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## BITUMINOUS BINDER COMPOSITION

The present invention relates to a bituminous binder composition. More particularly, the present invention relates to a composition comprising a bituminous component and an elastomeric block copolymer, which can be used as a binder in asphalt concrete compositions.

With the term "asphalt concrete composition" as used throughout the present specification is meant a composition containing on the one hand mineral components, such as aggregates and fines, and on the other hand a bituminous binder for adhering said mineral components together.

It will be appreciated that the present heavy traffic loadings make high demands upon the pavements. As the number of vehicles, and in particular the number of large, commercial vehicles, is ever increasing, said traffic loadings will only become heavier and consequently are a serious threat to the durability of pavements.

The inevitable result will be a reduction in the lifetime of the pavement, which in return will lead to increased maintenance costs. Moreover, the roads will be blocked more often due to maintenance activities. Hence, pavements having excellent performance characteristics - such as fatigue performance, resistance to permanent deformation, adhesive/cohesive strength and durability - are essential for an optimum infrastructure. Therefore, there is a continuous effort of improving the characteristics of asphalt concrete compositions.

As the nature and properties of the bituminous binder determine to a great extent the performance of the asphaltic pavement compositions, a lot of research has been and still is directed towards said binder.

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In the Shell Bitumen Review 64, pages 2-5, September 1989, a binder is described, comprising a polymer-compatible bitumen compounded with 7% by weight of a thermoplastic elastomer which is a styrene-butadiene-styrene (SBS) block copolymer. Said binder is commercially available since 1986 under the trade name Shell Cariphalte DM and has been successfully applied in practice on several roads and bridge decks. In general, in spite of the relatively high costs, thermoplastic elastomers are highly desired as bitumen modifiers, for they give an excellent balance of performance properties. As the presently applied SBS block copolymers have relatively high molecular weights, the SBS/bitumen binder compositions have relatively high viscosities. Consequently, the temperature at which compounding between binder and aggregates is conducted must be rather high in order to accomplish a workable viscosity of the SBS/bitumen binder. If said compounding temperature is not sufficiently high, the viscosity of the SBS/bitumen binder will be too high for effective compounding. It will be appreciated that compounding at as low as possible temperatures is preferred, mainly because of equipment costs, safety and ease of handling.

On the other hand, it is a generally accepted concept that thermoplastic elastomers to be applied as modifiers in bitumen, should have a relatively high molecular weight in order to be able to interact adequately with the bitumen. The thermoplastic elastomer namely, must form a, preferably continuous, polymer network through the bitumen upon addition to hot bitumen. The elastomer then absorbs maltenes from the bitumen in its elastomeric portion, swells and eventually forms a substantial volume fraction of the blend. It was generally accepted that at lower molecular weights of the elastomer, the elastomeric portions would not be capable of absorbing sufficiently maltenes from the bitumen to adequately interact with the bitumen to form a network through said bitumen.

Therefore, there is a need for an elastomeric binder having on the one hand a low viscosity at an as low as possible temperature

and on the other hand excellent binder characteristics resulting in a polymer-bitumen blend having a good balance of properties.

Surprisingly, it now has been found that blends of thermoplastic elastomers having a relatively low molecular weight - and consequently a relatively low viscosity at high temperatures - and bitumen are excellent binders for asphalt concrete compositions causing the asphalt concrete composition to exhibit a very good resistance to permanent deformation, which is one of the most important properties of asphalt concrete compositions.

Accordingly, the present invention relates to a bituminous binder composition comprising:

- (a) 1 to 10% by weight of a linear, radial or branched block copolymer comprising at least one monovinyl aromatic compound polymer block A and at least one conjugated diene polymer block B; and
- (b) 99 to 90% by weight of a bituminous component having a penetration (25 °C, 0.1 mm) in the range of from 40 to 300 dmm and having a softening point in the range of from 30 to 70 °C, characterized in that the content of monovinyl aromatic compound of said block copolymer is in the range of from 30 to 50% by weight based on the weight of total block copolymer and in that each initially prepared combination AB of said polymer blocks A and B has an apparent molecular weight in the range of from 45,000 to 80,000.

With the expression "apparent molecular weight" as used throughout this specification is meant the molecular weight as determined by gel permeation chromatography using polystyrene standards.

From the Journal of Applied Polymer Science, Vol. 43, 227-236 (1991), binders are known comprising a bitumen and a SBS block copolymer. However, it is stated that SBS block copolymers cannot form thermodynamically stable blends with road bitumen, due to which phase separation occurs, particularly at higher temperatures. This is detrimental for the performance properties.

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An alternative, thermally more stable, binder is proposed, in which ionic interactions between polymer and bitumen occur thus forming an ionomeric network. Said ionic interactions are achieved by treating the SBS block copolymer as well as the bitumen with maleic anhydride (step 1). After mixing the maleated SBS block copolymer and maleated bitumen (step 2) the acid groups still present in the blend are neutralized with zinc acetate trihydrate (step 3). However, the improved thermodynamic stability of the ionomeric SBS-bitumen blend inevitably implies a significant rise in the costs involved for material (maleic anhydride) and process (three-step process, additionally required equipment) and as a result the market price of the ionomeric binder will become significantly higher than the present price of SBS-bitumen binders, which already is considered high. Moreover, the benefits in respect of the performance properties of the ionomeric SBS-bitumen binder do not counterbalance the increase in costs.

From U.S. Patent No. 3,978,014 a bituminous composition is known comprising as a major component a bituminous component, an elastomeric block copolymer and a thermoplastic polymer, which is different from the elastomeric block copolymer and which has a molecular weight above 10,000. Said elastomeric block copolymer preferably is a polystyrene-poly(conjugated diene)-polystyrene block copolymer. Due to the presence of three different components, phase separation will occur more readily, which is detrimental for the stability of the composition.

In U.S. Patent No. 3,900,692 the treatment of an asphalt concrete composition is described comprising the impregnation of said asphalt concrete composition by applying to the surface thereof an oil in water emulsion. The oil phase, penetrating the asphalt, contains an elastomer which is insoluble in n-pentane to modify the asphaltene fraction and/or an elastomer which is soluble in n-pentane to modify the maltene fraction of the asphalt.

Examples of n-pentane insoluble elastomers are SBS block copolymers, usually having molecular weights above 100,000, and poly(chloroprene). Examples of n-pentane soluble elastomers are

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styrene-butadiene rubbers, natural rubber and poly(butadiene). A great disadvantage of the described method is that the binder in the asphalt concrete composition is rubberized only after it has been applied as pavement on a road, so that the process is hardly controllable. As a result, it is very unlikely that a reproducible and homogeneous distribution of the elastomers through the binder can be established, which is unfavourable of the performance properties of the asphalt concrete composition, in particular of the deformation resistance.

When the block copolymer to be used as component (a) in the binder composition according to the present invention is added to the hot bituminous component (b), it interacts with the maltenes in the bitumen by absorbing them, primarily in the conjugated diene portions of the block copolymer. As a result, the block copolymer swells to several times its original volume thereby forming a (continuous) polymer network throughout the bitumen. The amount of block copolymer required for obtaining such a network is in the range of from 1 to 10% by weight, preferably 2 to 8% by weight and most preferably 3 to 7% by weight, the remaining part of the binder composition being comprised of bituminous components. Although at lower block copolymer levels, i.e. 1 to 3% by weight, the formed polymer network may not be completely continuous throughout the entire bituminous component, the deformation resistance of the asphalt concrete composition is already extremely good due to the presence of several smaller polymer networks throughout the bitumen.

The monovinyl aromatic compound polymer blocks are essential in achieving the polymer network. In general, the hard poly(mono-vinyl aromatic compound) blocks agglomerate, thus forming hard domains which crosslink the poly(conjugated diene) entities to form a three-dimensional network. Upon heating to temperatures above 100 °C said hard domains soften, which enables the processing of the block copolymers by means of e.g. extruders and moulding machines. The exact processing temperature mainly depends on the size of the poly(monovinyl aromatic compound) blocks and on the

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size of the entire block copolymer molecules, i.e. on the content of monovinyl aromatic content and on the molecular weight of the block copolymer. Upon cooling, the block copolymer regains its original structure, strength and elasticity. Consequently, when the block copolymer is added to hot bitumen, the hard domains will soften and the block copolymer will flow due to the high temperature. As a result, mixing with the bitumen is considerably facilitated and a homogeneous distribution of the block copolymer through the bitumen can be established. The conjugated diene portions will absorb maltenes from the bitumen and upon cooling the monovinyl aromatic portions will harden again thus re-establishing the continuous polymer network described above.

Because the present invention involves low molecular weight block copolymers, implying that the poly(monovinyl aromatic compound) blocks are also relatively small, the number of said poly(monovinyl aromatic compound) domains throughout the bitumen must be sufficiently large. In this connection it was found that the content of said monovinyl aromatic compound in the block copolymer should be in the range of from 30 to 50% by weight, preferably 35 to 45% by weight, based on the total weight of block copolymer.

The block copolymers, which are useful as modifiers in the asphalt concrete compositions according to the present invention, may be prepared by any method known in the art including the well known sequential polymerization method and the coupling method, as illustrated in e.g. U.S. Patents Nos. 3,231,635; 3,251,905; 3,390,207; 3,598,887 and 4,219,627. In a preferred embodiment of the present invention, the block copolymer is prepared by coupling at least two diblock copolymer molecules AB together, with A representing a monovinyl aromatic compound polymer block and B representing a conjugated diene polymer block. Consequently, the resulting block copolymer has the general formula  $(AB)_n X$  with n being an integer of 2 or higher and X representing the residue of a coupling agent, which may be any polyfunctional coupling agent known in the art, such as dibromoethane, silicontetrachloride,



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diethyl adipate or divinylbenzene. Accordingly, a preferred block copolymer is a block copolymer which has been formed by coupling two or more, preferably two, diblock copolymers AB together by means of a polyfunctional coupling agent, wherein each diblock copolymer AB has an apparent molecular weight in the range of from 45,000 to 80,000, preferably from 50,000 to 70,000, and wherein the content of monovinyl aromatic compound of the final block copolymer is in the range of from 30 to 50% by weight, preferably 35 to 45% by weight, based on the total weight of block copolymer.

The preferred monovinyl aromatic compound is styrene, while the preferred conjugated diene is butadiene or isoprene with butadiene being most preferred.

One of the great advantages of the present invention is the low viscosity of the block copolymer-bitumen binder composition at high temperatures, as a result of which the workability of said binder composition is significantly improved, while the resistance to permanent deformation of the asphalt concrete composition containing said block copolymer is at least equal to the deformation resistance of asphalt concrete compositions containing the conventional high molecular weight SBS block copolymers.

Suitable bituminous components are those bitumen having a penetration (25 °C, 0.1 mm) in the range of from 40 to 300 dmm (decimillimeters) and having a softening point in the range of from 30 to 70 °C. Preferably, the bitumen has a low content of asphaltenes, i.e. less than 10% by weight. Bitumens having a penetration (25 °C, 0.1 mm) in the range of from 45 to 250 dmm and a softening point in the range of from 35 to 55 °C are preferred.

The present invention also relates to asphalt concrete compositions comprising the bituminous binder composition as hereinbefore described.

In order to adequately examine the resistance to permanent deformation of asphalt concrete compositions, the dynamic creep test is very useful. In this test a cylindrically shaped specimen of an asphalt concrete composition is subjected to repetitive, transient loads. More particularly, said cylindrically shaped

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specimen is alternately subjected to a transient load of 100 kPa during 0.2 seconds and a recovery period of 1.8 seconds. A base load of 1 kPa is permanently applied on the test specimen. Hence, each cycle lasts 2 seconds. The total number of cycles is 1800, corresponding to a cumulative loading time of 360 seconds. The test reveals several numerical values.

The "Amplitude" is the maximum accomplished deformation during the test, i.e. during the period of 1800 cycles (3600 seconds) and is expressed in millimeters (mm).

"Residual Strain" refers to the relative deformation and consequently the "Total Residual Strain" is the relative deformation after 1800 cycles. The "Strain Rate" refers to the rate of deformation and can be determined periodically, e.g. after 600 cycles (1200 seconds) and 1200 cycles (2400 seconds). In general, the Strain Rate can be determined at each point in time by determining the tangent of the Residual Strain and the cumulative loading time at that particular point in time.

The "Elastic Recovery" is a measure of the elasticity of the asphalt concrete composition and can be calculated as follows:

$$\text{Elastic recovery} = 100\% - \frac{\text{permanent deformation} * 100\%}{\text{Amplitude}}$$

The invention will be further illustrated by the following examples without restricting the scope of the invention to these specific embodiments.

#### Examples

##### Preparation of asphalt concrete test specimen

The binder was prepared by mixing the bitumen and the block copolymer in a high shear mixer. Typically, the bitumen was heated to 160 °C, after which an amount of block copolymer, corresponding to 5% by weight based on the total weight of bitumen plus block copolymer, was added. The bitumen and the block copolymer were subsequently mixed for 20 to 30 minutes under high shear, while the temperature was controlled to rise to a maximum temperature of

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185 °C, as at higher temperatures the block copolymer would degrade.

In all binder compositions a bitumen grade identified by PX-100 was used, which is a bitumen based on components from Arab Light crude having a softening point of about 45.0 °C, a penetration (25 °C, 0.1 mm) of about 100 and an asphaltene content of about 8% by weight.

After preparation of the binder, the asphalt concrete test specimen were prepared by mixing 5.8 parts by weight (pbw) of binder with 100 pbw of aggregates (Hollandse steenslag) at elevated temperature. This temperature - the so called "mixing temperature" - depends on the type of binder and more particularly on the type of block copolymer used in the binder. After mixing binder and aggregate at the mixing temperature, the obtained asphalt concrete composition was cooled to a temperature - the "compaction temperature" - at which the viscosity had increased to twice the viscosity of the asphalt concrete composition at the mixing temperature. In the present examples the viscosity at the mixing temperature was 150 mPa.s and the viscosity at the compaction temperature consequently was 300 mPa.s. At this "compaction" viscosity the asphalt concrete composition was packed by rolling with a steel wheel. The asphalt concrete composition was allowed to cool down to room temperature.

The various asphalt concrete compositions prepared according to the above described method are listed in Table I. Composition 1 is in accordance with the present invention, composition A is a comparative composition, while composition B is a reference composition.

Table I Asphalt concrete compositions

Comp.	Bitumen	Block copolymer			Tmix (°C)	Tcomp (°C)
		App.MW	diblock MW	styrene (% wt)		
1	PX-100	112,000	56,000	40	166	145
A	PX-100	168,000	89,000	30	191	168
B	PX-100	-	-	-	-	-

The block copolymer present in composition A is CARIFLEX TR 1101 (CARIFLEX is a trade mark), a styrene-butadiene-styrene block copolymer prepared by coupling two styrene-butadiene block copolymers with divinylbenzene.

5 From Table I it is becomes clear that composition 1 can be processed at lower temperatures than composition A, which in practice offers considerable advantages as to the workability of the asphalt concrete composition.

#### Example 1

10 From the asphalt concrete compositions as listed in Table I cylindrically shaped samples having a diameter of 10 mm and a height of 60 mm were subjected to a dynamic creep test at 40 °C.

The results are listed in Table II.

Table II Dynamic creep test at 40 °C

Composition	Tot.Res. Strain *10 <sup>-3</sup>	Strain Rate *10 <sup>-6</sup>	Amplitude mm	Elastic recovery %
1	26.4	3.0	0.09	99.86
A	30.0	3.3	-	99.82
B	46.0	7.1	-	99.48

Example 2

Asphalt concrete compositions were prepared according to the method described above. However, before cutting out cylindrical test samples from the prepared asphalt concrete compositions, said asphalt concrete composition were first treated in the Laboratory Test Track (LTT).

In general, the LTT has a circular track with an outer diameter of 3.25 m on which pavements of 0.7m wide can be tested at controlled temperatures up to 60 °C. In the present experiments the temperature was fixed at 40 °C and the wheel loading applied was 7 kN at a velocity of 15 km/h. The total number of wheel passes was 50,000.

After treatment in the LTT, cylindrical test samples of the same size as described in Example 1 were taken from the asphalt concrete compositions and subjected to the dynamic creep test.

The results are listed in Table III.

Table III Dynamic creep tests at 40 °C of samples ex LTT

Comp.	Tot.Res.	Strain rate		Amplitude mm	Elastic recovery %
	Strain *10 <sup>-3</sup>	t=1200 *10 <sup>-6</sup>	t=2400 *10 <sup>-6</sup>		
1	10.9	1.5	1.1	0.05	99.89
A	12.0	1.2	0.9	0.04	99.88
B	19.4	4.4	2.5	0.05	99.58

From Tables I, II and III it can be derived that the composition according to the present invention shows an unexpectedly good resistance to deformation, while its workability is significantly better than the known compositions.

C L A I M S

1. A bituminous binder composition comprising:
  - (a) 1 to 10% by weight of a linear, radial or branched block copolymer comprising at least one monovinyl aromatic compound polymer block A and at least one conjugated diene polymer block B; and
  - (b) 99 to 90% by weight of a bituminous component having a penetration (25 °C, 0.1 mm) in the range of from 40 to 300 dmm and having a softening point in the range of from 30 to 70 °C, characterized in that the content of monovinyl aromatic compound of said block copolymer is in the range of from 30 to 50% by weight based on the weight of total block copolymer and in that each initially prepared combination AB of said polymer blocks A and B has an apparent molecular weight in the range of from 45,000 to 80,000.
2. A bituminous binder composition according to claim 1, characterized in that it comprises component (a) in an amount of from 2 to 8% by weight and component (b) in an amount of from 98 to 90% by weight.
3. A bituminous binder composition according to claim 2, characterized in that it comprises component (a) in an amount of from 3 to 7% by weight and component (b) in an amount of from 97 to 93% by weight.
4. A bituminous binder composition according to any one of the claims 1 to 3, characterized in that the block copolymer is obtained by coupling two or more diblock copolymers AB together by means of a polyfunctional coupling agent, each diblock copolymer AB having an apparent molecular weight in the range of from 45,000 to 80,000.
5. A bituminous binder composition according to claim 4, characterized in that the block copolymer is obtained by coupling

two diblock copolymers, each having an apparent molecular weight in the range of from 50,000 to 70,000.

6. A bituminous binder composition according to any one of the claims 1 to 5, characterized in that the content of monovinyl aromatic compound in the block copolymer is in the range of from 35 to 45% by weight.
7. A bituminous binder composition according to any one of the claims 1 to 6, wherein the monovinyl aromatic compound is styrene.
8. A bituminous binder composition according to any one of the claims 1 to 7, wherein the conjugated diene is isoprene or butadiene.
9. A bituminous binder composition according to claim 8, wherein the conjugated diene is butadiene.
10. A bituminous binder composition according to any one of the claims 1 to 9, characterized in that the bituminous component has an asphaltene content of less than 10% by weight.
11. A bituminous binder composition according to any one of the claims 1 to 10, characterized in that the bituminous component has a penetration (25 °C, 0.1 mm) in the range of from 45 to 250 dmm and a softening point in the range of from 35 to 55 °C.
12. A bituminous binder composition according to claim 11, characterized in that the bituminous component is a bitumen having a penetration (25 °C, 0.1 mm) of about 100 dmm, a softening point of about 45 °C and an asphaltene content of about 8% by weight.
13. An asphalt concrete composition comprising a bituminous binder composition according to any one of the claims 1 to 12.



# INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/EP 93/02926

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 5 C08L95/00

// (C08L95/00, 53:02)

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 5 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 practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 001 440 (PHILLIPS PETROLEUM COMPANY) 18 April 1979 see page 2, paragraph 4 - page 3, line 2 see page 3, paragraph 5; claims ----	1-4, 6-9, 11, 13
X	FR,A,1 557 193 (SHELL INTERN. RESEARCH MAATSCH.) 14 February 1969 see "Résumé" : sections 1-3, 5 see page 2, line 15 - line 52 ----	1-9, 11, 13
A	EP,A,0 458 386 (EURON) 27 November 1991 -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

1 February 1994

Date of mailing of the international search report

24.02.94

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat	Application No
<b>PCT/EP 93/02926</b>	

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0001440	18-04-79	US-A- 4217259 AU-B- 507613 AU-A- 3930078 CA-A- 1105641 JP-A- 54057524	12-08-80 21-02-80 21-02-80 21-07-81 09-05-79
FR-A-1557193	14-02-69	BE-A- 710702 CH-A- 511267 DE-A, C 1720169 GB-A- 1177725 NL-A- 6801997 SE-B- 357374	13-08-68 15-08-71 02-10-69 14-01-70 16-08-68 25-06-73
EP-A-0458386	27-11-91	NONE	