein with reference to component (i) above, the term "polymer" encompasses oligomers and both homopolymers and copolymers; the prefix "poly" referring to two or more. Also, as used herein with reference to component (i) above, "crosslinked polymer" means that the chains of the polymer are linked to one another by covalent bonds so that the polymer, as a network, is insoluble in inert organic solvents and cannot be melted without decomposing.

[0029] The organic particulate that is included in the asphalt compositions described herein is, in certain embodiments, the by-product of a process used to manufacture an aromatic polyisocyanate. More particularly, in certain embodiments, the organic particulate is produced by drying a mixture comprising: (i) a residue, *i.e.*, a by-product, of a process for

producing an aromatic polyisocyanate by the reaction of a corresponding amine with phosgene; and (ii) a high-boiling hydrocarbon. As used herein, the term "high-boiling hydrocarbon" encompasses pure hydrocarbons and industrial mixtures that have a boiling point which is different from the boiling point of the polyisocyanate produced by the process resulting in the residue by at least 150°C at 15 mbar absolute pressure.

[0030] For example, in some embodiments, the organic particulate is the product of a process for the production of a pure, distilled aromatic polyisocyanate by (1) the reaction of the corresponding amine with phosgene in a suitable solvent and multi-stage distillative work-up of the isocyanate solution obtained to recover pure isocyanate, pure solvent and an isocyanate-containing residue, and (2) continuously feeding the residue obtained from the distillation process and from 2 to 50 weight % of a high-boiling hydrocarbon which is inert under the distillation conditions to a heated, product-agitating vacuum drier with a horizontal shaft. In such a process, the fraction of polyisocyanate still present is continuously distilled off from the residue at a temperature of from 160° to 280°C and a pressure of from 2 to 50 mbar. The remaining residue is continuously discharged as a pourable, non-dusting, granular material, which is cooled and ground to a desired particle size.

[0031] Residues from the synthesis of any of a variety of aromatic polyisocyanates are suitable for use in the inventions described in this specification. Suitable such aromatic polyisocyanates include, but are not limited to, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylxylene diisocyanate, 1,5-naphthalene diisocyanate, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate, 2,2'-diisocyanatodiphenylmethane, diphenylmethanediisocyanate, 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, benzene, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl, 2,4,6-triisopropyl-m-phenylene diisocyanate, and triphenylmethane-4,4',4"-triisocyanate, tris(p-isocyanatophenyl)thiophosphate, among others.

[0032] The residue stream, *i.e.*, that chemical mixture containing the by-product, being formed during distillation of the amine/phosgene reaction mixture often contains from 20 to 80 weight %, such as 40 to 60 weight %, of monomeric isocyanate in addition to polymeric products. In the practice of the process described above, this isocyanate-containing residue may be fed to the drier separately from the hydrocarbons in a plurality of partial streams. In certain embodiments, at least a portion of the isocyanate-containing

residue is mixed with the hydrocarbon and fed to the drier. The remainder of the residue may then be fed to the drier in one or more partial streams.

[0033] A continuously operating contact drier which has a double shell for heating, has a horizontal shaft which agitates the product and is heated is, in certain embodiments, used as the drier in the production of the organic particulate used in the asphalt compositions of the present specification. In certain embodiments, the drier has a plurality of nozzles for product admission, one nozzle for product discharge, and vapor discharge nozzles of large dimensions for the isocyanate and solvent which are separated from the residue during the distillation. Both single-shaft driers and double-shaft or screw feed apparatuses may be used.

[0034] Condensate formed from vapors generated during the process (e.g., in a vapor offtake system) may be used to remove dust deposits such as those which may be formed on the walls of the apparatus at the point where vapors are removed from the system (e.g., the vapor offtake system). These condensates are often separately discharged.

[0035] In certain embodiments of the process for preparing the organic particulates used in the asphalt compositions of the present specification, the reactor is operated at a temperature of from 160°C to 280°C, such as 200°C to 250°C, under a pressure of from 2 to 50 mbar, such as 10 to 20 mbar, at a throughput of up to 250 kg/hour per m² of heating surface. The continuous distillation is often conducted in a product-agitating drier with a horizontal shaft, to which a condensation system is attached. Distillation is carried out in the presence of one or more hydrocarbons, which are admixed in an amount of from 1 to 50 weight %, such as 3 to 10 weight %, based on the weight of the residue being treated. Suitable hydrocarbons include, but are not limited to, asphalts, such as those which occur industrially as by-products in the refining of crude oil. Specific non-limiting examples of suitable bitumens are those of grades 6/12, 10/20, 20/30, 30/40, 40/50, 60/70, 80/100, 100/120, and 180/200.

[0036] Suitable processes and equipment for producing the organic particulates suitable for use herein are also described in U.S. Patent No. 5,446,196, at col. 2, line 18 to col. 4, line 2, the cited portion of which being incorporated herein by reference.

[0037] In certain embodiments, for purposes of the inventions described in this specification, the organic particulate produced as described above is ground to a particle size of at least 0.1 micrometer, such as at least 1 micrometer, at least 5 micrometers, or, in some cases, at least 10 micrometers, at least 30 micrometers, at least 50 micrometers, or, in some cases, at least 90 micrometers and no more than 200 micrometers, such as no more than 150

micrometers or no more than 100 micrometer. For example, in some cases, the particle size is 90 to 200 micrometers. As used herein, "particle size" refers to a size designation determined according to ASTM D4749-87(2012). In certain embodiments, the organic particulate has a Mohs hardness of 2 to 4, and/or a specific gravity of 1.2 to 1.4. Furthermore, in certain embodiments, the ash content of the particulate is less than 0.5% by weight, and when heated under a nitrogen atmosphere, the particulate shows no discernable melting point. In certain embodiments, the particulate is insoluble in water at room temperature and pressure, and has a solubility of less than 5% at room temperature/pressure in any of the following organic solvents: acetone, chlorobenzene, xylenes, dimethylformamide, dimethylsulfoxide, dimethylacetamide, 1:1 mixture of acetone:aromatic 100, carbon disulfide, chloroform, methylene chloride, or tetrahydrofuran. It is not possible to analyze the particulate by SEC or NMR because of its insolubility in organic solvents. In certain embodiments, the content of high-boiling hydrocarbon in the organic particulate is from 1 to 10% by weight, such as 2 to 6% by weight, or 3 to 5% by weight, based on the total weight of the organic particulate. In certain embodiments, the organic particulate has a content of reactive NCO groups that is less than 6% by weight, based on the total weight of the organic particulate and/or is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

[0038] In certain embodiments, the organic particulate is present in the asphalt composition in an amount of at least 0.01%, such as at least 0.1%, at least 1%, at least 2%, or, in some cases, at least 3% by weight and/or up to 20%, such as up to 10%, up to 8%, up to 6%, or, in some cases, up to 5% by weight, based on the total combined weight of organic particulates and asphalt binder in the asphalt composition.

[0039] The asphalt compositions of the present disclosure may also comprise any of a variety of other optional ingredients, such as waxes, plasticizers, emulsifiers, adhesion promoters, compatibilizers, polymeric materials, such as rubber, polyethylene, and/or, polypropylene (and other plastics, including recycled plastics, such as recycled polyethylene and recycled polypropylene), and other fillers, mineral oil, and UV light absorbers, among other materials. In some embodiments, however, the organic particulates are not surface treated prior to combination with the asphalt binder.

[0040] The asphalt compositions of the present disclosure can be prepared by any of a variety of methods. In some embodiments, the organic particulate is dispersed in a paving grade asphalt binder by high shear mixing to disperse the particulates in the binder, followed

by heating, such as to a temperature of 150°C, to melt the asphalt binder. The asphalt binder, as modified by inclusion with the organic particulates, is then combined with aggregate to coat the aggregate prior to deposition to form a pavement.

[0041] It has been discovered that the use of the organic particulates described herein can have at least two benefits in asphalt compositions, neither of which would have been predictable. First, they can, in at least some cases, improve the high temperature performance of the asphalt composition. Second, the use of certain organic particulates described herein are orders of magnitude more stable in an asphalt binder, thereby, it is currently believed, making them easier to handle and providing a more consistent product.

[0042] In other aspects, it is currently believed that the organic particulates described herein can effectively act as a compatibilizer when used in combination with certain other polymeric modifiers, such as rubber and plastics, such as polyethylene and polypropylene (including recycled plastics, such as recycled polyethylene and recycled polypropylene), in an asphalt composition. As previously mentioned, while it is not uncommon to add such polymer modifiers to an asphalt binder to improve its high temperature performance, they suffer from poor storage stability. The organic particulates described herein, however, have polar groups that may have affinity for the asphalt binder and non-polar groups that should have affinity for the polymeric modifiers. As a result, it is currently believed that inclusion of the organic particulates described herein to an asphalt binder that also includes a polymeric modifier can improve and maintain the effective dispersion of such polymeric modifiers in the asphalt composition. Therefore, some embodiments of the inventions described in this specification are directed to asphalt compositions that further comprise a polymeric modifier.

[0043] In some of these aspects, the polymer modifier and the organic particulates described in this specification are present in the asphalt composition in a weight ratio of 1:10 to 10:1 or 1:5 to 5:1. In some cases, the polymer modifier is present in an amount at least as great as the organic particulate described in this specification, such as where the polymer modifier and the organic particulate are present in a weight ratio of 10:1 to 1:1 or 5:1 to 1:1.

[0044] These aspects of the asphalt compositions of the present disclosure can be prepared by any of a variety of methods. In some embodiments, the organic particulate is first dispersed in a paving grade asphalt binder by high shear mixing to disperse the particulates in the binder using a temperature of at least 150°C, such as 180 to 200°C, to melt the asphalt binder. Then, the polymer modifier is added and to the binder and dispersed. The asphalt binder, as modified by inclusion with the organic particulates and the

polymer modifier, is then combined with aggregate to coat the aggregate prior to deposition to form a pavement.

[0045] Various aspects of the subject matter described herein are set out in the following numbered examples:

[0046] Example 1. An asphalt composition comprising an aggregate coated with a coating, the coating comprising: (a) a paving grade asphalt binder, and (b) an organic particulate having a particle size of no more than 200 micrometers and comprising: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0047] Example 2. The asphalt composition of Example 1, wherein the paving grade asphalt binder has a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-16, PG 70-22, PG 76-22, or PG 70-28 when graded according to Standard AASHTO M 320-17.

[0048] Example 3. The asphalt composition of Example 1 to Example 2, wherein the paving grade asphalt binder is present in the asphalt composition in an amount of up to 99.99% by weight, up to 99.9% by weight, up to 99% by weight, up to 98% by weight, or up to 97% by weight and/or at least 80% by weight, at least 90% by weight, at least 92% by weight, at least 94% by weight, or at least 95% by weight, based on the total combined weight of the asphalt binder and the organic particulates in the asphalt composition.

[0049] Example 4. The asphalt composition of Example 1 to Example 3, wherein the organic particulate is an isocyanate-containing residue that is a byproduct of a process for producing an aromatic polyisocyanate by (1) the reaction of the corresponding amine with phosgene in a suitable solvent and multi-stage distillative work-up of the isocyanate solution obtained to recover pure isocyanate, pure solvent and an isocyanate-containing residue, and (2) continuously feeding the residue obtained from the distillation process and from 2 to 50 weight % of a high-boiling hydrocarbon which is inert under the distillation conditions to a heated, product-agitating vacuum drier with a horizontal shaft.

[0050] Example 5. The asphalt composition of Example 4, wherein the isocyanate comprises an aromatic polyisocyanates, such as 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylxylene diisocyanate, 1,5-naphthalene diisocyanate, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate, 2,2'-diisocyanatodiphenylmethane,

diphenylmethanediisocyanate, 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, benzene, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl, 2,4,6-triisopropyl-m-phenylene diisocyanate, or triphenylmethane-4,4',4''-triisocyanate, tris(p-isocyanatophenyl)thiophosphate.

[0051] Example 6. The asphalt composition of Example 1 to Example 5, wherein the high-boiling hydrocarbon comprises a bitumen of grade 6/12, 10/20, 20/30, 30/40, 40/50, 60/70, 80/100, 100/120, or 180/200.

[0052] Example 7. The asphalt composition of Example 1 to Example 6, wherein the organic particulate has a particle size of at least 0.1 micrometer, at least 1 micrometer, at least 5 micrometers, at least 10 micrometers, at least 30 micrometers, at least 50 micrometers, or at least 90 micrometers.

[0053] Example 8. The asphalt composition of Example 7, wherein the particle size is 90 to 200 micrometers.

[0054] Example 9. The asphalt composition of Example 1 to Example 8, wherein the organic particulate has a Mohs hardness of 2 to 4, and/or a specific gravity of 1.2 to 1.4.

[0055] Example 10. The asphalt composition of Example 1 to Example 9, wherein the ash content of the organic particulate is less than 0.5% by weight.

[0056] Example 11. The asphalt composition of Example 1 to Example 10, wherein the organic particulate is insoluble in water at room temperature and atmospheric pressure, and has a solubility of less than 5% at room temperature and atmospheric pressure in any of the following organic solvents: acetone, chlorobenzene, xylenes, dimethylformamide, dimethylsulfoxide, dimethylacetamide, 1:1 mixture of acetone: aromatic 100, carbon disulfide, chloroform, methylene chloride, or tetrahydrofuran.

[0057] Example 12. The asphalt composition of Example 1 to Example 11, wherein the content of high-boiling hydrocarbon in the organic particulate is from 1 to 10% by weight, 2 to 6% by weight, or 3 to 5% by weight, based on the total weight of the organic particulate.

[0058] Example 13. The asphalt composition of Example 1 to Example 12, wherein the organic particulate has a content of reactive NCO groups that is less than 6% by weight, based on the total weight of the organic particulate.

[0059] Example 14. The asphalt composition of Example 1 to Example 13, wherein the organic particulate is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

[0060] Example 15. The asphalt composition of Example 1 to Example 14, wherein the organic particulate is present in the asphalt composition in an amount of at least 0.01%, at least 0.1%, at least 1%, at least 2%, or at least 3% by weight and/or up to 20%, up to 10%, up to 8%, up to 6%, or up to 5% by weight, based on the total combined weight of organic particulates and asphalt binder in the asphalt composition.

[0061] Example 16. The asphalt composition of Example 1 to Example 15, wherein the asphalt composition further comprises a polymeric modifier, such as rubber, polyethylene, and/or polypropylene.

[0062] Example 17. The asphalt composition of Example 16, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1, 1:5 to 5:1, 10:1 to 1:1, or 5:1 to 1:1.

[0063] Example 18. A method of increasing the high temperature rutting resistance of asphalt pavement, comprising coating aggregate with an asphalt composition comprising an organic particulate dispersed in a paving grade asphalt binder, the organic particulate having a particle size of no more than 200 micrometers and comprising: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0064] Example 19. The method of Example 18, wherein the paving grade asphalt binder has a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-16, PG 70-22, PG 76-22, or PG 70-28 when graded according to Standard AASHTO M 320-17.

[0065] Example 20. The method of Example 18 to Example 19, wherein the paving grade asphalt binder is present in the asphalt composition in an amount of up to 99.99% by weight, up to 99.9% by weight, up to 99% by weight, up to 98% by weight, or up to 97% by weight and/or at least 80% by weight, at least 90% by weight, at least 92% by weight, at least 94% by weight, or at least 95% by weight, based on the total combined weight of the asphalt binder and the organic particulates in the asphalt composition.

[0066] Example 21. The method of Example 18 to Example 20, wherein the organic particulate is an isocyanate-containing residue that is a byproduct of a process for producing an aromatic polyisocyanate by (1) the reaction of the corresponding amine with phosgene in a suitable solvent and multi-stage distillative work-up of the isocyanate solution obtained to recover pure isocyanate, pure solvent and an isocyanate-containing residue, and (2) continuously feeding the residue obtained from the distillation process and from 2 to 50

weight % of a high-boiling hydrocarbon which is inert under the distillation conditions to a heated, product-agitating vacuum drier with a horizontal shaft.

[0067] Example 22. The method of Example 21, wherein the isocyanate comprises an aromatic polyisocyanates, such as 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylxylene diisocyanate, 1,5-naphthalene diisocyanate, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate, 2,2'-diisocyanatodiphenylmethane, diphenylmethanediisocyanate, 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, benzene, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl, 2,4,6-triisopropyl-m-phenylene diisocyanate, or triphenylmethane-4,4',4"-triisocyanate, tris(p-isocyanatophenyl)thiophosphate.

[0068] Example 23. The method of Example 18 to Example 22, wherein the high-boiling hydrocarbon comprises a bitumen of grade 6/12, 10/20, 20/30, 30/40, 40/50, 60/70, 80/100, 100/120, or 180/200.

[0069] Example 24. The method of Example 18 to Example 23, wherein the organic particulate has a particle size of at least 0.1 micrometer, at least 1 micrometer, at least 5 micrometers, at least 10 micrometers, at least 30 micrometers, at least 50 micrometers, or at least 90 micrometers.

[0070] Example 25. The method of Example 24, wherein the particle size is 90 to 200 micrometers.

[0071] Example 26. The method of Example 18 to Example 25, wherein the organic particulate has a Mohs hardness of 2 to 4, and/or a specific gravity of 1.2 to 1.4.

[0072] Example 27. The method of Example 18 to Example 26, wherein the ash content of the organic particulate is less than 0.5% by weight.

[0073] Example 28. The method of Example 18 to Example 27, wherein the organic particulate is insoluble in water at room temperature and atmospheric pressure, and has a solubility of less than 5% at room temperature and atmospheric pressure in any of the following organic solvents: acetone, chlorobenzene, xylenes, dimethylformamide, dimethylsulfoxide, dimethylacetamide, 1:1 mixture of acetone: aromatic 100, carbon disulfide, chloroform, methylene chloride, or tetrahydrofuran.

[0074] Example 29. The method of Example 18 to Example 28, wherein the content of high-boiling hydrocarbon in the organic particulate is from 1 to 10% by weight, 2 to 6% by weight, or 3 to 5% by weight, based on the total weight of the organic particulate.

[0075] Example 30. The method of Example 18 to Example 29, wherein the organic particulate has a content of reactive NCO groups that is less than 6% by weight, based on the total weight of the organic particulate.

[0076] Example 31. The method of Example 18 to Example 30, wherein the organic particulate is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

[0077] Example 32. The method of Example 18 to Example 31, wherein the organic particulate is present in the asphalt composition in an amount of at least 0.01%, at least 0.1%, at least 1%, at least 2%, or at least 3% by weight and/or up to 20%, up to 10%, up to 8%, up to 6%, or up to 5% by weight, based on the total combined weight of organic particulates and asphalt binder in the asphalt composition.

[0078] Example 33. The method of Example 18 to Example 32, wherein the asphalt composition further comprises a polymeric modifier, such as rubber, polyethylene, and/or polypropylene.

[0079] Example 34. The method of Example 33, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1, 1:5 to 5:1, 10:1 to 1:1, or 5:1 to 1:1.

[0080] Example 35. An asphalt pavement comprising an aggregate coated with an asphalt composition comprising a paving grade asphalt binder having an organic particulate dispersed therein, the organic particulate having a particle size of no more than 200 micrometers and comprising: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon.

[0081] Example 36. The pavement of Example 35, wherein the paving grade asphalt binder has a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-16, PG 70-22, PG 76-22, or PG 70-28 when graded according to Standard AASHTO M 320-17.

[0082] Example 37. The pavement of Example 35 to Example 36, wherein the paving grade asphalt binder is present in the asphalt composition in an amount of up to 99.99% by weight, up to 99.9% by weight, up to 99% by weight, up to 98% by weight, or up to 97% by weight and/or at least 80% by weight, at least 90% by weight, at least 92% by weight, at least 94% by weight, or at least 95% by weight, based on the total combined weight of the asphalt binder and the organic particulates in the asphalt composition.

[0083] Example 38. The pavement of Example 35 to Example 37, wherein the organic particulate is an isocyanate-containing residue that is a byproduct of a process for

producing an aromatic polyisocyanate by (1) the reaction of the corresponding amine with phosgene in a suitable solvent and multi-stage distillative work-up of the isocyanate solution obtained to recover pure isocyanate, pure solvent and an isocyanate-containing residue, and (2) continuously feeding the residue obtained from the distillation process and from 2 to 50 weight % of a high-boiling hydrocarbon which is inert under the distillation conditions to a heated, product-agitating vacuum drier with a horizontal shaft.

[0084] Example 39. The pavement of Example 35, wherein the isocyanate comprises an aromatic polyisocyanates, such as 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylxylene diisocyanate, 1,5-naphthalene diisocyanate, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate, 2,2'-diisocyanatodiphenylmethane, diphenylmethanediisocyanate, 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, benzene, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl, 2,4,6-triisopropyl-m-phenylene diisocyanate, or triphenylmethane-4,4',4''-triisocyanate, tris(p-isocyanatophenyl)thiophosphate.

[0085] Example 40. The pavement of Example 35 to Example 39, wherein the high-boiling hydrocarbon comprises a bitumen of grade 6/12, 10/20, 20/30, 30/40, 40/50, 60/70, 80/100, 100/120, or 180/200.

[0086] Example 41. The pavement of Example 35 to Example 40, wherein the organic particulate has a particle size of at least 0.1 micrometer, at least 1 micrometer, at least 5 micrometers, at least 10 micrometers, at least 30 micrometers, at least 50 micrometers, or at least 90 micrometers.

[0087] Example 42. The pavement of Example 41, wherein the particle size is 90 to 200 micrometers.

[0088] Example 43. The pavement of Example 35 to Example 42, wherein the organic particulate has a Mohs hardness of 2 to 4, and/or a specific gravity of 1.2 to 1.4.

[0089] Example 44. The pavement of Example 35 to Example 43, wherein the ash content of the organic particulate is less than 0.5% by weight.

[0090] Example 45. The pavement of Example 35 to Example 44, wherein the organic particulate is insoluble in water at room temperature and atmospheric pressure, and has a solubility of less than 5% at room temperature and atmospheric pressure in any of the following organic solvents: acetone, chlorobenzene, xylenes, dimethylformamide,

dimethylsulfoxide, dimethylacetamide, 1:1 mixture of acetone: aromatic 100, carbon disulfide, chloroform, methylene chloride, or tetrahydrofuran.

[0091] Example 46. The pavement of Example 35 to Example 45, wherein the content of high-boiling hydrocarbon in the organic particulate is from 1 to 10% by weight, 2 to 6% by weight, or 3 to 5% by weight, based on the total weight of the organic particulate.

[0092] Example 47. The pavement of Example 35 to Example 46, wherein the organic particulate has a content of reactive NCO groups that is less than 6% by weight, based on the total weight of the organic particulate.

[0093] Example 48. The pavement of Example 35 to Example 47, wherein the organic particulate is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

[0094] Example 49. The pavement of Example 35 to Example 48, wherein the organic particulate is present in the asphalt composition in an amount of at least 0.01%, at least 0.1%, at least 1%, at least 2%, or at least 3% by weight and/or up to 20%, up to 10%, up to 8%, up to 6%, or up to 5% by weight, based on the total combined weight of organic particulates and asphalt binder in the asphalt composition.

[0095] Example 50. The pavement of Example 35 to Example 49, wherein the asphalt composition further comprises a polymeric modifier dispersed therein, such as rubber, polyethylene, and/or polypropylene.

[0096] Example 51. The pavement of Example 50, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1, 1:5 to 5:1, 10:1 to 1:1, or 5:1 to 1:1.

[0097] Example 52. A method of making an asphalt pavement, comprising coating aggregate with an asphalt composition, wherein the asphalt composition comprises (i) a paving grade asphalt binder, (ii) a polymeric modifier, and (iii) an organic particulate having a particle size of no more than 200 micrometers and that is a byproduct of a process for producing an aromatic isocyanate.

[0098] Example 53. The method of Example 52, wherein the organic particulate comprises: (a) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (b) a high-boiling hydrocarbon.

[0099] Example 54. The method of Example 52 to Example 53, wherein the paving grade asphalt binder has a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-

16, PG 70-22, PG 76-22, or PG 70-28 when graded according to Standard AASHTO M 320-17.

[00100] Example 55. The method of Example 52 to Example 54, wherein the paving grade asphalt binder is present in the asphalt composition in an amount of up to 99.99% by weight, up to 99.9% by weight, up to 99% by weight, up to 98% by weight, or up to 97% by weight and/or at least 80% by weight, at least 90% by weight, at least 92% by weight, at least 94% by weight, or at least 95% by weight, based on the total combined weight of the asphalt binder and the organic particulates in the asphalt composition.

[00101] Example 56. The method of Example 52 to Example 55, wherein the organic particulate is an isocyanate-containing residue that is a byproduct of a process for producing an aromatic polyisocyanate by (1) the reaction of the corresponding amine with phosgene in a suitable solvent and multi-stage distillative work-up of the isocyanate solution obtained to recover pure isocyanate, pure solvent and an isocyanate-containing residue, and (2) continuously feeding the residue obtained from the distillation process and from 2 to 50 weight % of a high-boiling hydrocarbon which is inert under the distillation conditions to a heated, product-agitating vacuum drier with a horizontal shaft.

[00102] Example 57. The method of Example 56, wherein the isocyanate comprises an aromatic polyisocyanates, such as 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylxylene diisocyanate, 1,5-naphthalene diisocyanate, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate, 2,2'-diisocyanatodiphenylmethane, diphenylmethanediisocyanate, 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, benzene, 1-[(2,4-diisocyanatophenyl)methyl]- 3-isocyanato-2-methyl, 2,4,6-triisopropyl-m-phenylene diisocyanate, or triphenylmethane-4,4',4"-triisocyanate, tris(p-isocyanatophenyl)thiophosphate.

[00103] Example 58. The method of Example 56 to Example 57, wherein the high-boiling hydrocarbon comprises a bitumen of grade 6/12, 10/20, 20/30, 30/40, 40/50, 60/70, 80/100, 100/120, or 180/200.

[00104] Example 59. The method of Example 52 to Example 58, wherein the organic particulate has a particle size of at least 0.1 micrometer, at least 1 micrometer, at least 5 micrometers, at least 10 micrometers, at least 30 micrometers, at least 50 micrometers, or at least 90 micrometers.

[00105] Example 60. The method of Example 59, wherein the particle size is 90 to 200 micrometers.

[00106] Example 61. The method of Example 52 to Example 60, wherein the organic particulate has a Mohs hardness of 2 to 4, and/or a specific gravity of 1.2 to 1.4.

[00107] Example 62. The method of Example 52 to Example 61, wherein the ash content of the organic particulate is less than 0.5% by weight.

[00108] Example 63. The method of Example 52 to Example 62, wherein the organic particulate is insoluble in water at room temperature and atmospheric pressure, and has a solubility of less than 5% at room temperature and atmospheric pressure in any of the following organic solvents: acetone, chlorobenzene, xylenes, dimethylformamide, dimethylsulfoxide, dimethylacetamide, 1:1 mixture of acetone: aromatic 100, carbon disulfide, chloroform, methylene chloride, or tetrahydrofuran.

[00109] Example 64. The method of Example 56, wherein the content of high-boiling hydrocarbon in the organic particulate is from 1 to 10% by weight, 2 to 6% by weight, or 3 to 5% by weight, based on the total weight of the organic particulate.

[00110] Example 65. The method of Example 52 to Example 64, wherein the organic particulate has a content of reactive NCO groups that is less than 6% by weight, based on the total weight of the organic particulate.

[00111] Example 66. The method of Example 52 to Example 65, wherein the organic particulate is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

[00112] Example 67. The method of Example 52 to Example 66, wherein the organic particulate is present in the asphalt composition in an amount of at least 0.01%, at least 0.1%, at least 1%, at least 2%, or at least 3% by weight and/or up to 20%, up to 10%, up to 8%, up to 6%, or up to 5% by weight, based on the total combined weight of organic particulates and asphalt binder in the asphalt composition.

[00113] Example 68. The method of Example 52 to Example 67, wherein the polymeric modifier comprises rubber, polyethylene, and/or polypropylene.

[00114] Example 69. The method of Example 52 to Example 68, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1, 1:5 to 5:1, 10:1 to 1:1, or 5:1 to 1:1.

EXAMPLES

[00115] SUPERPAVE™ Performance Grading ("PG") is used to assess the quality of asphalt binders. The PG grading system specifies limitations at various temperature and aging levels. In particular, to account for temperature and aging, PG grading specifies limitations at specific temperatures and aging levels:

- **High Temperature $G^*/\sin\delta$:** A minimum $G^*/\sin\delta$ of 1 kPa and 2.2 kPa are specified in the un-aged and short term aged condition, respectively. $G^*/\sin\delta$ represents the asphalt binder's stiffness and elasticity; where a higher G^* represents a higher stiffness and a lower δ represents a higher elasticity. It is desirable to increase the asphalt binder stiffness and elasticity at high temperatures to guard against permanent pavement deformation.
- **Intermediate Temperature $G^*\sin\delta$:** A maximum $G^*\sin\delta$ of 5000 kPa is specified after long term aging. Asphalt binders are susceptible to durability cracking for extended oxidative aging times at intermediate temperatures. Binders that are too stiff and inelastic are prone to durability cracking.
- **Low Temperature Stiffness and M-value:** A maximum stiffness of 300 MPa and minimum m-value of 0.300 are specified in the long term aging condition. M-value represents an asphalt binder's ability to relax stress at low temperatures. As asphalt binder cools in the field, thermal stresses build in the asphalt pavement. If the asphalt binder cools such that the thermal stresses exceed the strength of the pavement, a crack will form. Binders that are able to relax thermal stresses and maintain lower levels of stress are less prone to thermal cracks.

Example 1

[00116] In order to determine the effect of including solid toluene diisocyanate residue particles on the properties of asphalt binders, PG grading was conducted on asphalt binders with and without such particles included. The solid toluene diisocyanate residue particles comprised: (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and (ii) a high-boiling hydrocarbon, and were prepared according to the process described in U.S. Patent No. 5,446,196. The solid particles were processed in a laboratory ball mill followed by subjecting the processed material to size classification using a stack of progressively finer stainless steel sieves

similar to what is generally described in ASTM D4749-87(2012) to give powders with distinct and characteristic particle sizes as follows: (a) only solid powder passing through a U.S. Tyler sieve #500 and therefore with nominal characteristic dimension less than about 22 micrometers ("Ultra-fine particles"); (b) only solid powder passing through a U.S. Tyler sieve #230 but retained on a U.S. Tyler sieve #400 and therefore with nominal characteristic dimension less than about 63 micrometers but greater than about 36 micrometers ("Fine particles"); and (c) only solid powder passing through a U.S. Tyler sieve #70 but retained on a U.S. Tyler sieve #170 and therefore with nominal characteristic dimension less than about 200 micrometers but greater than about 90 micrometers ("Coarse particles").

[00117] Prior to PG grading, the particles were high shear blended in an asphalt binder using with radial paddles spinning at speed around 5,000 RPMs. After high shear blending at 150°C for one hour to attempt to melt and disperse the particles within the asphalt binder, representative samples were smeared onto glass slides. The particles were still observable after one hour of high shear blending, indicating that the particles did not melt or dissolve after blending.

[00118] FH 64-22 graded asphalt binder was modified with Coarse particles, Fine particles, and Ultra Fine particles respectively. Each binder was modified at the same concentration of 4% by weight of particles, based on the total weight of the binder. Once modified, each binder was high temperature PG graded in the un-aged (Figure 1a) and short term aged (Figure 1b) condition. Results are illustrated in Figures 1a and 1b respectively. The horizontal dashed line in each Figure represents the PG specification minimum threshold. The high temperature PG grade of the unmodified binder is 64. A PG grade of 64 indicates that the $G^*/\sin\delta$ for both the un-aged and short term aged binder is greater than 1 kPa and 2.2 kPa, respectively. Modification of the binder with Coarse particles was sufficient to change the PG grade from 64 to 70, but not sufficient to change it to 76. An increase from 64 to 70 indicates that the Coarse particles improved the high temperature performance of the FH 64-22 binder. Further inspection of the Figures 1a and 1b shows that while binder modification with Fine or Ultra-fine particles improved the performance, the change was not sufficient to raise the PG to 70. Coarse TDI particles were then selected to be tested with an additional binder source, Val 58-22, to capture any binder chemistry dependence.

[00119] High temperature PG testing was then performed on Val 58-22 and FH 64-22 graded asphalt binders. The goal of this testing was to understand if the effects of Coarse particles were sensitive to asphalt binder chemistry, at concentrations of 4% by weight and

8% by weight of Coarse particles, based on the total weight of the binder. Results are illustrated in Figure 2. Figure 2 illustrates the results of $G^*/\sin\delta$ measurements for the two different binders at the PG temperature. For the unmodified FH 64-22 and Val 58-22 binders the PG temperature is 64°C and 58°C, respectively. The two aging conditions for the testing were un-aged and short term aged (RTFO). Figure 2 shows that the results were sensitive to binder chemistry. Evidence for this would be to compare the results between FH 64 and Val 58, unmodified and with Coarse particles. For the Val58 the use of the Coarse particles caused noticeably less change in the response than occurred with the FH64 binder. Because the two binders differed in their detailed chemical compositions, the differences in response were attributed to the interactions of these differences with the action of the Coarse particles in the high temperature PG grading test.

[00120] Additional tests were conducted at intermediate and low temperatures with the FH 64-22 binder to understand effects of TDI modification at different temperature ranges in the PG grading system.

[00121] According to the PG grading, asphalt binders are required to have a $G^*\sin\delta$ (fatigue factor) of less than 5000 kPa at intermediate temperatures after long term oxidative aging in a Pressure Aging Vessel (PAV). For example, in order to be considered a PG 64-22, an asphalt binder must have a PAV-aged $G^*\sin\delta$ of less than 5000 kPa at 25°C. Figure 3 illustrates the intermediate temperature testing results with and without Coarse particle modification (4% by weight, based on total binder weight).

[00122] For a PG 70-22 binder, the required intermediate temperature is 28°C. As is apparent, FH 64-22 asphalt binder modified with Coarse particles (4% by weight, based on total binder weight) passed the 5000 kPa criteria at 25°C, thus becoming PG70-22 graded. Although a grade increase from 64-22 to 70-22 was achieved, an increased stiffness was a negative consequence of modification. Common types of asphalt binder softening agents, e.g. oil modifiers, would decrease the stiffness at intermediate temperatures, which would be indicative of improved fatigue performance.

[00123] According to the PG grading, an asphalt binder must meet stiffness and relaxation specification limits at typical low service temperatures to guard against thermal cracking. Low temperature cracking is generally found in older pavements; therefore the test is performed on the long-term aged material (PAV aged). Two parameters: creep stiffness and m-value are specified in the PG system. The stiffness of asphalt binder should be below 300 MPa and m value should be greater than 0.300 at the low temperature grade test temperature (e.g. -22°C). Table 1 shows a comparison between the unmodified and

Coarse particle modification (4% by weight, based on total binder weight) after low temperature grading. Binders were tested 10°C higher than the low temperature they are graded; a -22°C grade was tested at -12°C.

Table 1

FH 64-22 + 4% Coarse Particles						
<i>Temperature</i>	<i>Stiffness</i>	<i>Average</i>	<i>Criteria</i>	<i>m-value</i>	<i>Average</i>	<i>Criteria</i>
-12°C	281	281	≤ 300 MPa	0.297	0.296	≥ 0.3
	267			0.295		
-6°C	128	128	≤ 300 MPa	0.352	0.352	≥ 0.3
	122			0.352		
FH 64-22 Without Particles						
<i>Temperature</i>	<i>S</i>	<i>Average</i>	<i>Criteria</i>	<i>m</i>	<i>Average</i>	<i>Criteria</i>
-12°C	193	193	≤ 300 MPa	0.351	0.344	≥ 0.3
	197			0.336		
-18°C	424	424	≤ 300 MPa	0.265	0.265	≥ 0.3
	430			0.265		

[00124] Results showed that the modified asphalt binder increased the low temperature PG grade to -16. This indicates that after modification the asphalt binder was more susceptible to thermal cracking.

[00125] Results indicated that the particles behaved like mineral filler when dispersed in asphalt binder. In the asphalt industry, the amount of fine mineral filler added into asphalt binder is regulated based on the total asphalt binder in the mixture; called the dust to binder ratio (D:B) and is maintained between 0.6 to 1.6 depending on the state. Pavement constructability and performance is directly related to the D:B ratio. If the D:B is too high, the pavement may be too stiff and difficult to construct. If the D:B is too low, the pavement may be "tender" or susceptible to high temperature rutting. Despite its importance, mineral filler is inexpensive and plentiful in the asphalt industry. It was concluded that the solid isocyanate residue particles tested could act as a substitute for mineral filler in asphalt binder applications.

Example 2

[00126] Testing described in Example 1 indicated that certain solid toluene diisocyanate residue particles may be able to increase the high temperature rutting resistance of asphalt binders. High temperature ruts occur when truck traffic deforms the asphalt pavement layer in the form of wheel tracks. Asphalt binders that are susceptible to rutting damage are often soft binders used in warm climates (e.g. Southern United States) with low $G^*/\sin\delta$ values at high PG temperatures.

[00127] Although these particles showed promise in improving the PG high temperature grade of binders, a common challenge for particulate modifiers is storage stability. When binders modified with particulate additives are stored in asphalt tanks, the particulates may settle to the bottom or float to the top of the storage tanks; commonly called storage instability. Storage instability results in high material variability and practical challenges for asphalt producers. The most common particulate additive used today is recycled Tire Rubber (TR) which is known to have storage stability issues and thus is used with significant difficulty due to the need of continuous agitation and monitoring.

[00128] To understand the potential for toluene diisocyanate residue particles to show storage problems, storage stability and PG grading tests were conducted on Fine particles and Ultra-fine particles. Both were compared to using the 60 mesh TR modified binders. All of the binders were blended at a temperature of 150°C using a shear rate of 5000 RPMs. A modified version of the ASTM D 5976 standard was utilized to measure storage stability of each modified binder. To conduct this procedure, modified binders are poured into aluminum tubes. The aluminum tubes were then placed vertically into an oven at 163°C for 48 hours. Next, the tubes were moved into a freezer for a minimum of 4 hours to freeze the sample. Once the modified binders are frozen solid, the aluminum tubes were cut into thirds. Samples were taken from the top and bottom third of the aluminum tube for each modified binder and the $G^*/\sin\delta$ was measured at 64 and 70°C. Table 2 shows the $G^*/\sin\delta$ and calculated percent difference values for each modified binder.

Table 2

<u>Filler Type</u>	<u>Temperature</u>	<u>G*/sinδ</u> <u>(Top)</u>	<u>G*/sinδ</u> <u>(Bottom)</u>	<u>Difference</u>
Fine Particles	64°C	2.06 kPa	2.04 kPa	1%
Fine Particles	70°C	0.97 kPa	0.97 kPa	0%
Ultra-fine Particles	64°C	2.50 kPa	2.22 kPa	11%
Ultra-fine Particles	70°C	1.17 kPa	1.04 kPa	11%
TR Particles	64°C	4.40 kPa	15.45 kPa	251%
TR Particles	70°C	2.08 kPa	7.79 kPa	275%

[00129] The results set forth in Table 2 indicate that the Fine particles and Ultra-fine particles were more stable than the TR particles in the asphalt binder. Despite the clear advantage for storage stability of the Fine particle and Ultra-fine particle modified binders, the $G^*/\sin\delta$ at high temperatures was much larger for the rubber modified binder in comparison. Further PG testing was conducted at the same concentration, 5% by weight, based on total weight of the binder, to quantify the potential for each modification type to increase rutting resistance of asphalt binders.

[00130] Particles and asphalt binder were blended using the same high shear procedure as previously used. Each binder was measured for the high temperature PG $G^*/\sin\delta$ parameter at 64 and 70°C. Results are illustrated in Figure 4 and show that the TR particles increased the $G^*/\sin\delta$ to a larger degree than the use of either the Fine particles or the Ultra-fine particles, notably at the higher temperatures. The results of Example 1, however, indicate that Coarse particles may be able to provide an equivalent $G^*/\sin\delta$ as TR particles at a use level of 5% in asphalt binder.

[00131] In a further round of experiments, a different 64-22 graded asphalt binder was employed with solid toluene diisocyanate residue particles which were not subjected to any post-process size reduction of the particles. These “AS IS” (particle sizes ranging from several hundred micrometers to several millimeters) granular solids were high shear blended in the asphalt binder at different use levels using process conditions as described earlier for the attempted melting and dispersion of the size reduced particles, see paragraph [0090]. In comparison these “AS IS” granular solids were much more difficult to disperse in the asphalt binder and they required blend times of 4, 6, and up to 8 hours of high shear mixing at 150 degrees C to obtain a serviceable suspension suitable for further testing according to AASHTO standard.

[00132] As indicated in Table 3, the asphalt binder was modified with toluene diisocyanate residue particles at levels of 2, 4, 10 and 20 % (w/w), and compared to asphalt binder modified instead with 5 % (w/w) of recycled tire rubber (TR). Each binder was high temperature PG graded in the aged and short term aged condition as per the standard. The high temperature PG grade of the unmodified binder is 64. A PG grade of 64 indicates that when tested at a temperature of 64 degrees C, the $G^*/\sin\delta$ for both the un-aged and short term aged binder are greater than 1 kPa and 2.2 kPa, respectively. Asphalt binder modified with “AS IS” non-size reduced particles was tested at 70 degrees C, but as is evident in Table 3, the value of $G^*/\sin\delta$ was in no case sufficient to meet the requirements at the levels tested. On the other hand there is an increasing trend in the values of $G^*/\sin\delta$ as the level of the particles rises, indicating that the use of the particles was not detrimental merely not sufficient to improve the high temperature performance of the asphalt binder in this high temperature test. In contrast, the asphalt binder modified with 5 % tire rubber easily passed the PG grade of 70.

Table 3: AASHTO Testing of Non-size Reduced Particles using PG 64-22 Asphalt Binder.

High temperature PG testing of modified binders conducted at 70 degrees C.

	2% modified	4% modified	10% modified	20% modified	5 % tire rubber	units	Spec Limit
Unaged $G^*/\sin\delta$	0.83	0.83	0.84	0.85	1.22	kPa	Min. 1.00
Short term aged $G^*/\sin\delta$	2.00	2.07	2.06	2.17	3.11	kPa	Min. 2.20

[00133] These results with the PG 64-22 binder and the “AS IS” non-size reduced particles indicate that the particle size matters and that particles that do not fall within an optimal size range may not be as effective in raising the performance grade of the asphalt binder. It is apparent that the overall optimum size of the solid toluene diisocyanate residue particles corresponds to the “Coarse particles” as described herein which generally speaking is a particle size in the range of 90 to 200 micrometers as determined by material that successfully passes through sieves or screens with U.S. Tyler sieve #70 but is generally retained on screens with U.S. Tyler sieve # 170.

[00134] Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. An asphalt composition comprising an aggregate coated with a coating, the coating comprising:
 - (a) a paving grade asphalt binder, and
 - (b) an organic particulate having a particle size of no more than 200 micrometers and comprising:
 - (i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and
 - (ii) a high-boiling hydrocarbon.
2. The asphalt composition of claim 1, wherein the paving grade asphalt binder has a performance grade rating of PG 58-22, PG 64-22, PG 64-16, PG 64-28, PG 52-34, PG 52-28, PG 58-28, PG 67-10, PG 64-10, PG 67-22, PG 70-10, PG 70-16, PG 70-22, PG 76-22, or PG 70-28 when graded according to Standard AASHTO M 320-17 .
3. The asphalt composition of claim 2, wherein the paving grade asphalt binder has a performance grade rating of PG 64-22 when graded according to Standard AASHTO M 320-17.
4. The asphalt composition of claim 1, wherein the paving grade asphalt binder is present in an amount of at least 80% by weight, based on the total weight of the asphalt composition.
5. The asphalt composition of claim 4, wherein the paving grade asphalt binder is present in an amount of at least 90% by weight, based on the total weight of the asphalt composition.
6. The asphalt composition of claim 5, wherein the paving grade asphalt binder is present in an amount of at least 95% by weight, based on the total weight of the asphalt composition.
7. The asphalt composition of claim 1, wherein the organic particulate (b) is the dried product of a mixture comprising:

- (1) a residue of an aromatic polyisocyanate production process; and
- (2) a high-boiling hydrocarbon.

8. The asphalt composition of claim 7, wherein the polyisocyanate comprises a toluene diisocyanate.
9. The asphalt composition of claim 7, wherein the high-boiling hydrocarbon comprises a bitumen.
10. The asphalt composition of claim 1, wherein the particle size is 90 to 200 micrometers.
11. The asphalt composition of claim 10, wherein the paving grade asphalt binder has a performance grade rating of PG 64-22 when graded according to Standard AASHTO M320-17.
12. The asphalt composition of claim 1, wherein the organic particulate (b) is present in an amount of at least 0.1% and up to 10% by weight, based on the total weight of the paving grade asphalt binder in the asphalt composition.
13. The asphalt composition of claim 12, wherein the organic particulate (b) is present in an amount of at least 1% and up to 6% by weight, based on the total weight of the paving grade asphalt binder in the asphalt composition.
14. The asphalt composition of claim 1, wherein the asphalt composition further comprises a rubber, polyethylene, and/or polypropylene polymeric modifier, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1.
15. A method of increasing the high temperature rutting resistance of asphalt pavement, comprising coating aggregate with an asphalt composition comprising an organic particulate dispersed in a paving grade asphalt binder, the organic particulate having a particle size of no more than 200 micrometers and comprising:

(i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and

(ii) a high-boiling hydrocarbon.

16. The method of claim 15, wherein:

(a) the paving grade asphalt binder has a performance grade rating of PG 64-22 when graded according to Standard AASHTO M320-17 and is present in an amount of at least 90% by weight, based on the total weight of the asphalt composition; and

(b) the organic particulate has a particle size of 90 to 200 micrometers and is present in an amount of at least 0.1% and up to 10% by weight, based on the total weight of the paving grade asphalt binder in the asphalt composition.

17. The method of claim 15, wherein the organic particulate is the dried product of a mixture comprising: (1) a residue of a toluene diisocyanate polyisocyanate production process; and (2) a high-boiling hydrocarbon comprising bitumen.

18. The method of claim 15, wherein the asphalt composition further comprises a rubber, polyethylene, and/or polypropylene polymeric modifier, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1.

19. An asphalt pavement comprising an aggregate coated an asphalt composition comprising a paving grade asphalt binder having an organic particulate dispersed therein, wherein the organic particulate has a particle size of no more than 200 micrometers and comprises:

(i) a crosslinked polymer comprising aromatic groups, biuret groups, urea groups, and carbodiimide groups; and

(ii) a high-boiling hydrocarbon.

20. The asphalt pavement of claim 19, wherein:

(a) the paving grade asphalt binder has a performance grade rating of PG 64-22 when graded according to Standard AASHTO M320-17 and is present in an amount of at least 90% by weight, based on the total weight of the asphalt composition; and

(b) the organic particulate has a particle size of 90 to 200 micrometers and is present in an amount of at least 0.1% and up to 10% by weight, based on the total weight of the paving grade asphalt binder in the asphalt composition.

21. The asphalt pavement of claim 20, wherein the organic particulate is the dried product of a mixture comprising: (1) a residue of a toluene diisocyanate polyisocyanate production process; and (2) a high-boiling hydrocarbon comprising bitumen.

22. The asphalt pavement of claim 18, wherein the asphalt composition further comprises a rubber, polyethylene, and/or polypropylene polymeric modifier, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1.

23. A method of making an asphalt pavement, comprising coating aggregate with an asphalt composition, wherein the asphalt composition comprises:

(i) a paving grade asphalt binder,

(ii) a polymeric modifier, and

(iii) an organic particulate having a particle size of no more than 200 micrometers and that is a byproduct of a process for producing an aromatic isocyanate.

24. The method of claim 23, wherein the organic particulate is the phosgenation product of toluene diamine containing less than 0.5% by weight of ortho-toluenediamine isomers, based on the total weight of toluene diamine.

25. The method of claim 23, wherein the polymeric modifier comprises rubber, polyethylene, and/or polypropylene.

26. The method of claim 25, wherein the polymeric modifier and the organic particulate are present in the asphalt composition in a weight ratio of 1:10 to 10:1, 1:5 to 5:1, 10:1 to 1:1, or 5:1 to 1:1.

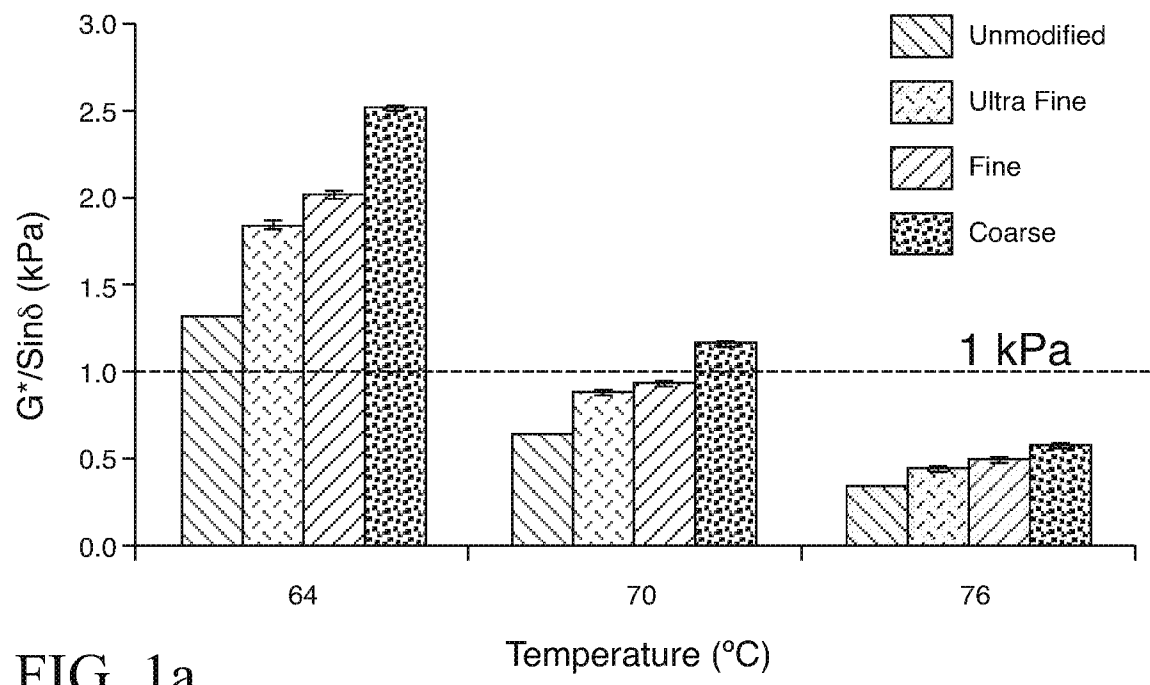


FIG. 1a

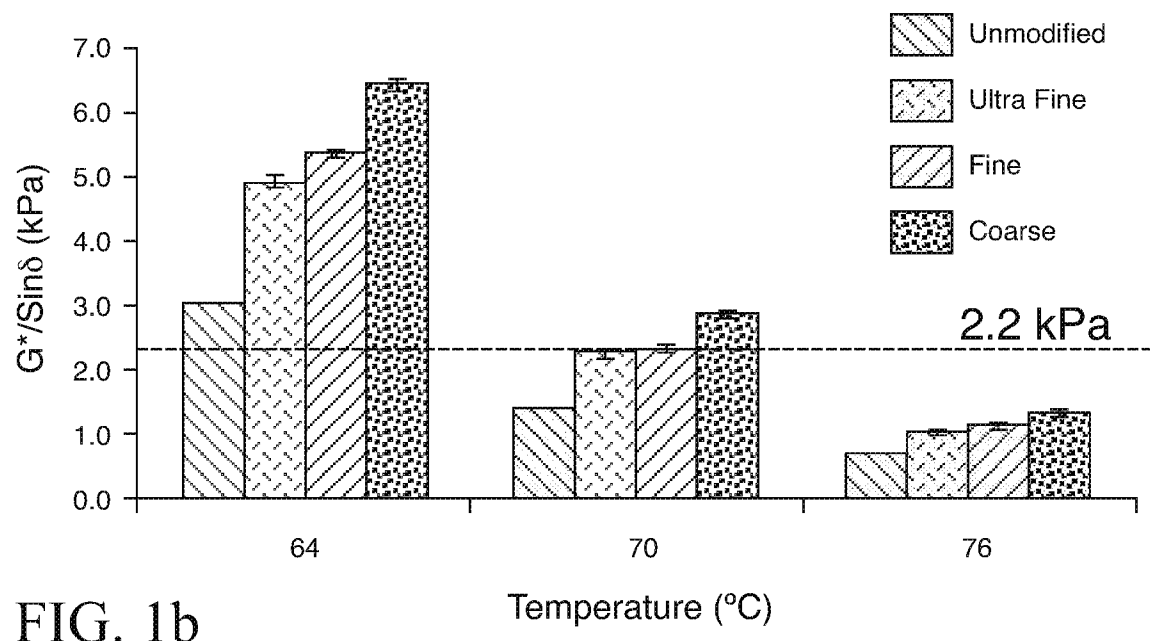


FIG. 1b

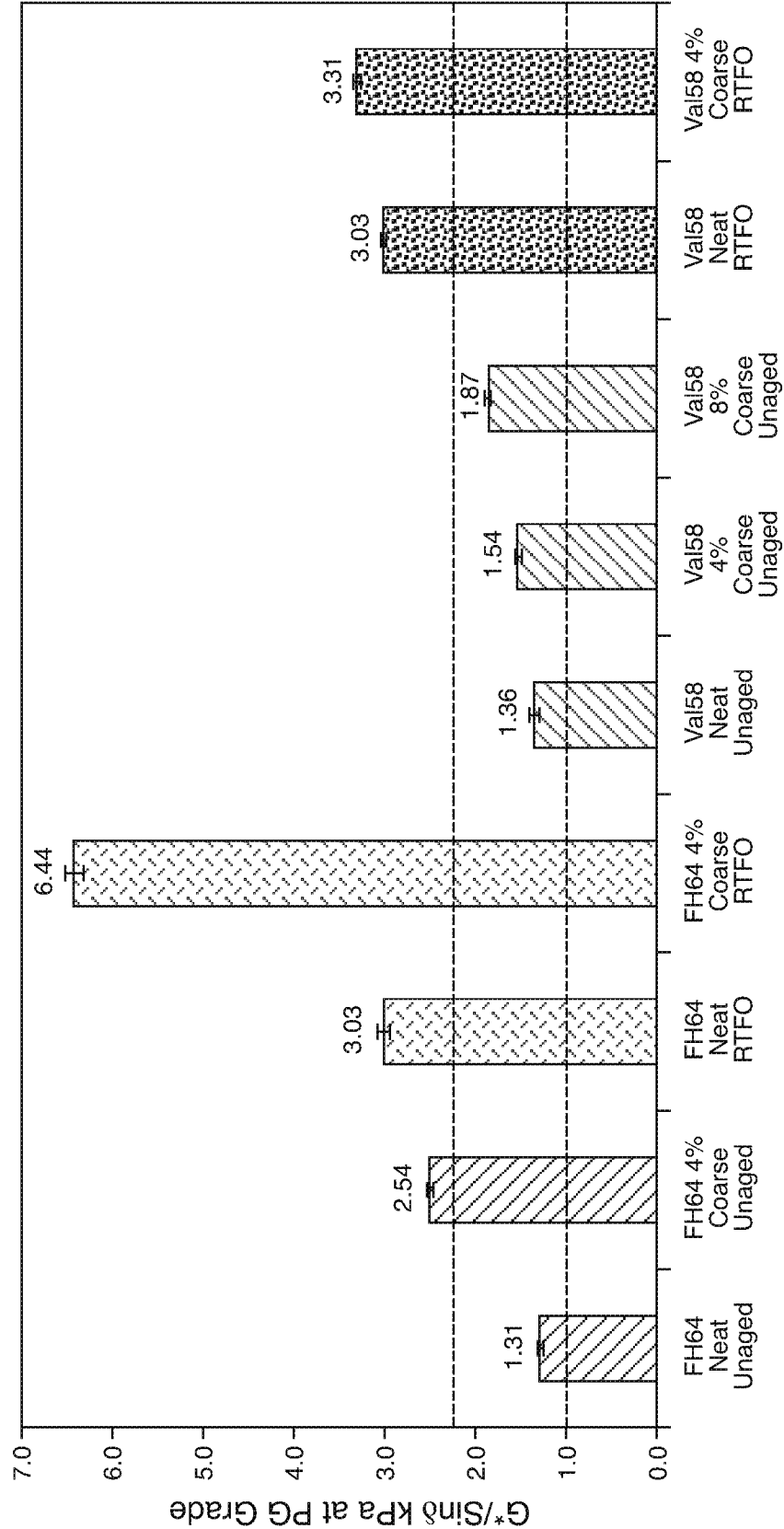


FIG. 2

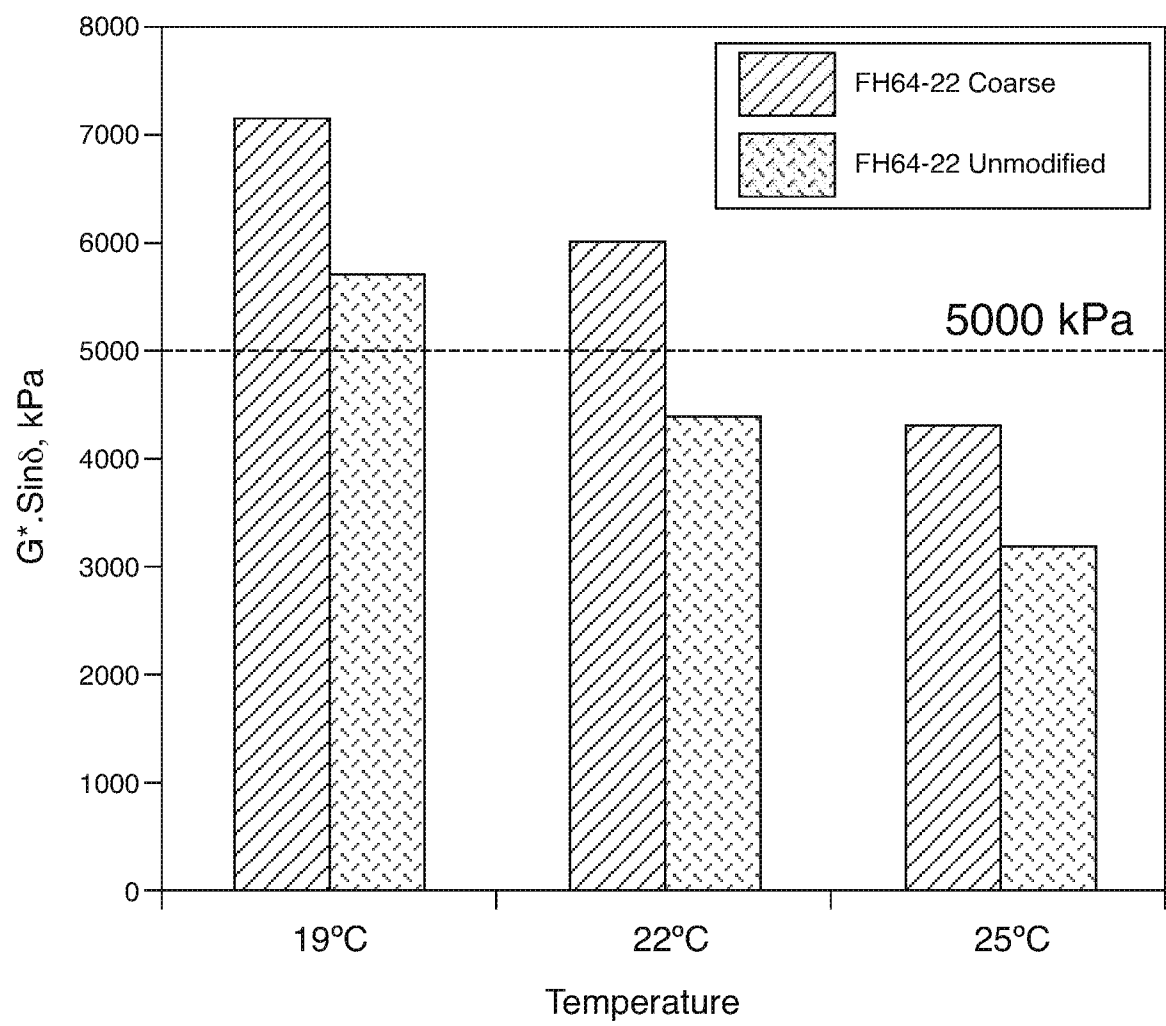


FIG. 3

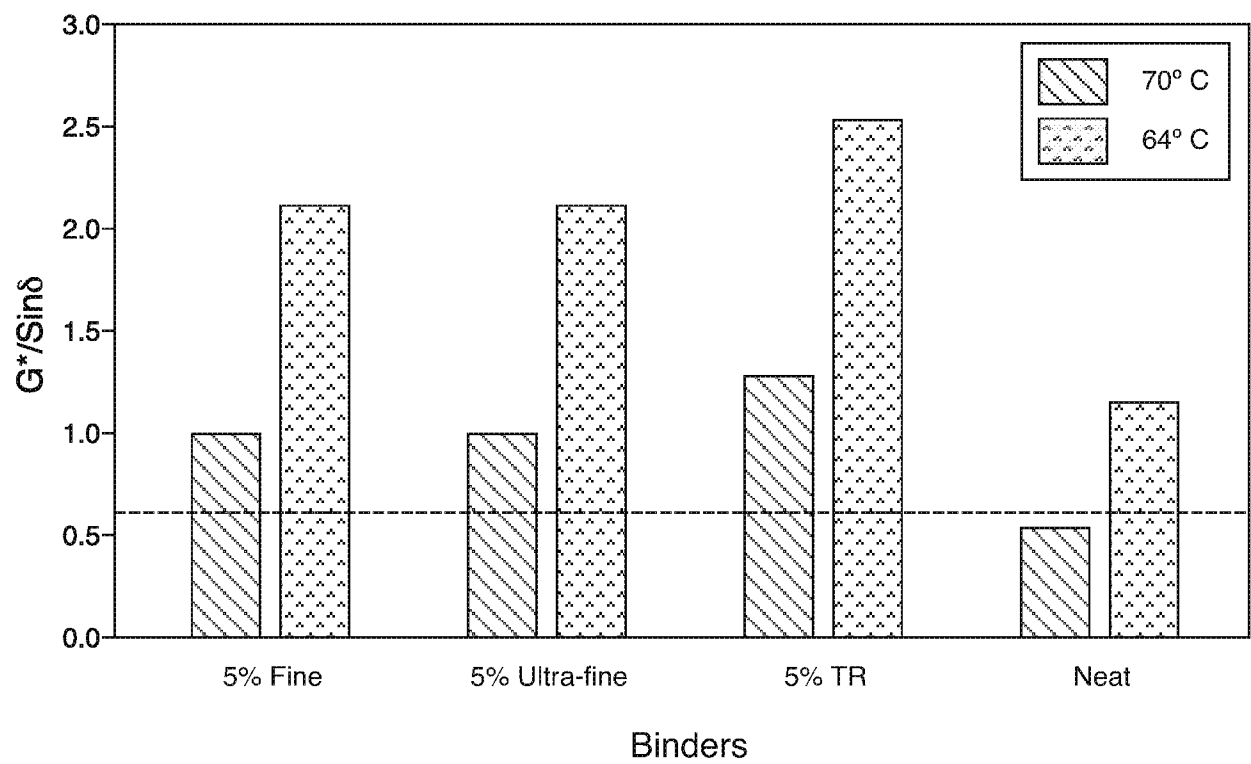


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/047438

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L95/00 C07C71/00 C08G18/06
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 C07C C08G

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)

EP0-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.
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Y	US 4 143 008 A (ZWOLINSKI LEON M ET AL) 6 March 1979 (1979-03-06) column 3, line 50 - column 4, line 2; examples 3,11 ----- -/--	1-26

☒ Further documents are listed in the continuation of Box C.

☒ 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

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"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

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Date of the actual completion of the international search

25 September 2019

Date of mailing of the international search report

09/10/2019

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INTERNATIONAL SEARCH REPORT

International application No
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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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