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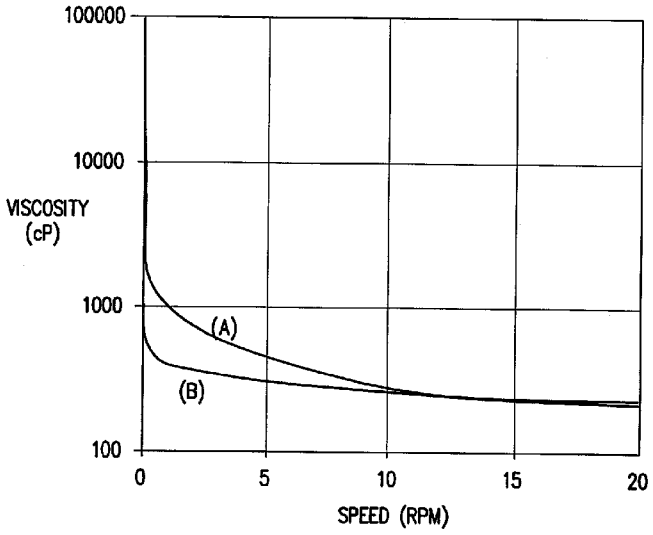
(54) Title: STABILIZED BITUMEN COMPOSITIONS, METHOD FOR PRODUCING THE SAME AND THEIR USE AS CONSTRUCTION MATERIALS

FIG. 1



(57) Abstract: Stabilized bitumen compositions with improved properties are disclosed. The bitumen is stabilized by a composition comprising the mineral porcelanite and an activating agent. The compositions are stable and meet performance requirements according to national standards. The compositions have superior viscoelastic and anti-stripping properties and are more economical than existing stabilized bitumen compositions.

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STABILIZED BITUMEN COMPOSITIONS, METHOD FOR PRODUCING THE SAME AND THEIR USE AS CONSTRUCTION MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

Reference is made to U.S. Provisional Patent Application Serial No. 61/489,341, filed May 24, 2011 and entitled STABILIZED BITUMEN COMPOSITIONS, METHOD FOR PRODUCING THE SAME AND THEIR USE AS CONSTRUCTION MATERIALS, the disclosure of which is hereby incorporated by reference and priority of which is hereby claimed pursuant to 37 CFR 1.78(a)(4) and (5)(i).

FIELD OF THE INVENTION

The present invention relates to stabilized bitumen compositions with improved properties useful as construction materials and to a method for producing the compositions.

BACKGROUND OF THE INVENTION

The following publications are believed to represent the current state of the art:

U.S. Patent Nos. 4,278,470, 4,710,229, 4,818,373, 6,100,317; and

U.S. Patent Publication Nos. 2008/0184913, 2009/0133604, 2010/0229757.

SUMMARY OF THE INVENTION

The present invention seeks to provide a stabilized bitumen composition that has superior properties and is more economical than existing bitumen compositions.

Accordingly, there is provided in accordance with one embodiment of the present invention a stabilized bitumen composition including bitumen, and a structurizer including porcelanite and an activating agent. Preferably, the activating agent includes a quaternary ammonium compound.

Preferably, the quaternary ammonium compound includes at least two alkyl chains of 10 – 30 carbons, more preferably 15 – 18 carbons. Most preferably, the quaternary ammonium compound is di(hydrogenated tallow)dimethylammonium chloride.

In accordance with a preferred embodiment of the present invention, the activating agent includes the quaternary ammonium compound in an amount of about 1 – 15% of the porcelanite weight, more preferably about 1 – 10% of the porcelanite weight. Preferably, the composition includes about 0.5 – 25% of the structurizer by weight, more preferably about 5 - 15% of the structurizer by weight.

Preferably, the bitumen is selected from asphalt cement, asphalt binder and performance grade bitumen. The composition preferably includes about 20 – 90% of the bitumen by weight, more preferably about 30 – 80% of the bitumen by weight, and most preferably about 40 – 70% of the bitumen by weight.

In accordance with a preferred embodiment of the present invention, the composition further includes a diluent. The diluent is preferably a light hydrocarbon, more preferably naphtha. The compositions preferably includes about 10 – 30% diluent by weight, more preferably, about 15 – 25% diluent by weight.

Preferably, the composition further includes at least one additive selected from a solvent, a polymer and a filler. The solvent is preferably selected from kerosene, toluene and trichloroethylene, most preferably toluene. Preferably, the composition includes not more than about 15% solvent by weight.

In accordance with a preferred embodiment of the present invention, the polymer is selected from polyurethane, silicones, atactic polypropylene (APP), ethylene-vinyl acetate (EVA), styrene-butadiene (SB) and styrene-butadiene-styrene

(SBS), more preferably APP and SBS. The composition preferably includes not more than about 20% polymer by weight, more preferably not more than about 15% polymer by weight.

Preferably, the filler is selected from calcium carbonate, coal ash, clay, limestone and dolomite, most preferably calcium carbonate. The composition preferably includes not more than about 30% filler by weight, more preferably not more than about 25% filler by weight.

There is also provided in accordance with another embodiment of the present invention a method of providing a stabilized bitumen composition including providing bitumen at a temperature of about 100 – 140°C, adding a structurizer including porcelanite and an activating agent to the bitumen and mixing to form a homogenous composition.

Preferably, the method further includes cooling the composition to ambient temperature. In one embodiment, the structurizer is added to the bitumen before the cooling. In an alternative embodiment, the structurizer is added to the mixture after the cooling. Preferably, the method further includes adding a diluent to the bitumen.

In accordance with a preferred embodiment of the present invention, the method further includes heating the bitumen to about 160 – 200°C, adding a polymer to the bitumen, mixing the polymer with the bitumen for up to two hours, and cooling the bitumen to provide bitumen at about 100 – 140°C. Preferably, the method further includes adding to the composition at least one additive selected from a solvent, a polymer and a filler.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will be understood and appreciated more fully from the following detailed description, taken in conjunction with the drawing in which:

Fig. 1 is a graph showing the thixotropic properties of the stabilized bitumen composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Bitumen-containing compositions are among the most widely used materials for road construction, waterproofing, damp proofing, corrosion-resistance, insulation, coating applications and other uses. These materials typically comprise bitumen, fillers, solvents, diluents and other additives.

However, the bitumen itself, as the most important ingredient and often the basis for these materials, has a number of defects, the most significant of which are: narrow working temperature range, limited elasticity and short operating life. Oxidation due to atmospheric influences destroys the bitumen, resulting in crack formation and splitting.

The modification of bitumen – the change of its properties by addition of different additives – is one of the ways of improving of the stability of bitumen-containing materials under heavy stresses and extreme ambient temperatures. One of the most common modification methods is to blend bitumen with a polymer, such as polyurethane, silicones and atactic polypropylene (APP). The tri-block copolymer styrene-butadiene-styrene (SBS) is also widely used, usually at about 1-15% of the bitumen weight.

The different physicochemical nature of polymer structural blocks leads to the creation of self-organizing three-dimensional polymer network in the volume of the polymer-bitumen binding agent due to the physical stitching of the polymer macromolecules. Owing to this, the polymer-bitumen composition acquires elastomeric properties, such as reduction of fragility at low temperatures, and increased shear resistance at high operational temperatures.

However, there is a negative aspect of such modification – the polymer modifier can increase the cost of the bitumen by 100% or more. As bitumen is already the most expensive component of construction materials, the increased cost of polymer modification affects the overall construction cost significantly.

Another problem with polymer-modified bitumens is their lack of adhesion to hydrophilic surfaces such as stone and metal. Since the polymer-modified bitumens are highly hydrophobic, there is a tendency for water to creep into the space between the bitumen and the surface to which it is applied and strip the bitumen away from the surface. Unmodified bitumen suffers the same stripping from hydrophilic surfaces.

Another method of modifying bitumen is the addition of filaments, usually cellulose or mineral fibers to the mix. Polymer fibers can also be used for this purpose. The usual content of fibers in construction materials is about 5%. While fibers impart stability to bitumen, they also cause an increase in viscosity which renders mixing difficult.

A modifier for use in asphalt mixes is disclosed in WO 2010/116354, assigned to the assignee of the present invention and incorporated by reference herein in its entirety. It has now been discovered that this modifier is useful in stabilizing bitumen by creating a three-dimensional elastic reticular structure within the bitumen. Stabilized bitumen compositions comprising this modifier have superior thixotropic properties, which make the compositions especially suitable for use in construction materials.

In accordance with a first embodiment of the present invention, there is provided a stabilized bitumen composition comprising bitumen and a stabilizing composition, referred to hereinafter as a "structurizer".

The bitumen is preferably asphalt cement grade bitumen in accordance with ASTM D 3381, such as AC-20 or AC-30. In this standard, the number refers to the viscosity of the bitumen at 60 °C in units of 100 Poise. For example, AC-20 has a viscosity of 2000 P at 60 °C.

The bitumen may also be asphalt binder or performance grade bitumen, such as PG-64, PG-70 or PG-76, according to a national standard. The stabilized bitumen composition preferably comprises about 20 – 90% bitumen by weight, more preferably about 30 – 80% bitumen by weight, most preferably about 40 – 70% bitumen by weight

The structurizer comprises porcelanite, a mineral found, *inter alia*, in deposits in the Dead Sea area of Israel and described in detail in WO 2010/116354, and an activating agent. In one preferred embodiment, the activating agent is a quaternary ammonium compound.

The quaternary ammonium compound preferably has at least two long carbon chains. The long carbon chains preferably comprise between 10 and 30 carbon atoms, more preferably from 15 to 18 carbon atoms. An especially preferred compound is di(hydrogenated tallow)dimethylammonium chloride, available from Akzo-Nobel (Stockholm, Sweden) as Arquad 2HT-75 (hereinafter "2HT-75").

Activation of the porcelanite is preferably achieved by crushing the porcelanite to about 3 – 8 mm particle size granules, adding the activating agent, and blending the mixture until the desired particle size is achieved. Alternatively, the porcelanite can be blended for about 5 minutes, followed by addition of the activating agent and further blending for an additional 1 – 5 minutes.

The weight of the quaternary ammonium compound is preferably between 1 and 15% of the porcelanite weight. More preferably, the weight of the quaternary ammonium compound in the structurizer is between 1 and 10% of the porcelanite weight. The stabilized bitumen composition preferably comprises about 0.5 – 25% structurizer by weight, more preferably about 5 – 15% structurizer by weight.

The stabilized bitumen composition optionally contains a diluent. The diluent can be any liquid miscible with bitumen. The diluent preferably comprises light hydrocarbons. Most preferably, the diluent is naphtha. When present, the diluent comprises about 10 – 30% of the stabilized bitumen composition by weight, more preferably about 15 – 25% of the stabilized bitumen composition by weight.

The stabilized bitumen composition optionally further includes additives preferably selected from polymers, fillers, and solvents. The total additives comprise up to about 40% of the stabilized bitumen composition. The stabilized bitumen composition has reduced amounts of the polymers, fibers and other additives necessary to prepare comparable bitumen compositions lacking the structurizer.

The polymer is preferably selected from typical polymers used to modify bitumen, such as polyurethane, silicones, atactic polypropylene (APP), ethylene-vinyl acetate (EVA), styrene-butadiene (SB) and styrene-butadiene-styrene (SBS). The polymer is preferably included in an amount that is less than the amount of polymer used in a comparable material without the structurizer. Preferably the stabilized bitumen composition comprises no more than about 20% polymer, more preferably no more than about 15% polymer.

The filler is preferably a solid inorganic compound. The filler can be in amorphous or crystalline form. Particularly preferably fillers are calcium carbonate, coal ash, clay and other similar soft, fine ground minerals such as limestone and dolomite. Preferably the stabilized bitumen composition comprises no more than about 30% filler, more preferably no more than about 25% filler.

The solvent can be any solvent that is miscible with bitumen and helps to solubilize the polymer. Preferably, the solvent is a hydrocarbon solvent such as kerosene, an aromatic hydrocarbon solvent such as toluene or a chlorinated hydrocarbon solvent such as trichloroethylene. The solvent is preferably present in an amount of up to 15% of the stabilized bitumen composition by weight.

The stabilized bitumen composition of the present invention is preferably prepared by the following procedure: bitumen is heated to about 100 – 140°C and optionally mixed with a diluent. Optionally, a polymer is added. Structurizer is added and the composition is mixed for about 30 minutes while cooling to ambient temperature. Other ingredients such as fillers, solvents and other additives can be added together with the structurizer or after cooling to ambient temperature. Alternatively, the structurizer can be added after cooling to room temperature.

In some embodiments, in order to achieve full mixing with the polymer, bitumen is first heated to about 160 – 200°C and mixed with the polymer additive for up to about two hours. The bitumen-polymer mixture is then cooled to about 100 – 140°C, and the other components are added as described above.

EXAMPLES

The activated porcelanite structurizer was prepared as follows: 100 g of crushed porcelanite with a particle size between 3 and 8 mm was mixed with 5 g of 2HT-75 in a laboratory blender at 20,000 RPM for 5 minutes. The particle size distribution was measured by Malvern Mastersizer 2000. Maximum particle size was 40 μm. This structurizer was used in all of the following Examples.

Example 1 – Characterization of Structurized Bitumen

Structurized bitumen was prepared by heating PG-70 grade bitumen to about 140 °C and adding structurizer in an amount of 15% of the bitumen weight. The viscosities of the structurized bitumen and pure bitumen at 160 °C were measured as a function of shear rate. The results are shown in Fig. 1.

As can be seen in Fig. 1, under high shear stresses the structurized bitumen (A) behaves like unmodified bitumen (B), but under low shear stresses the viscosity of the

structurized bitumen is 10 times greater or more than unmodified bitumen. This thixotropic, shear thinning property makes the structurized bitumen easy to apply to a surface and very stable after it has been applied and is at rest.

This property can be utilized, for example, for waterproofing a vertical surface. The requirements for the thickness of the waterproofing layer according to local specifications in Israel is not less than 3 mm. Bitumen must be heated in order to be applied to the surface, since cold bitumen is too viscous. It is impossible to apply a pure bitumen layer of the required thickness in one pass by spraying or with a brush, since the hot bitumen is too thin and will run down the surface before cooling. Adding about 15% of structurizer to the bitumen will impart high resting viscosity once the bitumen is applied and at rest, and will facilitate the application of a 3 mm thick layer of in one pass.

Other properties of bitumen are not significantly affected by the addition of the structurizer. The softening point, the temperature at which a material softens beyond some arbitrary softness, of pure bitumen and bitumen containing 5% structurizer, was measured in accordance with ASTM D 36. Pure bitumen had a softening point of 61 °C, while the softening point of the structurized bitumen was 63 °C.

The penetration test in accordance with ASTM D5 – 97 is used as a measure of consistency of a bituminous material expressed as the distance in tenths of a millimeter that a 100 g standard needle vertically penetrates a sample of the material for 5 seconds at a temperature of 25°C. Higher values of penetration indicate a softer consistency of the bituminous material. Pure bitumen had a penetration of 53 (1/10 mm) while the structurized bitumen had a penetration of 51 (1/10 mm).

Example 2 – Polymer-Modified Waterproofing Mastic

Two bitumen containing materials were prepared, the first containing structurizer and the second being a reference material. The materials were prepared as follows: bitumen was heated to 160 °C and SBS was added followed by mixing for two hours. The mixture was cooled to 100 °C, calcium carbonate, naphtha and toluene were added, and the mixture was mixed for 30 minutes while cooling to room temperature. For material 1, structurizer was also added together with the calcium carbonate. Compositions of the two materials are shown in Table 1.

Table 1: Compositions of Waterproofing Materials

Component	Composition (wt %)	
	Reference Material 1	Material 1
Bitumen	40	40
Calcium Carbonate	20	20
Naphtha	20	20
SBS	7	4
Toluene	13	11
Structurizer		5

Material 1 and Reference Material 1 were subjected to the following test in accordance with ASTM D 5329: a layer of 4 mm thickness is applied to an aluminum panel, and the panel is placed in vertical position in a 60 °C oven for five hours. The flow of the layer from its initial position is measured. The permitted shift according to ASTM D 5329 is 5 mm.

Both Material 1 and Reference Material 1 had a flow of 0 mm. It can be seen from here that the structurizer is able to replace, at least partially, the polymer stabilizer without compromising the thermal stability of the material. This replacement of the polymer provides an economic advantage, as the polymer additive is much more expensive than the structurizer.

Additionally, the structurizer imparts anti-stripping properties to the bitumen composition. Since the structurizer is a surfactant, it facilitates binding of the hydrophobic bitumen to the hydrophilic surfaces such as stone and metal. This superior binding prevents the stripping phenomenon described hereinabove that is common in unmodified and polymer-modified bitumen compositions.

Example 3 – Anti-Corrosion Mastic for Automobiles

Two bitumen containing materials were prepared, the first containing structurizer and the second being a reference material containing fibers. The materials were prepared as follows: bitumen was heated to 160 °C and APP was added followed by mixing for two hours. The mixture was cooled to 100 °C, calcium carbonate was added, together with glass fibers for Reference Material 2 and structurizer for Material

2, and the mixture was mixed for 30 minutes while cooling to room temperature. Compositions of the two materials are shown in Table 2.

Table 2: Compositions of Anti-Corrosion Materials

Component	Composition (wt %)	
	Reference Material 2	Material 2
Bitumen	50	50
Calcium Carbonate	25	25
APP	20	15
Glass fibers	5	
Structurizer		10

Material 2 and Reference Material 2 were subjected to the following test in accordance with ASTM D 5329: a layer of 4 mm thickness is applied to an aluminum panel, and the panel is placed in vertical position in a 60 °C oven for five hours. The flow of the layer from its initial position is measured. The permitted shift according to ASTM D 5329 is 5 mm.

Both Material 2 and Reference Material 2 had a flow of 0 mm. It can be seen from here that the structurizer is able to replace, at least partially, the polymer stabilizer and to completely replace the fiber stabilizer without compromising the thermal stability of the material. This replacement of the polymer provides an economic advantage and imparts anti-stripping properties to the material. Removing fibers from the composition improves the mixing properties as the increase in viscosity caused by the fibers is avoided.

Example 4 – Anti-Corrosion Lacquer for Metal Construction

Two bitumen containing materials were prepared, the first containing structurizer and the second being a reference material containing a commercial anti-stripping agent. The materials were prepared as follows: bitumen was heated to 100 °C and naphtha was added. Carbon black and Wetfix® N were added for Reference Material 3, and structurizer was added for Material 3. The mixture was mixed for 30

minutes while cooling to room temperature. Compositions of the two materials are shown in Table 3.

Table 3: Compositions of Anti-Corrosion Materials

Component	Composition (wt %)	
	Reference Material 3	Material 3
Bitumen	70	70
Naphtha	25	25
Carbon black filler	4	
Wetfix® N (anti-stripping)	1	
Structurizer		5

Material 3 and Reference Material 3 were subjected to the following test in accordance with ASTM D 714: a steel plate is covered with a 100 micron thick layer of the material and placed in 15% concentration solution of NaCl in water at 60 °C for one week. The plates are then observed for signs of blistering.

Both Material 3 and Reference Material 3 were free of blistering. It can be seen from here that structurizer is able to replace the commercial anti-stripping agent and the filler without compromising the corrosion resistance of the material. This replacement of the anti-corrosion agent and filler provides an economic advantage to the material.

It will be appreciated by persons skilled in the art that the present invention is not limited to what has been particularly shown and described hereinabove. Rather the scope of the present invention includes both combinations and subcombinations of various features described hereinabove as well as modifications thereof which would occur to a person of skill in the art upon reading the foregoing description and which are not in the prior art.

CLAIMS

1. A stabilized bitumen composition comprising:
bitumen, and
a structurizer comprising porcelanite and an activating agent.

2. The stabilized bitumen composition according to claim 1, wherein said activating agent comprises a quaternary ammonium compound.

3. The stabilized bitumen composition according to claim 2, wherein said quaternary ammonium compound comprises at least two alkyl chains of 10 – 30 carbons.

4. The stabilized bitumen composition according to claim 3, wherein said at least two alkyl chains have 15 – 18 carbons.

5. The stabilized bitumen composition according to any one of claims 2 to 4, wherein said quaternary ammonium compound is di(hydrogenated tallow)dimethylammonium chloride.

6. The stabilized bitumen composition according to any one of claims 2 to 5, wherein said activating agent comprises said quaternary ammonium compound in an amount of about 1 – 15% of the porcelanite weight.

7. The stabilized bitumen composition to claim 6, wherein said quaternary ammonium compound is in an amount of about 1 – 10% of the porcelanite weight.

8. The stabilized bitumen composition according to any one of claims 1 to 7, wherein said composition comprises about 0.5 – 25% of said structurizer by weight.

9. The stabilized bitumen composition according to claim 8, wherein said composition comprises about 5 - 15% of said structurizer by weight.

10. The stabilized bitumen composition according to any one of claims 1 to 9, wherein said bitumen is selected from asphalt cement, asphalt binder and performance grade bitumen.

11. The stabilized bitumen composition according to any one of claims 1 to 10, wherein said composition comprises about 20 – 90% of said bitumen by weight.

12. The stabilized bitumen composition according to claim 11, wherein said composition comprises about 30 – 80% of said bitumen by weight.

13. The stabilized bitumen composition according to claim 12, wherein said composition comprises about 40 – 70% of said bitumen by weight.

14. The stabilized bitumen composition according to any one of claims 1 to 13, further comprising a diluent.

15. The stabilized bitumen composition according to claim 14, wherein said diluent is a light hydrocarbon.

16. The stabilized bitumen composition according to claim 15, wherein said light hydrocarbon is naphtha.

17. The stabilized bitumen composition according to any one of claims 14 to 16, wherein said composition comprises about 10 – 30% diluent by weight.

18. The stabilized bitumen composition according to claim 17, wherein said composition comprises about 15 – 25% diluent by weight.

19. The stabilized bitumen composition according to any one of claims 1 to 18, further comprising at least one additive selected from a solvent, a polymer and a filler.

20. The stabilized bitumen composition according to claim 19, wherein said solvent is selected from kerosene, toluene and trichloroethylene.

21. The stabilized bitumen composition according to claim 20, wherein said solvent is toluene.

22. The stabilized bitumen composition according to any one of claims 19 to 21, wherein said composition comprises not more than about 15% solvent by weight.

23. The stabilized bitumen composition according to any one of claims 19 to 22, wherein said polymer is selected from polyurethane, silicones, atactic polypropylene (APP), ethylene-vinyl acetate (EVA), styrene-butadiene (SB) and styrene-butadiene-styrene (SBS).

24. The stabilized bitumen composition according to claim 23, wherein said polymer is selected from atactic polypropylene (APP) and styrene-butadiene-styrene (SBS).

25. The stabilized bitumen composition according to any one of claims 19 to 24, wherein said composition comprises not more than about 20% polymer by weight.

26. The stabilized bitumen composition according to claim 25, wherein said material comprises not more than about 15% polymer by weight.

27. The stabilized bitumen composition according to any one of claims 19 to 26, wherein said filler is selected from calcium carbonate, coal ash, clay, limestone and dolomite.

28. The stabilized bitumen composition according to claim 27, wherein said filler is calcium carbonate.

29. The stabilized bitumen composition according to any one of claims 19 to 28, wherein said composition comprises not more than about 30% filler by weight.

30. The stabilized bitumen composition according to claim 29, wherein said composition comprises not more than about 25% filler by weight.

31. A method of providing a stabilized bitumen composition comprising:

providing bitumen at a temperature of about 100 – 140°C;

adding a structurizer comprising porcelanite and an activating agent to said bitumen; and

mixing to form a homogenous composition.

32. The method according to claim 31, further comprising cooling said composition to ambient temperature.

33. The method according to claim 32, wherein said structurizer is added to said bitumen before said cooling.

34. The method according to claim 32, wherein said structurizer is added to said mixture after said cooling.

35. The method according to any one of claims 31 to 34, further comprising adding a diluent to said bitumen.

36. The method according to any one of claims 31 to 35, further comprising:

heating said bitumen to about 160 – 200°C;

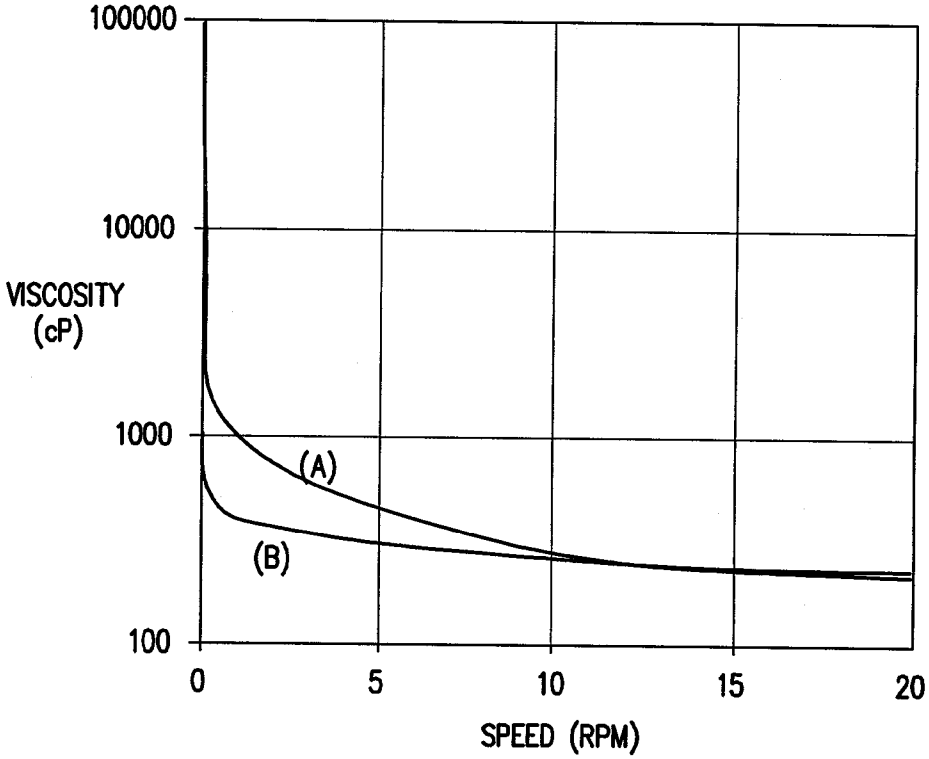
adding a polymer to said bitumen;

mixing said polymer with said bitumen for up to two hours;

cooling said bitumen to provide bitumen at about 100 – 140°C.

37. The method according to any one of claims 31 to 36, further comprising adding to said composition at least one additive selected from a solvent, a polymer and a filler.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2012/000204

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08L 95/00 (2012.01)
USPC - 106/281.1
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)
IPC(8) - C04B 24/36; C08L 95/00; E01C 7/22, 26 (2012.01)
USPC - 106/235, 273.1, 281.1; 523/450

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)
Orbit.com, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/0255982 A1 (PELED et al) 07 October 2010 (07.10.2010) entire document	1-5, 31
Y		32-35
Y	CN 101948622 A (YONGLI et al) 19 January 2011 (19.01.2011) entire document	32-34
Y	US 2002/0114940 A (CLEMENS et al) 22 August 2002 (22.08.2002) entire document	35

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

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Date of the actual completion of the international search	Date of mailing of the international search report
14 September 2012	04 OCT 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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International application No.
PCT/IL2012/000204

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-30, 36, 37
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.