(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 June 2018 (28.06.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/114907 A1

(51) International Patent Classification:
C08L 95/00 (2006.01) *C08K 3/32* (2006.01)
C08L 25/10 (2006.01) *C08L 91/00* (2006.01)
C08L 53/02 (2006.01)

(21) International Application Number:
PCT/EP2017/083479

(22) International Filing Date:
19 December 2017 (19.12.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201641043661 21 December 2016 (21.12.2016) IN

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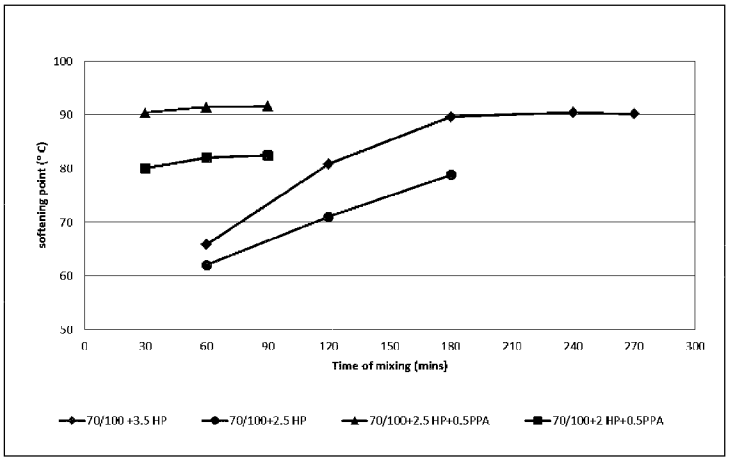
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,

WO 2018/114907 A1

(54) Title: USE OF POLYPHOSPHORIC ACID (PPA) AND/OR OIL AS MIXING TIME REDUCING ADDITIVE FOR OBTAINING BITUMEN/BLOCK COPOLYMER MIXES

Figure 4



(57) Abstract: Use of an additive for reducing the preparation time of a polymer-modified bitumen composition in a process which comprises blending: (a) from 0.5 to 5 wt%, by weight of the polymer-modified bitumen composition, of a fully or partially hydrogenated block copolymer; (b) from 85.0wt% to 99.4 wt%, based on the total weight of the polymer-modified bitumen composition, of a bitumen component; (c) from 0.1 to 10 wt%, by weight of the polymer-modified bitumen composition, of an additive selected from (i) polyphosphoric acid, (ii) a flux component selected from aromatic, naphthenic or paraffinic flux oils, and petroleum extracts, and mixtures thereof; and (iii) mixtures of (i) and (ii); and (d) optionally one or more additional components.

[Continued on next page]

KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

USE OF POLYPHOSPHORIC ACID (PPA) AND/OR OIL AS MIXING TIME REDUCING ADDITIVE FOR OBTAINING BITUMEN/BLOCK COPOLYMER MIXES

Field of the Invention

This invention relates to the use of an additive for reducing the preparation time of preparing a polymer-modified bitumen composition.

Background of the Invention

Bitumen is used as a binder in road asphalt mixtures, and has developed continually to meet ever-increasing performance demands from road building constructors. In general bitumen performs well in road asphalt, but increasingly heavy traffic loads and high traffic volume have led to the wear of many roads through rutting and cracking of the surface.

In their article entitled "Polymer modification of bitumen: Advances and challenges", published in May 2014 in the European Polymer Journal, volume 54, pages 18-38, J. Zhu et al. describe the modification of bitumen with polymers. By polymer modification of bitumen is herein understood to mean the incorporation of polymers in bitumen, for example by mechanical mixing or by chemical reaction. According to J. Zhu et al. polymer modification is reported to lead to improved properties, such as higher stiffness at high temperatures, a higher cracking resistance at low temperatures, a better moisture resistance and/or a longer fatigue life. J. Zhu et al, however, indicated that in addition to the reported advantages, researchers also encountered various challenges, including high costs and poor storage stability.

WO2015/170739 describes an asphalt composition used for e.g. road surfacing containing 0.5 to 20 parts mass

of a block copolymer and 100 parts mass of asphalt. The block copolymer comprises a polymer block (A) containing 20-60% mass vinyl aromatic monomer units as main component, and copolymer block (B) containing conjugated diene monomer units and vinyl aromatic monomer units. The content of copolymer block (A) in the block copolymer is 10-40% mass. The hydrogenation rate of double bonds in the conjugated diene monomer units of the block copolymer is 40-100%.

It would be an advancement in the art to provide a process for producing a polymer-modified bitumen that allows for a significant reduction in the preparation time of the polymer-modified bitumen as well as obtaining a high softening point, whilst maintaining good storage stability, good road application properties and good rutting and cracking properties.

Summary of the Invention

According to the present invention there is provided the use of an additive for reducing the preparation time of a polymer-modified bitumen composition in a process which comprises blending:

(a) from 0.5 to 5 wt%, by weight of the polymer-modified bitumen composition, of a fully or partially hydrogenated block copolymer;

(b) from 85.0 wt% to 99.4 wt%, based on the total weight of the polymer-modified bitumen composition, of a bitumen component;

(c) from 0.1 to 10 wt%, by weight of the polymer-modified bitumen composition, of an additive selected from (i) polyphosphoric acid, (ii) a flux component selected from aromatic, naphthenic or paraffinic flux oils, and petroleum extracts, and mixtures thereof; and (iii) mixtures of (i) and (ii); and

(d) optionally one or more additional components.

The use of the additive described herein surprisingly leads to a reduction in the time taken to prepare a polymer-modified bitumen using the process described herein.

Brief Description of the Drawings

Figure 1 is a plot of the results shown in Table 1

Figure 2 is a plot of the results shown in Table 2

Figure 3 is a plot of the results shown in Table 3

Figure 4 is a plot of the results shown in Table 4.

Detailed Description of the Invention

The process herein comprises blending together components (a), (b), (c) and optionally (d).

Component (a) is a fully or partially hydrogenated block copolymer. In the process herein, the fully or partially hydrogenated block copolymer is used at a level of from 0.5 to 5 wt%, by weight of the polymer-modified bitumen composition. Preferably, the block copolymer is present in an amount of from 1 wt% to 5 wt%, preferably from 1.5 wt% to 4 wt%, even more preferably from 2 wt% to 3.5 wt%, by weight of the polymer-modified bitumen composition.

The block copolymer for use herein preferably comprises at least one polymer block derived from a vinyl aromatic hydrocarbon monomer and at least one polymer block derived from a conjugated diene monomer. The block copolymer may be linear or radial, symmetric or asymmetric, and may have a structure represented by the formula A-B, A-B-A, B-A-B, A-B-A-B etc. wherein A is the polymer block of a vinyl aromatic hydrocarbon and B is polymer block of a conjugated diene. The block copolymer preferably contains up to 40% by weight of vinyl aromatic hydrocarbon, more preferably from 30 to 40% by weight of

vinyl aromatic hydrocarbon.

The vinyl aromatic hydrocarbon is preferably styrene, *o*-methylstyrene, *p*-methylstyrene, *p*-tert-butylstyrene, 1,3-dimethylstyrene, α-methylstyrene, vinylnaphthalene or vinylanthracene, most preferably styrene. Mixtures of vinyl aromatic hydrocarbons may be used.

The conjugated diene preferably has from 4 to 8 carbon atoms, and is more preferably selected from 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene. Most preferably the conjugated diene is 1,3-butadiene or isoprene. Mixtures of conjugated dienes may be used.

The block copolymer is fully or partially hydrogenated which means that all or a certain percentage of the double bonds in the conjugated diene moieties are hydrogenated. Preferably the block copolymer is from 40 to 100 wt% hydrogenated, more preferably 40 to 99.5 wt% hydrogenated, even more preferably from 50 to 90 wt% hydrogenated, and especially from 60 to 90 wt% hydrogenated.

Examples of suitable fully or partially hydrogenated block copolymers for use herein include a fully or partially hydrogenated styrene-β-isoprene polymer (SEP), a fully or partially hydrogenated styrene-β-isoprene-β-styrene polymer (SEPS), a fully or partially hydrogenated styrene-isoprene-styrene polymer (SIS), a fully or partially hydrogenated styrene-β-butadiene-β-styrene copolymer (SEBS), and a fully or partially hydrogenated styrene-β-isoprene/butadiene-β-styrene copolymer (SEEPS).

In a preferred embodiment herein, the block copolymer comprises a polymer block (A) comprising vinyl aromatic monomer units as main component, and copolymer block (B)

comprising conjugated diene monomer units and vinyl aromatic monomer units, wherein the content of the vinyl aromatic monomer units in the block copolymer is in the range from 20 to 60 mass%, the content of the copolymer block (A) in the block copolymer is in the range from 10 to 40 mass% and the hydrogenation rate of double bonds in the conjugated diene monomer units of the block copolymer is in the range from 40 to 100%, preferably in the range from 50 to 90%, more preferably in the range from 60 to 90%. Polymers of this type are disclosed in WO2015/170739, incorporated herein by reference in its entirety.

In a preferred embodiment herein, the conjugated diene monomers units of the block copolymer comprise (a) conjugated diene monomer units derived from 1,2-bonds and/or 3,4-bonds and (b) conjugated diene monomer units derived from 1,4-bonds, and if the total content of conjugated monomer diene units is taken to be 100 mass%, the content of alkenyl monomer units (a1) obtained by hydrogenating the conjugated diene monomer units (a) is in the range from 10 to 50 mass%, the content of alkenyl monomer units (b1) obtained by hydrogenating the conjugated diene monomer units (b) is in the range from 0 to 80 mass%, and the total content of unhydrogenated conjugated diene monomers units (a2) following hydrogenation and unhydrogenated conjugated diene monomer units (b2) following hydrogenation is in the range from 0 to 90 mass%.

Preferably, the content of conjugated diene monomer units (a) derived from 1,2-bonds and/or 3,4-bonds is in the range from 10 to 50 mass% relative to the total content of the conjugated diene monomer of the block copolymer.

The weight average molecular weight of the block copolymer for use herein is preferably in the range of from 50,000 to 300,000.

In a preferred embodiment herein the block copolymer has at least one type of functional group selected from hydroxyl groups, acid anhydride groups, epoxy groups, amino groups, amide groups, silanol groups and alkoxysilane groups.

Component (b) is a bitumen component. The bitumen component used in the process of the present invention may be a residue from the distillation of crude oil, a cracked residue, naturally occurring bitumen or a blend of various bitumen types. Examples of bitumen that may be conveniently used in the present invention include distillation or "straight run" bitumen, precipitation bitumen, e.g. propane bitumen, oxidized or blown bitumen, naphthenic bitumen, paraffinic bitumen or mixtures thereof.

Various grades of bitumen may be used in the process of producing the polymer-modified bitumen described herein, such as, for example, 35/50, 50/70, 60/70, 70/100, 80/100, 100/150, 160/220 grades.

The bitumen component is present in the polymer-modified bitumen composition at a level of from 85 wt% to 99.4 wt%, preferably from 90 wt% to 95 wt%, based on the total weight of the polymer-modified bitumen.

Component (c) is an additive selected from (i) polyphosphoric acid, (ii) a flux component selected from aromatic, naphthenic or paraffinic flux oils, petroleum extracts, and mixtures thereof; and (iii) mixtures of (i) and (ii).

Component (c) is used at a level of from 0.1 wt% to 10 wt%, preferably from 0.1 wt% to 5 wt%, more preferably

from 0.5 wt% to 5 wt%, and even more preferably from 0.5 to 2 wt%, by weight of the polymer-modified bitumen composition.

Polyphosphoric acid (PPA) is a polymeric product of thermal dehydration and polycondensation of orthophosphoric acid (H_3PO_4). Besides orthophosphoric forms, it contains a mixture of polymeric forms whose content increases with increasing acid concentration. Commercially available PPA is a mixture of linear polyacids of general formula $H_{n+2}P_nO_{3n+1}$, wherein $n \geq 2$. Those acids are produced either from the dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4. In the latter method, longer chains are obtained. Polyphosphoric acid is highly hydroscopic and easily hydrolyses in moist air. Its viscosity and physical form at room temperature depends on the content of P_2O_5. Polyphosphoric acid is available in various grades, for example, concentrations of 105, 110 and 114% H_3PO_4 are used (the % exceeds 100% since it reflects the calculation of H_3PO_4 concentration on the base of P_2O_5 content in the inorganic polymer). 105%, 110% and 114% H_3PO_4 is equivalent to 75.9%, 79.8% and 82.6% P_2O_5, respectively.

The flux component (ii) for use herein is selected from aromatic, naphthenic or paraffinic flux oils, petroleum extracts, e.g. aromatic extracts, distillates or residues, mineral derived or synthetic base oils, and vegetable oils. Specific examples of suitable flux components include bright stock furfuryl extract (BFE), Fischer-Tropsch derived base oils such as HVI 160B supplied by Shell, lubricating base oils such as re-refined SN150 supplied by Whelan Refining Limited, Sneyd Hill, Burslem, Stoke-on-Trent, ST6 2DZ, UK and Vivatec 500

(a refined solvent mineral oil) supplied by H&R group, and De-asphalted cylinder oil (DACO).

Preferred flux components for use herein are SN150 (from Whelan Refining Limited) and HVI 160B (from Shell). Shell HVI 160B is a paraffinic base oil with good oxidation stability and high viscosity/temperature behaviour. HVI 160B is classified as a Group I base stock slate within the API/ATIEL Guidelines. SN150 is a Group I base oil.

When additive component (c) is a flux component, a preferred level of flux component is from 0.5 to 10 wt%, by weight of the polymer-modified bitumen composition.

In a preferred embodiment herein, component (c) is polyphosphoric acid. A preferred level of polyphosphoric acid is 0.5 to 5 wt%, by weight of the polymer-modified bitumen composition.

The polymer-modified bitumen composition may also comprise one or more additional components (d) suitable for use in a bitumen formulation. Such additional components are well known to those skilled in the art and include, for example, waxes, anti-stripping agents, viscosity modifiers, penetration correctors (for example, Gilsonite), softening agents, process oils, GTL oils, aromatic oils, paraffinic oils, and petroleum distillates, and the like.

During preparation of the polymer-modified bitumen composition, high shear mixing is preferably used for blending of components (a), (b), (c) and optionally (d). As used herein, the term "high shear mixing" means mixing at a speed from 1500 to 6000, preferably 3000 to 6000, even more preferably from 4000 to 6000 rpm. Preferably, high shear mixing involves the use of a Silverson high shear mixer.

The use of an additive component (c) enables a reduction in the time taken for the production of a polymer-modified bitumen using the process described herein. Preferably, the time taken to produce the polymer-modified bitumen is reduced by at least 30%, preferably at least 50%, more preferably at least 60%, even more preferably at least 70%, especially at least 80%, compared with the time taken to produce a polymer-modified bitumen in an analogous process which doesn't include the use of an additive component (c).

In a preferred embodiment, the blending of components (a), (b), (c) and optionally (d) in the process herein is carried out at a temperature of less than 180°C, preferably less than 170°C, more preferably less than 165°C. The use of additive (c) enables the process of preparing the polymer-modified bitumen composition to be carried out at a lower temperature compared to the temperature used in an analogous process which does not use additive (c).

The softening point of the polymer-modified bitumen is preferably 60°C or greater, more preferably 70°C or greater, even more preferably 80°C or greater, especially 90°C or greater.

The final polymer-modified bitumen composition should meet the desired polymer-modified bitumen specification.

The final polymer-modified bitumen composition produced herein can be used as a binder in an asphalt composition for road paving applications.

The invention is further illustrated by the following non-limiting examples.

Examples

Various polymer-modified bitumen compositions were produced by blending a bitumen component, a polymer and

polyphosphoric acid using a Silverson high shear mixer.

The bitumen grades used were 60/70 (from Bahrain Petroleum Company), 60/70 (from Shell Eastern Petroleum Limited), 80/100, and 70/100. The polymer was a partially hydrogenated polymer as disclosed and prepared in WO2015/170739.

Tables 1 to 4 set out the grades of bitumen and the levels of each component, as well as mixing times, mixing temperatures and softening points measured at various intervals in the production process. For each of the polymer-modified bitumen compositions produced, the softening points were measured at various intervals (mixing times) using the EN 1427-2015 test method. The polymer-modified bitumen compositions are deemed to be stable when the change in softening point stabilizes.

Table 1

Bitumen grade	Polymer (wt%)	PPA(wt%)	Softening Point (°C)	Mixing time (mins)	Mixing temperature (°C)
60/70 (from Bahrain Petroleum Company)	3	0.5	94	30	180
			94.2	60	180
			93.8	90	180
60/70	2.5	0.5	86	30	180
			86.2	60	180
			86.2	90	180
60/70	3.5	0	62	60	180
			69	120	180
			73.4	180	180
60/70	2	0.4	56	30	180
60/70	2.2	0.4	73.8	30	180

60/70	2.5	0.4	84.6	30	180
60/70	2.7	0.4	89.4	30	180
60/70	3	0.5	94	30	180
60/70	2.5	0.5	85	30	165
			86	60	165
			86.2	90	165

Table 2

Bitumen grade	Polymer (wt%)	PPA (wt%)	Softening point (°C)	Mixing time (mins)	Mixing temperature °C
60/70 (from Shell Eastern Petroleum Limited)	3.5	0	72.4	60	180
			84.5	120	180
			89.2	180	180
60/70	3	0.5	86.6	30	180
			88.8	60	180
			90.5	90	180
60/70	3	0.5	85.2	30	165
			87	60	165
			92	90	165

Table 3

Bitumen grade	Polymer (wt%)	PPA (wt%)	Softening point (°C)	Mixing time (mins)	Mixing temperature °C
80/100 (from Argentina)	3.5	0	64.4	60	180
			69.4	120	180
			67.1	180	180

			67	240	180
80/100	2.5	1	91	30	180
			92.4	60	180
			92.2	90	180
80/100	2.2	1	86	30	180
			86.4	60	180
			86.2	90	180
80/100	3	0.5	99.8	60	180
			100.8	120	180
			101	180	180

Table 4

Bitumen grade	Polymer (wt%)	PPA (wt%)	Softening point (°C)	Mixing time (mins)	Mixing temperature °C
70/100 (from Godorf refinery Germany)	3.5	0	65.8	60	180
			80.8	120	180
			89.6	180	180
			90.4	240	180
			90.1	270	180
70/100	2	0.5	82.2	30	180
			82.2	60	180
			82.6	90	180
70/100	2.5	0.5	90.4	30	180
			91.4	60	180
			91.6	90	180
70/100	2.5		62	60	180
			71	120	180
			78.8	180	180
70/100	2	0.5	80	30	180
			82	60	180

			82.4	90	180

Figure 1 is a plot of the softening point against the mixing time results shown in Table 1.

Figure 2 is a plot of the softening point against the mixing time results shown in Table 2

Figure 3 is a plot of the softening point against the mixing time results shown in Table 3

Figure 4 is a plot of the softening point against the mixing time results shown in Table 4.

In Figures 1-4, "HP" means "hydrogenated polymer".

Discussion

The results shown in Tables 1-4 and Figures 1-4 show that the use of PPA helps to significantly reduce the time taken to make a stable polymer-modified bitumen composition comprising a partially hydrogenated polymer.

C L A I M S

1. Use of an additive for reducing the preparation time of a polymer-modified bitumen composition in a process which comprises blending:

(a) from 0.5 to 5 wt%, by weight of the polymer-modified bitumen composition, of a fully or partially hydrogenated block copolymer;

(b) from 85.0 wt% to 99.4 wt%, based on the total weight of the polymer-modified bitumen composition, of a bitumen component;

(c) from 0.1 to 10 wt%, by weight of the polymer-modified bitumen composition, of an additive selected from (i) polyphosphoric acid, (ii) a flux component selected from aromatic, naphthenic or paraffinic flux oils, and petroleum extracts, and mixtures thereof; and (iii) mixtures of (i) and (ii); and

(d) optionally one or more additional components.

2. Use according to Claim 1 wherein the blending takes place at a temperature of less than 180°C.

3. Use according to Claim 1 or 2 wherein the blending takes place at a temperature of less than 170°C.

4. Use according to any of Claims 1 to 3 wherein the blending takes place at a temperature of less than 165°C.

5. Use according to any of Claims 1 to 4 wherein the fully or partially hydrogenated block copolymer comprises a polymer block (A) comprising vinyl aromatic monomer units as main component, and a copolymer block (B) comprising conjugated diene monomer units and vinyl aromatic monomer units, wherein the content of the vinyl aromatic monomer units in the block copolymer is in the range from 20 to 60 mass%, the content of the copolymer

block (A) in the block copolymer is in the range from 10 to 40 mass% and the hydrogenation rate of double bonds in the conjugated diene monomer units of the block copolymer is in the range from 40 to 100%.

6. Use according to Claim 5 wherein the hydrogenation rate of double bonds in the conjugated diene monomer units of the block copolymer is in the range from 50 to 90%.

7. Use according to Claim 5 or 6 wherein the hydrogenation rate of double bonds in the conjugated diene monomers units of the block copolymer is in the range from 60 to 90%.

8. A process according to any of Claims 5 to 7 wherein the conjugated diene monomer units of the block copolymer comprise (a) conjugated diene monomer units derived from 1,2-bonds and/or 3,4-bonds and (b) conjugated diene monomer units derived from 1,4-bonds, and if the total content of conjugated monomer diene units is taken to be 100 mass%, the content of alkenyl monomer units (a1) obtained by hydrogenating the conjugated diene monomer units (a) is in the range from 10 to 50 mass%, the content of alkenyl monomer units (b1) obtained by hydrogenating the conjugated diene monomer units (b) is in the range from 0 to 80 mass%, and the total content of unhydrogenated conjugated diene monomers units (a2) following hydrogenation and unhydrogenated conjugated diene monomer units (b2) following hydrogenation is in the range from 0 to 90 mass%.

9. Use according to any of Claims 5 to 8 wherein the fully or partially hydrogenated block copolymer has a weight average molecular weight in the range from 50,000 to 300,000.

10. Use according to any of Claims 5 to 9 wherein the

block copolymer has at least one type of functional group selected from hydroxyl groups, acid anhydride groups, epoxy groups, amino groups, amide groups, silanol groups and alkoxysilane groups.

11. Use according to any of Claims 5 to 10 wherein the content of conjugated diene monomer units (a) derived from 1,2-bonds and/or 3,4-bonds is in the range from 10 to 50 mass% relative to the total content of the conjugated diene monomer of the block copolymer.

12. Use according to any of Claims 1 to 11 wherein the additive is polyphosphoric acid.

Figure 1

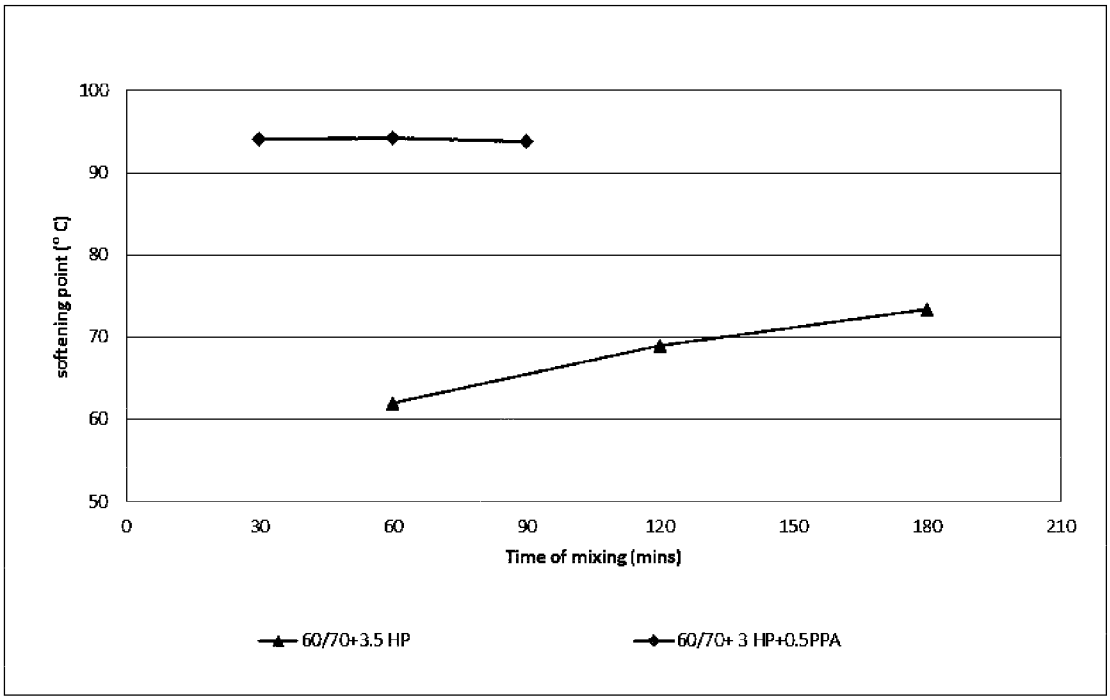
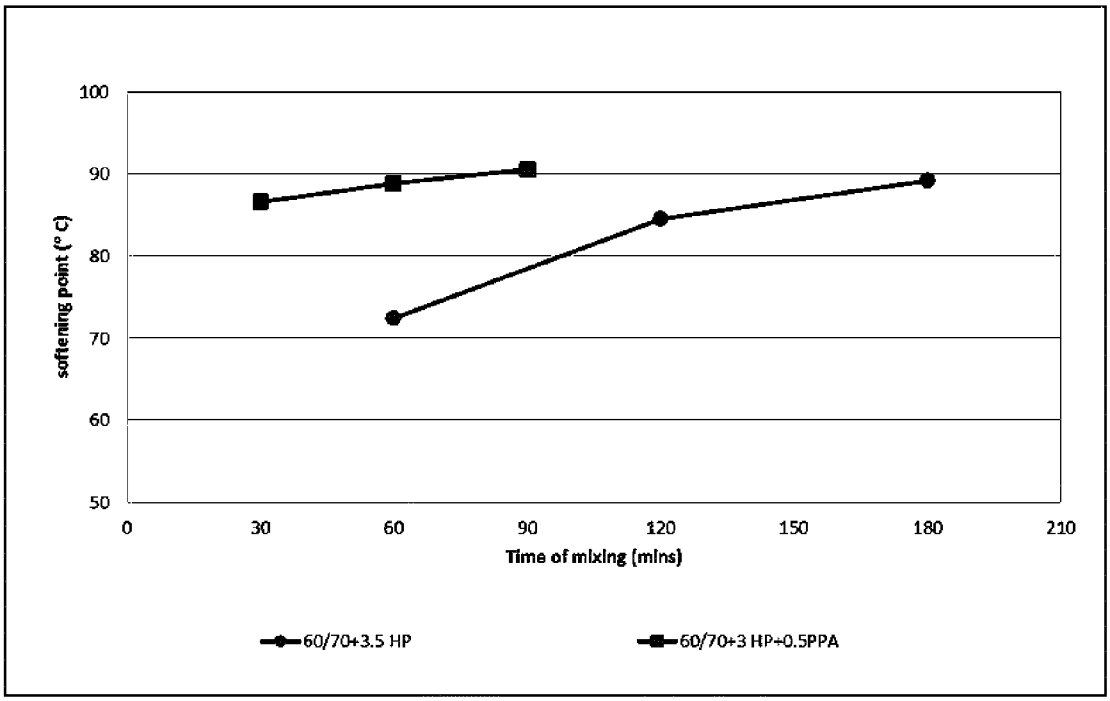

100
90
80
70
60
50
softening point (° C)
0
30
60
90
120
150
180
210
Time of mixing (mins)
60/70+3.5 HP
60/70+ 3 HP+0.5PPA

Figure 2


100
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50
softening point (° C)
0
30
60
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180
210
Time of mixing (mins)
60/70+3.5 HP
60/70+3 HP+0.5PPA

Figure 3

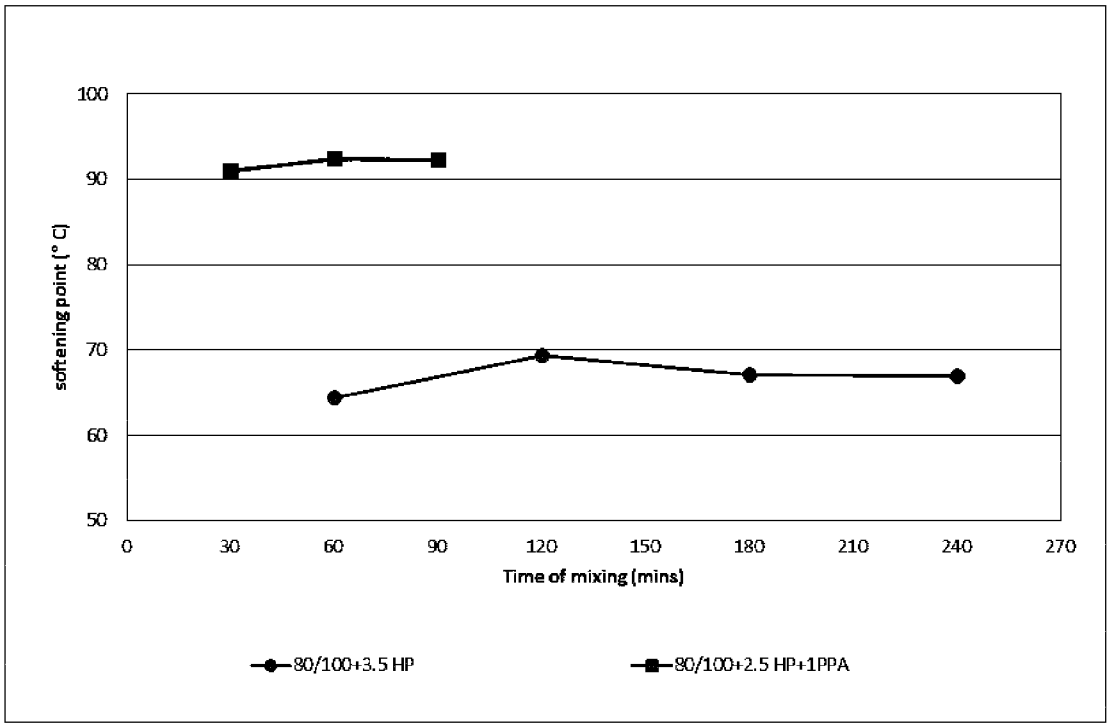
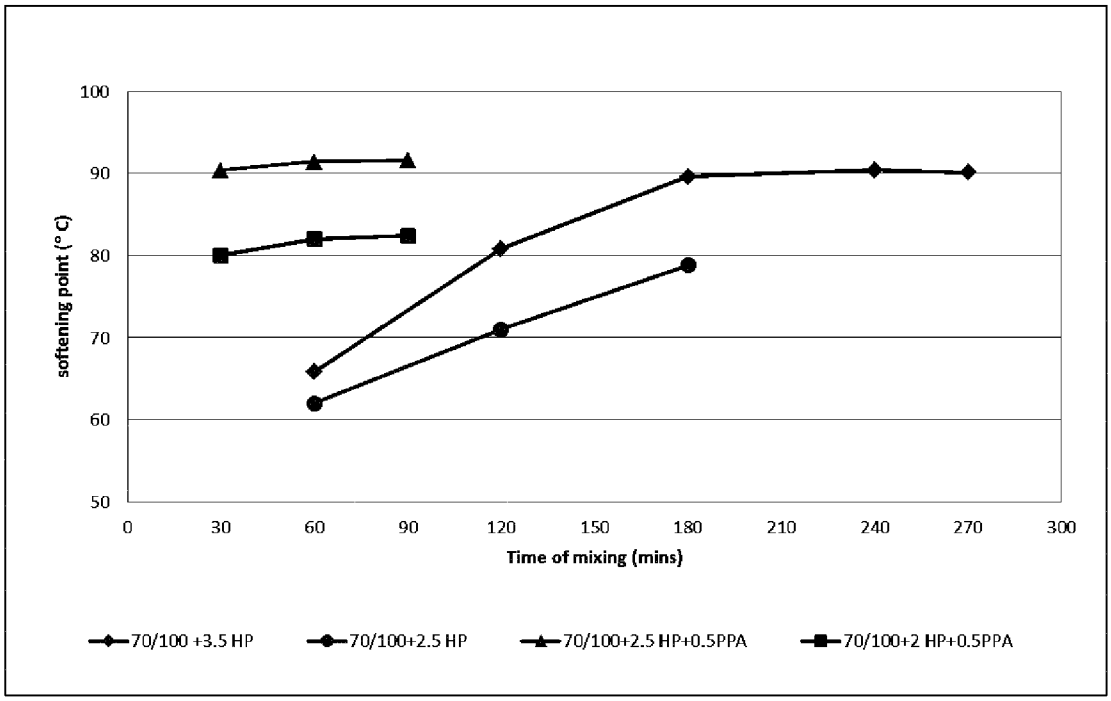

100
90
80
70
60
50
softening point (° C)
0
30
60
90
120
150
180
210
240
270
Time of mixing (mins)
80/100+3.5 HP
80/100+2.5 HP+1PPA

Figure 4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softening point (° C)
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90
120
150
180
210
240
270
300
Time of mixing (mins)
70/100 +3.5 HP
70/100+2.5 HP
70/100+2.5 HP+0.5PPA
70/100+2 HP+0.5PPA

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/083479

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L95/00 C08L25/10 C08L53/02 C08K3/32 C08L91/00
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/170739 A1 (ASAHI KASEI CHEMICALS CORP [JP]) 12 November 2015 (2015-11-12) cited in the application	1-12
Y	the whole document & EP 3 141 584 A1 (ASAHI CHEMICAL IND [JP]) 15 March 2017 (2017-03-15)	1-12
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 March 2018	22/03/2018

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

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Anonymous: "Polyphosphoric Acid Modification of Asphalt Binders, E-C160", Transportation Research Circular January 2012, 8 April 2009 (2009-04-08), pages 1-172, XP055066169, Retrieved from the Internet: URL:www.tbr.org [retrieved on 2013-06-11]	1-12
Y	page 1 - page 7 pages 132,134 the whole document	1-12

X	Robert N. Hunter ET AL: "The Shell Bitumen Handbook, sixt edition" In: "The Shell Bitumen Handbook, sixt edition", 1 January 2015 (2015-01-01), ICE Publishing, Westminster, London, UK, XP055459540, ISBN: 978-0-7277-5837-8 pages 165-166,	1-12
Y	the whole document	1-12

Y	Jim May ET AL: "Heating, Mixing and Storing Modified Asphalt, Technical Paper T-133", , 1 January 1996 (1996-01-01), pages 1-24, XP055459543, Chattanooga, Tennessee, USA Retrieved from the Internet: URL:http://www.heatec.com/literature/technical/T-133.pdf [retrieved on 2018-03-15] the whole document	1-12

Y	X. Lu ET AL: "SBS Modified Bitumens: Does Their Morphology and Storage Stability Influence Asphalt Mix Performance?", , 12 April 2010 (2010-04-12), pages 1-10, XP055459550, Retrieved from the Internet: URL:http://data.abacus.hr/h-a-d/radovi_s_kongresa/nagoya_japan_2010/90227.pdf [retrieved on 2018-03-15] the whole document	1-12

	-/--	

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Szabolcs Biro ET AL: "Asphalt rubber versus other modified bitumens", ROAD MATERIALS AND PAVEMENT DESIGN, Vol X, 1 October 2015 (2015-10-01), pages 1-17, XP055458455, Abingdon DOI: 10.1080/14680629.2015.1004865 Retrieved from the Internet: URL:http://ra-foundation.org/wp-content/uploads/2013/02/020-PAP_017.pdf [retrieved on 2018-03-12]	1-12
Y	paragraph [2.1.6;2.2.1]	1-12
X	Mônica Fernandes ET AL: "Rheological evaluation of polymer-modified asphalt binders", Materials Research, 1 September 2008 (2008-09-01), pages 381-386, XP055458725, DOI: 10.1590/S1516-14392008000300024 Retrieved from the Internet: URL:http://www.scielo.br/pdf/mr/v11n3/24.pdf [retrieved on 2018-03-13]	1-12
Y	paragraphs [02.1], [02.2]; figure 1; table 3 the whole document	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/083479

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015170739 A1	12-11-2015	CN 106232729 A	14-12-2016
		EA 201692021 A1	28-02-2017
		EP 3141584 A1	15-03-2017
		JP WO2015170739 A1	20-04-2017
		KR 20160122817 A	24-10-2016
		SG 11201608866W A	29-12-2016
		TW 201546192 A	16-12-2015
		US 2017073519 A1	16-03-2017
		WO 2015170739 A1	12-11-2015