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**WPI Abstract Accession No. 96-236271/24 & JP
080092486 A WPI Abstract Accession No.
78-022661A/02 & JP 500135114 A**

(58) Field of Search

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(54) **Preparation process for polymer-modified bitumen**

(57) A method for improving the storage stability of a polymer-modified bituminous composition, which comprises using as a compatibilising agent a disulphide that does not release sulphur during the preparation of the composition at elevated temperature. The disulphide may be diphenyl, bis(2,4,5-trichlorophenyl) bis(4-aminophenyl), bis(3-t-butyl-6-methyl-methyl-4-hydroxy-phenyl) or bis(orthobenzoic acid) disulphide.

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PREPARATION PROCESS FOR POLYMER-MODIFIED BITUMEN

Polymer-modified bitumens are widely used in road construction, roofing, sealing etc. Most interest commercially lies in bitumens modified with styrenic thermoplastic rubbers, particularly styrene-butadiene block-copolymers, for which the mechanical properties are in many ways superior to conventionally used bitumens.

Polymer-bitumen blends are two phase systems. Bitumen itself is a complex mixture of molecular structures which include maltenes and asphaltenes. The addition of, e.g., thermoplastic rubbers disturbs the phase equilibrium and leads to phase separation particularly on hot storage into a polymer-rich layer and an asphaltene-rich layer. Each of these two phases has distinctly different properties. Therefore storage stability is an important requirement for polymer-modified bitumens. This is especially so for the road industry.

There have been a large number of proposals for ensuring or improving storage stability.

Firstly, phase separation can be avoided or reduced by the use of compatible bitumens which have low asphaltene content and high aromaticity. On their own compatible base bitumens have poorer properties for, e.g., road usage than incompatible base bitumens, but with a polymer-modified system the effect is reversed - blends based on compatible bitumens generally outperform blends based on incompatible bitumens. However, because of limited availability of compatible base bitumens, there is a strong need for a mechanism to render incompatible bitumen-polymer blends storage stable.

It has been proposed to use high shear mixing at temperatures of from 260°C to 310°C in special equipment (U.S. Patent Specification No. 4,314,921); to prolong the hot mix time to avoid separation (European Patent Specification No. 0 458 386 A1); and to use various additives such as an inorganic acid (U.S. Patent Specification No. 5,070,123), an unsaturated dicarboxylic aliphatic acid or anhydride (European Patent Specification No. 0 496 457 A1) and carbon black (U.S. Patent Specification No. 5,036,119).

The additives proposed are often to be added to one or other of the polymer and bitumen components to modify the component and/or to cause chemical coupling of polymer and bitumen to encourage the long-term stability of the resulting blend.

More commonly, sulphur and also peroxides have been proposed as such coupling agents. Peroxides in polymer-bitumen compositions have been proposed, inter alia, in U.S. Patent Specifications Nos. 3,634,293 and 4,503,176, and the use of sulphur in, for example, U.S. Patent Specifications Nos. 3,634,293 and 4,154,710, in British Patent Specification No. 2,025,986, in U.S. Patent Specification No. 5,120,777 and in European Patent Specification Nos. 0 360 656 A and 0 096 638 B1. In the latter three documents the sulphur source may be a compound which acts as a sulphur-donor or agent which yields free, elemental or radical sulphur during the polymer-modified bitumen preparation process. Such sulphur sources include various dialkyl disulphides and diaryl disulphides, thiuram disulphides and amino disulphides. Some of these are known as vulcanisation agents (morpholino disulphides and polyalkyl phenol disulphides) and vulcanisation accelerators (tetramethylthiuram disulphide). All disclosures require free sulphur during the blending process to

give rise to the coupling necessary for homogenisation and storage stability.

Peroxides are expensive and highly reactive; because of their reactivity such agents can adversely affect the composition of the polymer-bitumen blend and its properties. Free sulphur is a cheaper, less reactive alternative but it is not always efficient (with some blends homogenisation does not occur and with others gellation can be a severe problem) and most importantly it gives rise to hydrogen sulphide formation at the elevated temperature of the blending process which is environmentally unacceptable.

As noted above certain disulphides are well known as vulcanisation accelerators. Tetramethylthiuram disulphide is proposed to be added (as an alternative to elemental sulphur) to a homogenised rubber-bitumen blend to produce cross-linked rubber in an asphalt composition to utilise, e.g., waste tyre rubber particles, in International Patent Specification No. WO 93/17076.

In U.S. Patent Specification No. 3,611,888 small amounts of a mixture of dixylyl disulphides are used in a polymer-bitumen blend to prevent any tendency of the elastomer to cure during heating in the manufacture or use of the resulting sealant composition. No indication is given as to when such an additive is incorporated into the polymer-modified bitumen composition but the general process outlined and the use of the additive suggests that it is necessary to incorporate it into the polymer component prior to mixing with the other components, which include a resin and a plasticizer in addition to asphalt (bitumen) selected to produce a composition which remains stable on heating.

None of the documents above discloses the use of disulphides as a compatibiliser for polymer-bitumen

blends except as a source of free sulphur to act as a conventional coupling agent in the blending process.

Against these conventional proposals, it has now surprisingly been found that a number of disulphides
5 which do not yield sulphur under the usual high temperature polymer-bitumen blending processes are highly useful compatibilising agents which render polymer-bitumen blends homogeneous and storage stable with none of the disadvantages arising from free-
10 sulphur and also give rise to polymer-bitumen compositions with well-balanced properties and an improved low temperature performance.

Accordingly, the present invention provides a method for improving the storage stability of a
15 polymer-modified bituminous composition, which comprises using as a compatibilising agent a disulphide that does not release sulphur during the preparation of the composition at elevated temperature.

It is well within the knowledge and expertise of
20 the skilled person in the art to assess whether a disulphide will release sulphur or not under high temperature blending compositions. For example, under the blending conditions sulphur-donating compounds such as morpholino disulphides and polyalkylphenol
25 disulphides give rise to a release of hydrogen sulphide (as indicated above) which is easily detectable.

Conventionally blending of polymer and bitumen is carried out at elevated temperature, i.e. above room temperature, usually at a temperature in the range of
30 from 100°C to 250°C. Suitably the blending temperature is maintained in the range of from 150°C to 200°C and preferably at 180°C. Generally the mixing of polymer and bitumen is carried out with stirring and often using a high-speed or high-shear mixer.

35 The disulphide compatibilising agent may be added initially to the polymer component, to the bitumen

component or to a preblended mixture of the two, or the polymer, bitumen and compatibilising agent may be mixed together all at once.

5 It has been found useful to preblend the polymer and bitumen, prior to adding the disulphide, for a short time period of sufficient length to provide an even distribution of polymer in the bitumen, suitably using a high-shear mixer and at elevated temperature. The mixing time is envisaged as of the order of an hour
10 or less, and is suitably 30 minutes. Whilst an even distribution is achieved, should no compatibiliser be added the two components would normally separate on storage once the mixing had stopped. After addition of the disulphide the high-shear mixing at elevated
15 temperature is suitably continued for a time sufficient to achieve full homogenisation, this may be for up to 15 hours but may be from 1 to 10 hours. With certain systems this additional mixing time may be in the range of from 3 to 5 hours.

20 The disulphide is suitably added to the polymer-bitumen components in an amount of from 0.1 to 10% by weight of the final composition. Preferably in the range of from 0.1 to 2% by weight is used, and especially 1% by weight.

25 If other components are to be added to the composition this may occur at any suitable stage in the blending process.

30 By the method of the invention, it is also possible to compatibilise blends prepared by other methods but which have separated wholly or partially on storage.

The disulphide is preferably a diaryl disulphide which is not a sulphur-donor under the blending conditions. Useful results have been achieved where each aryl portion is an unsubstituted or substituted phenyl, suitably a phenyl group unsubstituted or
35 substituted by one or more of the same or different

substituents selected from C₁₋₆ alkyl, preferably C₁₋₄ alkyl and especially methyl groups, halogen atoms, especially chlorine atoms, hydroxy groups, amino groups and carboxylic acid groups or their derivatives such as salts, esters amides and anhydrides. Alkyl herein includes linear and branched alkyl groups and halogen is to be understood as including fluorine, chlorine, bromine and iodine.

Preferably a diaryl disulphide is used in which each aryl group is a phenyl group unsubstituted or substituted by one or more of the same or different substituents selected from methyl groups, t-butyl groups, chlorine atoms and carboxylic acid groups.

Mixtures of disulphides may be used provided that none is utilised which is sulphur-donating. Where disulphides exist in different isomeric forms then either the pure isomer or a mixture of isomers may be used.

The polymers of the polymer-bituminous composition may be any polymer normally used in such compositions. Thus it may, for example, be a polyisoprene, polybutene, polyacrylate or polymethacrylate polymer or a block copolymer of a conjugated diene, e.g. butadiene, isoprene, pentadiene or hexadiene, and a monovinyl aromatic hydrocarbon e.g. styrene, methylstyrene, vinylnaphthalene, vinyltoluene or vinylxylene.

Advantageously the polymer is a styrene-butadiene block copolymer, especially the triblock copolymer commonly known as an SBS block copolymer. Such copolymers may be linear or radial, and of any useful styrene content. Suitably the styrene content is in the range of from 10 to 55% by weight, as measured by ASTM 3314, more preferably 30 to 40% by weight. Such copolymers may be prepared by any method known in the

art including by sequential polymerisation or by the coupling of prepolymerised blocks.

The SBS polymer may be present in an amount in the range of from 1 to 15% by weight of the final composition.

The bituminous component present in the bituminous composition may be a naturally occurring bitumen or derived from a mineral oil. Also petroleum pitches obtained by a cracking process and coal tar can be used as the bituminous component as well as blends of various bituminous materials. Examples of suitable components include distillation of "straight-run bitumens", precipitation bitumens, e.g. propane bitumens, blown bitumens, e.g. catalytically blown bitumen or "Multiphalte", and mixtures thereof. Other suitable bituminous components include mixtures of one or more of these bitumens with extenders (fluxes) such as petroleum extracts, e.g. aromatic extracts, distillates or residues, or with oils. Suitable bituminous components (either "straight-run bitumens" or "fluxed bitumens") are those having a penetration of in the range of from 50 to 250 dmm at 25°C; therefore quite hard bitumens of a penetration of from 60 to 70 dmm may be used, but generally a straight run or distilled bitumen having a penetration in the range of from 150 to 250 dmm will be the most convenient to use. Both compatible as well as incompatible bitumens may be used.

Naturally the most benefit from this invention comes from use with incompatible bitumens, however the improved and well balanced properties of the resulting polymer-bitumen blend suggest that the disulphide additive may be of use with compatible bitumen-polymer blends not just to assist homogenisation but also to provide an improvement of the resulting properties of the composition.

The bituminous composition may also contain other ingredients such as may be required for the end-use envisaged. Thus fillers may be included, for example talc, calcium carbonate and carbon black, or other components including resins, oils, stabilisers or flame retardants may be incorporated. The content of such fillers and other components may be in the range of from 0 to as much as 40% by weight.

The storage stable compositions resulting from the present invention find use in any of the areas in which polymer-modified bitumens are utilised, for example in road, roofing, sound deadening, vibration damping, adhesive, coating and sealant applications.

The beneficial properties imparted to the compositions by use of the disulphide compatibiliser in the present invention make the resulting polymer-modified bitumens of particular use as binders in asphalt compositions for road and paving construction and repair. For such usage polymer-modified bitumens containing in the range of from 1 to 10%, especially from 3 to 7%, by weight are preferred.

The present invention further provides the use of the above diaryl disulphides as compatibilising agents for polymer-modified bituminous compositions.

The present invention still further provides a polymer-modified composition which comprises as a compatibilising agent a disulphide that does not release sulphur during the preparation of the composition at elevated temperature.

The following Examples illustrate the present invention.

Examples 1 to 6

A blend of 5% weight-by-weight of polymer in bitumen was prepared for each of Examples 1 to 6 and Comparison Examples A and B by the following procedure in which a Silverson L4R high shear mixer was used.

An incompatible bitumen of Venezuelan origin having a penetration of 80 was heated to 160°C and subsequently the polymer, a linear styrene-butadiene-styrene (SBS) block copolymer with a molecular weight of 180,000 gr/mol and a styrene content of 30% by weight sold by Shell under the code KRATON D 1101(c), was added. During polymer addition the temperature increased to 180°C as a result of the energy input of the mixer. The blend was stirred at high shear for 30 minutes and the mixing temperature maintained at 180°C by switching the mixer on and off as necessary.

For Examples 1 to 6, and Comparison B, 1% weight-by-weight of the test disulphide was then added to the blend with the stirring continued at half the maximum speed and the temperature maintained at 180°C. The homogeneity of the blend was checked frequently with fluorescence microscopy (homogeneity as determined by fluorescence microscopy corresponds to hot storage stability) and for Examples 1 to 6 the blending process was stopped when a single yellow phase was observed; the mixing time to achieve a single phase was noted. For comparison B, when after 12 hours of mixing no homogeneity was observed, the mixing was stopped.

The properties of the prepared blends were assessed using the following test methods:

Softening point	:	ASTM D 36
Penetration at 25°C	:	ASTM D5
Viscosity	:	evaluated at 150°C using a Haeke roto-viscometer and a shear rate of 100s ⁻¹

The results are given in Table I below. It can be seen that

Table I

Example	Disulphide	Homogenisation Time (hrs)	Penetration (dmm)	Softening Point (°C)	Viscosity (m Pas)
1	diphenyl	8	53	72	930
2	bis(2,4,5-trichlorophenyl)	9	46	69	770
3	bis(4-aminophenyl)	7	46	74	1000
4	bis(3-t-butyl-6-methyl-methyl-4-hydroxy-phenyl) ¹	10	40	76	1000
5	bis(orthobenzoic acid)	4	45	64	690
A	None	-	43	75	1100
B	tetramethylthiuram	n.h. ²	39	78	1300

¹ as sold by Monsanto as an anti-oxidant under the trade name SANTONOX

² "not homogeneous"

the sulphur-donating tetramethylthiuram disulphide did not impart homogeneity of the polymer-bitumen blend whereas homogeneity was achieved with all of the other disulphides tested with the good balance of properties for such blends maintained and in some instances improved.

C L A I M S

1. A method for improving the storage stability of a polymer-modified bituminous composition, which comprises using as a compatibilising agent a disulphide that does not release sulphur during the preparation of the composition at elevated temperature.
5
2. A method as claimed in claim 1, wherein the disulphide is a diaryl disulphide.
3. A method as claimed in claim 2, wherein the diaryl group of diaryl disulphide is a phenyl group which is unsubstituted or substituted by one or more of the same or different substituents selected from C₁₋₆ alkyl groups, halogen atoms, amino groups, and carboxylic acid groups or derivatives thereof.
10
4. A method as claimed in any one of claims 1 to 3, wherein the polymer is a styrene-butadiene-styrene block copolymer.
15
5. A method as claimed in claim 4, wherein the polymer is present in the composition in an amount in the range of from 1 to 15% by weight.
- 20 6. A method as claimed in any one of claims 1 to 5, wherein the disulphide is used in an amount in the range of from 0.1 to 10% by weight of the total prepared composition.
- 25 7. A process for the preparation of a polymer-modified bituminous composition which comprises contacting the polymer and bitumen at elevated temperature in the presence of a disulphide that does not release sulphur under the blending conditions in order to achieve a storage stable homogeneous blend.
- 30 8. A process as claimed in claim 7, wherein the polymer and bitumen are pre-blended at elevated temperature.

9. A method as claimed in claim 1 or a process as claimed in claim 7 which is carried out substantially as described in respect of anyone of Examples 1 to 6 herein.

5 10. A polymer-modified bituminous composition which comprises as a compatibilising agent a disulphide that does not release sulphur during the preparation of the composition at elevated temperature.



Application No: GB 9610517.6
Claims searched: 1-10

Examiner: K. Macdonald
Date of search: 22 August 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): C3N
Int CI (Ed.6):
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1442112 (TOYO SODA) see Claims 1,2	1,7 and 10 at least
X	GB 1419093 (COAL INDUSTRY) see Example	1,7 and 10 at least
X	EP 0360656 A1 (ELF FRANCE) see page 4, lines 21-41	1, 7 and 10 at least
X	US 5399598 (ALPHAFLEX) see Claim 1	1,7 and 10 at least
X	US 5120777 (ELF FRANCE) see column 6, line 41- column 7, line 10	1,7 and 10 at least
X	US 5087652 (DU PONT) see Claim 1	1,7 and 10 at least
X	US 3611888 (UNIROYAL) see Example 1	1,7 and 10 at least
XP	WPI Abstract Accession No. 96-236271/24 & JP 080092486 A (JSR CELL ELASTOMA) 09.04.96 (see abstract)	1,7 and 10 at least
X	WPI Abstract Accession No. 78-02661A/02 & JP 500135114 A (JSR) 27.10.75 (see abstract)	1,7 and 10 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.