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**BITUMINOUS COMPOSITION**
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(57) The present invention provides a bituminous composition which comprises a bituminous component and a block copolymer composition comprising at least one block of a conjugated diene and at least one block of a monovinylaromatic hydrocarbon, wherein the block copolymer composition has a vinyl content of at least 25% by weight based on the total diene content and a diblock content of 25 wt% or less, and any diblock copolymer present has an apparent molecular weight which is in the range of from 100,000 to 170,000; and the block copolymer composition per se.

A B S T R A C T

Bituminous Composition

The present invention provides a bituminous composition which comprises a bituminous component and a block copolymer composition comprising at least one block of a conjugated diene and at least one block of a monovinylaromatic hydrocarbon, wherein the block copolymer composition has a vinyl content of at least 25% by weight based on the total diene content and a diblock content of 25 wt% or less, and any diblock copolymer present has an apparent molecular weight which is in the range of from 100,000 to 170,000; and the block copolymer composition per se.

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Invention Title: Bituminous Composition



The following statement is a full description of this invention, including the best method of performing it known to me/us:-

### Bituminous Composition

The present invention concerns bituminous compositions having advantageous high and low temperature properties which are maintained over time giving an improved estimated service life when used in, for example, roofing applications. These advantageous properties are imparted by the use of a thermoplastic elastomeric block co-polymer having a high vinyl content and a particular diblock content.

Butadiene homopolymers with a high vinyl content (determined by infrared examination essentially the same as that set forth in "The Analysis of Natural and Synthetic Rubbers by Infrared Spectroscopy" H.L. Dinsmore and D.C. Smith in Naval Research Laboratory Report No. P-2861, August 20, 1964) are known from U.S. Patent Specification No. 3,301,840 and are preparable by utilising a hydrocarbon solvent such as tetrahydrofuran during polymerisation.

U.S. Patent Specification No. 4,129,541 describes, as a comparison polymer, a block co-polymer which has a vinyl content of 47% by weight (also determined by infrared (IR) techniques) which can be prepared utilising tetrahydrofuran by a process described in U.S. Patent Specification No. 3,639,521. The authors of U.S. 4,129,541 are seeking an asphalt (also known as bitumen)-containing composition which in use as a pipeline coating in the low temperature environment of off-shore pipeline installations would provide for a longer service life by improving resistance to cracking. Their findings show that at temperatures of 0°C there is generally a gradual decrease in crack time improvement as the conjugated diene level is increased, regardless of the method of polymer preparation, but that for polymers such as the high vinyl polymer A the

crack time is actually decreased (i.e. worse) from that of compositions which contain no polymer at all.

5 The use of high vinyl conjugated diene/monovinyl aromatic block copolymers as modifiers for rubber-modified-asphalt roofing or waterproofing materials is described in U.S. Patent Specification No. 4,530,652. Such block copolymers have a vinyl content of at least 25%, exemplified as 33, 40 and 45%, based on total diene content, and were found to improve at least one 10 of dispersability in asphalt, viscosity (measured at 177°C), high temperature flow resistance and low temperature break resistance. Most preferred are said to be radial teleblock copolymers containing 30 to 40% styrene, 40% vinyl unsaturation, and having a number 15 average molecular weight between 150,000 and 250,000. The copolymer asphalt blends tested indeed all show very good low temperature properties but have highly variable and unpredictable high temperature properties for viscosity and flow resistance.

20 High temperature viscosity is an important parameter for bitumen blend processing, particularly where polymer-modified compositions are prepared by high temperature (in excess of 150°C), high shear blending. Block copolymer bitumen blends desirably 25 have a viscosity measured at 180°C of less than 8 Pas, advantageously of 4 Pas or less, and most suitably 2 or 3.

30 Additionally, polymer-modified bitumens when used as roofing materials in external locations need to have both acceptable high temperature and low temperature properties to be of use in a large number of environments, and to retain those properties over time in order to provide a long service time, thereby 35 delaying, for as long as possible, the need for replacement of the roofing materials.

The polymer-modified asphalt compositions of U.S.- 4,530,652 whilst having very acceptable low temperature

properties for the main part, have unsuitable high temperature viscosities and/or flow resistant properties for most of the blends disclosed. Indeed the results are so variable for these high temperature properties that it is difficult to draw any conclusions about what sub group of compositions could have both acceptable, and consistent, high and low 5 temperature properties; neither is there any guidance in U.S.-4,530,652 as to the expected service life of the compositions tested.

It has now been found that consistently improved low and high temperature properties can be achieved in a high vinyl content block copolymer modified bitumen and furthermore that such properties can be more attractively retained over time than for 10 conventional polymer-modified bitumens.

Accordingly, the present invention provides a bituminous composition which comprises a bituminous component and a block copolymer comprising at least one block of a conjugated diene and at least one block of a monovinylaromatic hydrocarbon, wherein the block copolymer has a vinyl content of at least 25% by weight based on the 15 total diene content and a diblock content of 25 wt% or less, and any diblock copolymer present has an apparent molecular weight in the range of from 100,000 to 170,000.

With the term "apparent molecular weight" as used throughout the specification is meant the molecular weight of a polymer, as measured with gel permeation chromatography (GPC) using poly(styrene) calibration standards (according to ASTM 20 3536).

By "diblock content", there should be understood the amount of non-coupled diblock copolymer that is finally present in the prepared block copolymer composition. Where the block copolymer is prepared via the full sequential preparation method, essentially

only triblock copolymers are formed having an apparent molecular weight in the range from 200,000 to 340,000.

The diblock content is preferably less than 20 %wt, more preferably 15 wt% or less.

5       The block copolymer composition constituents may be either linear or radial; good results have been given by both copolymer types. The block copolymer composition constituents include linear triblock copolymers (ABA), multi-armed block copolymers ((AB)<sub>n</sub>X) and diblock copolymers (AB), with A representing a monovinyl aromatic hydrocarbon polymer block, B representing a conjugated diene polymer block, n being an integer of 2 or higher, preferably between 2 and 6 and X representing the residue of a coupling agent.  
10       The coupling agent may be any di- or polyfunctional coupling agent known in the art, for example, dibromoethane, silicon tetrachloride, diethyl adipate, divinylbenzene, dimethyldichlorosilane, methyl dichlorosilane. Particularly preferred in such a preparation route is the use of non-halogen containing coupling agents, for example gamma-glycidoxypropyl-trimethoxysilane (Epon 825), and diglycidylether of bisphenol A.

25       The block copolymers, which are useful as modifiers in the bituminous compositions according to the present invention, may be prepared by any method known in the art including the well known full sequential polymerisation method, optionally in combination with reinitiation, 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 and EP 0413294 A2, 0387671 B1, 0636654 A1, WO 04/22931.

30       The block copolymer may therefore, for example, be prepared by coupling at least two diblock copolymer molecules AB together.

35       Techniques to enhance the vinyl content of the conjugated diene portion are well known and may involve



the use of polar compounds such as ethers, amines and other Lewis bases and more in particular those selected from the group consisting of dialkylethers of glycols. Most preferred modifiers are selected from dialkyl  
5 ether of ethylene glycol containing the same or different terminal alkoxy groups and optionally bearing an alkyl substituent on the ethylene radical, such as monoglyme, diglyme, diethoxyethane, 1,2-diethoxy-  
10 propane, 1-ethoxy-2,2-tert-butoxyethane, of which 1,2-diethoxypropane is most preferred.

The apparent molecular weight of diblock copolymer (AB) is in the range of from 100,000 to 170,000. Preferably, said diblock copolymer apparent molecular weight is in the range of from 110,000 to 150,000, more  
15 preferably from 115,000 to 125,000.

The content of monovinyl aromatic hydrocarbon of the final block copolymer is suitably in the range of from 10 to 55% by weight, preferably in the range of from 20 to 45, and more preferably 25 to 40, % by  
20 weight based on the total block copolymer.

Suitable monovinyl aromatic hydrocarbons include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene,  $\alpha$ -methylstyrene, vinylnaphthalene, vinyltoluene and vinylxylene, or  
25 mixtures thereof of which styrene being the most preferred.

The total vinyl content of the block copolymer is at least 25% by weight. Suitably the vinyl content is in the range of from 30 to 80 % by weight, preferably  
30 from 35 to 65% by weight, more preferably from 45 to 55% by weight, and most preferably from 50 to 55 % by weight, especially more than 50 %wt.

Suitable conjugated dienes include those having from 4 to 8 carbon atoms, for example 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene. Mixture  
35 of such dienes may also be used. Preferred conjugated

dienes are 1,3-butadiene and isoprene, with 1,3-butadiene being the most preferred.

It will be appreciated that with the term "vinyl content" actually is meant that a conjugated diene is polymerised via 1,2-addition. Although a pure "vinyl" group is formed only in the case of 1,2 addition polymerisation of 1,3 butadiene, the effects of 1,2 addition polymerisation of other conjugated dienes on the found final properties of the block copolymer and the blends of it with bitumen will be the same.

It is thought that the block copolymer composition used as modifier in the bituminous composition of the invention is novel, and therefore the present invention also extends to any of the block polymer compositions per se as described hereinbefore.

The bituminous component present in the bituminous compositions according to the present invention 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 or "straight-run bitumens", precipitation bitumens, e.g. propane bitumens, blown bitumens, e.g. catalytically blown bitumen or "Multiphate", 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.

5 The bituminous composition may also, optionally, 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 10 range of from 0 to as much as 40% by weight. Of course, if advantageous, other polymer modifiers may also be included in the bituminous composition of the invention.

15 The useful low temperature and high temperature properties of the polymer-bitumen blends of the present invention coupled with the improved ageing resistance enables such blends to be of significant benefit in uses where the blends are exposed to external weather conditions, such as use in roofing and road 20 applications, especially in roofing applications. When used in roofing applications the block copolymer composition is suitably present in the bituminous composition in an amount in the range of from 6, or more preferably 10 to 15 % by weight, based on total 25 bituminous composition. When used in road applications the block copolymer composition is suitably present in the bituminous composition in an amount in the range of from 1 to 10 % by weight, more preferably of from 2 to 8 % by weight, based on total bituminous composition. 30 The usefully low high-temperature viscosity not just means that the polymer-bitumen blends can be more easily processed but also means that they enable a greater amount of filler to be incorporated before the maximum allowable processing viscosity is achieved, and 35 thus leads to a cheaper product in those applications where fillers are commonly used.

Other applications in which the polymers themselves may be of use are in sound deadening, in adhesive, sealant or coating compositions and/or in vibration dampening compositions.

5 The following Examples illustrate the present invention.

Examples 1 to 16

A number of block copolymer compositions of the invention, and for comparison, were prepared by a  
10 conventional polymerisation method based on one of the general procedures given below:

A. Preparation of linear and/or radial coupled block copolymer compositions

B. Full Sequential Polymerisation

15 General Procedure A

By the following process, the coupled block copolymer compositions of the present invention were prepared:

180 g styrene was added to 6 litres of cyclohexane  
20 at 50°C, after which 8.31 mmol of sec-butyl lithium was added. The reaction was completed after 40 minutes. Hereafter, 1.46 mL diethoxypropane was added, followed by the addition of 418 g of butadiene in 10 minutes. The temperature of the reaction mixture rose to 60°C.  
25 The polymerisation was allowed to proceed at this temperature for 85 minutes. At this point in the polymerisation a sample is taken from the reaction and analysed by GPC ASTM D3536. Then the coupling agent as listed in Table 1 was added. For polymers 1 to 5 and  
30 10 to 17 the molar amount of coupling agent added, is half of that of the mmols of sec-butyl lithium. For polymers 8 to 9 and 18 the molar amount of coupling agent added is 0.25 times that of the mmols of sec-butyl lithium.

35 The reaction mixture was allowed to stand for 30 minutes at

60°C. After cooling down the reaction mixture, 0.6% by weight of IONOL on polymer was added for stabilisation. The product was isolated by steam stripping to give white crumbs.

5 Except for the coupling agent, the variation of the block copolymer compositions listed in Table 1 is obtained by altering the amount of sec-butyl lithium and/or amount of DEP to get the apparent molecular weight as listed in column 4 in Table 1.

10 General Procedure B

90 g styrene was added to 6 litres of cyclohexane at 50°C, after which 4.16 mmol of sec-butyl lithium was added. The reaction was completed after 40 minutes. Hereafter, 1.46 mL diethoxypropane was added, followed  
15 by the addition of 418 g of butadiene in 10 minutes. The temperature of the reaction mixture rose to 60°C. The polymerisation was allowed to proceed at this temperature for 85 minutes. Hereafter the second portion of 90 g styrene is added in 1 minute. The  
20 polymerisation is allowed to proceed at 60°C for 15 minutes before 0.5 mL of ethanol is added to terminate the polymerisation. After cooling down the reaction mixture, 0.6 wt% of IONOL, relative to the weight of  
25 the polymer were added for stabilisation. The product was isolated by steam stripping to give white crumbs.

The variation of the block copolymer compositions listed in Table 1 is obtained by altering the amount of sec-butyl lithium and amount of DEP to get the apparent molecular weight as listed in column 5 for polymer 6, 7  
30 and 16 in Table 1.

Details of comparison polymer compositions are given in Table 2 below.

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Table 1

Block copolymer composition of Ex. No.	Poly-styrene Content (%) <sup>1</sup>	Vinyl Content (%) <sup>2</sup>	Diblock (Mw) kg/mol (x 10 <sup>3</sup> ) <sup>(3)</sup>	Final Mw kg/mol (x 10 <sup>3</sup> ) <sup>(3)</sup>	Preparation Route	Coupling Agent (4)	Coupling Efficiency (%)
1	30	58	161	299	A	MDCS	95
2	30	47	165	304	A	MDCS	89
3	30	64	136	255	A	MDCS	97
4	30	42	145	268	A	MDCS	91
5	32	52	124	236	A	MDCS	96
6	31	52	-	235	B	-	full seq.
7	31	55	-	268	B	-	full seq.
8	31	51	120	415	A	GPTS	86
9	31	52	147	502	A	GPTS	82
10	20	69	141	280	A	DMDCS	96
11	30	68	124	248	A	DMDCS	98
12	30	69	140	280	A	DMDCS	80
13	33	50	148	413	A	GPTS	80

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Table 1 (continued)

Block copolymer composition of Ex. No.	Poly-styrene Content (%) <sup>1</sup>	Vinyl Content (%) <sup>2</sup>	Diblock (Mw) kg/mol ( $\times 10^3$ ) <sup>(3)</sup>	Final Mw kg/mol ( $\times 10^3$ ) <sup>(3)</sup>	Preparation Route	Coupling Agent (4)	Coupling Efficiency (%)
14	30	59	120	235	A	MDCS	83
15	30	61	115	386	A	SiCl <sub>4</sub>	78
16	30	66	-	321	B	-	full seq.

Key

- 1 by weight; measured according to ASTM 3314
- 2 by weight of butadiene block, measured by IR spectroscopy generically as in ASTM 3677
- 3 weight average molecular weight; measured by GPC (ASTM 3536) as detected by UV absorption.
- 4 weight ratio of amount of material formed by coupling to the total amount of living "diblock" present before coupling

DMDCS: dimethyldichlorosilane  
MDCS: methyldichlorosilane  
SiCl<sub>4</sub>: silicon tetrachloride  
GPTS: gamma-glycidypropyltrimethoxysilane

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Table 2

Comparison Block copolymer composition	Poly-styrene Content (%) <sup>1</sup>	Vinyl Content (%) <sup>2</sup>	Diblock Mw kg/mol (x 10 <sup>3</sup> ) <sup>3</sup>	Final kg/mol (x 10 <sup>3</sup> ) <sup>3</sup>	Preparation Route	Coupling Agent	Coupling Efficiency (%)
C1	30	37	176	325	A	MDCS	96
C2	30	44	176	321	A	MDCS	96
C3	30	53	176	332	A	MDCS	96
C4	30	64	176	326	A	MDCS	95
C5	30	64	181	335	A	MDCS	92
C6	30	53	199	363	A	MDCS	94
C7	30	45	202	368	A	MDCS	94
C8	30	10	127	435	A	DEAP	86
C9	31	10	91	177	A	DBE	83

DEAP : diethyladipate

DBE : dibromoethane



Example 17

A blend of 12% by weight of block copolymer composition in bitumen was prepared for each of Examples 1 to 9 and for each of the comparison Examples  
5 by the following procedure in which a Silverson LR2 high shear mixer was used:

The bitumen was heated to 160°C and subsequently the block copolymer composition was added. during polymer addition the temperature increased to 180°C, which is  
10 caused by the energy input of the mixer. At 180°C the temperature was kept constant by on/off switching of the high shear mixer. Blending was continued until a homogeneous blend was obtained which was monitored by fluorescence microscopy. Generally the blending time  
15 was around 60 minutes.

The bitumen grade used for this example is a compatible bitumen, designated PX-200 and having a penetration of 200.

The block copolymer-bitumen blends were then tested  
20 for suitability for roofing applications. The evaluations for both cold temperature and high temperature performance initially and after 6 months ageing time for the block copolymer blends of the invention and for the comparison blends are given in  
25 Table 3 below. The test methods used were:

Viscosity : evaluated at 180°C using a Haeke roto-  
viscometer and a shear rate of 20s<sup>-1</sup> and 100s<sup>-1</sup>

Cold bend (CB) : evaluated under DIN 52123

Flow Resistance Temperature: evaluated under DIN 52123

30 The ageing characteristics of the block copolymer-bitumen blends were determined by a laboratory ageing test recommended by UEAtc (Union Européenne pour L'Agrément Technique dans la Construction) which involves treatment in a dark air-ventilated oven at 70°C  
35 for 6 months. In Table 3, the initial and the 6 months' aged values are given; the difference between the two (the Δ value) is also given. Desirably the Δ

value should be as low as possible. The higher the value the shorter the estimated lifetime for the tested composition.

5 From Table 3 it can clearly be seen that although generally the low temperature properties and stability as shown by the cold bend temperature are good for all blends containing high vinyl-containing block copolymers compositions, the present block copolymer compositions additionally show advantageous high  
10 temperature properties of a generally lower viscosity and a retained flow resistance temperature over time which reflects an advantageously longer estimated service life in use. The comparison examples C<sub>1</sub>-C<sub>7</sub> generally have a higher viscosity and a far higher  $\Delta$   
15 value for the flow resistance temperature showing a significant reduction in this high temperature property over time. It is further observed that blends containing low vinyl-containing block copolymer compositions (comparison examples C<sub>8</sub> and C<sub>9</sub>) display a  
20 far less attractive retention of low temperature properties and stability and relatively poor high temperature properties when compared with the present bitumen blends.



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Table 3

Block copolymer of Ex. No.	Viscosity at 180°C (Pas)		Flow Resistance Temperature (°C)		Cold Bend Temperature (°C)	
	20 s <sup>-1</sup>	100 s <sup>-1</sup>	Initial	Aged	Initial	Aged
1	6	4	110	85	-20	-10
2	7	5	110	90	-25	-25
3	3	3	100	80	-20	-15
4	4	4	100	80	-25	-20
5	2	2	95	80	-25	-20
6	2	2	95	90	-25	-20
7	3	3	105	100	-20	-30
8	2	2	95	90	-25	-20
9	5	3	105	100	-20	-25
C1	8	6	110	80	-25	-15
C2	8	6	115	85	-25	-20

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Table 3 (continued)

Block copolymer of Ex. No.	Viscosity at 180°C (Pas)		Flow Resistance Temperature (°C)			Cold Bend Temperature (°C)		
	20 s <sup>-1</sup>	100 s <sup>-1</sup>	Initial	Aged	Δ	Initial	Aged	Δ
C3	6	5	110	80	30	-25	-15	10
C4	5	4	115	85	30	-20	-15	5
C5	6	4	105	75	30	-20	-20	0
C6	7	5	115	80	35	-20	-30	-10
C7	8	6	120	80	40	-20	-20	0
C8	4	4	95	75	20	-30	-10	20
C9	1	1	80	70	10	-35	-20	15

Example 18

For the block copolymer compositions of Examples 10 to 16, 12% by weight polymer blends in bitumen grade PX-200 were prepared by the blending procedure of Example 17 and the initial high and low temperature properties were evaluated. The results are given in Table 4.

Table 4

Block co-polymer of Ex. No.	Viscosity at 180°C (Pas) 20 s <sup>1</sup>	Flow Resistance Temperature (°C)	Cold Bend Temperature (°C)
10	3	80	-15
11	2	90	-10
12	3	90	-5
13	3	115	-20
14	2	90	-25
15	2	95	-20
16	4	95	-25

The block copolymer blends of Table 4 also exhibit favourable "high temperature" viscosity, and acceptable flow resistance and cold bend temperatures.

Example 19

In this Example, the block copolymer compositions of Examples 6 and 8 and comparison Example C8 were blended, using the blending procedure of Example 17, with a different, incompatible bitumen grade, designated B-180, having a penetration of 180, to establish whether the advantageous properties noted above extend consistently to blends with other bitumens.

Details of the resulting evaluations of the high and low temperature properties (carried out as in Example 17) are given in Table 5 below.

It will be clear from Table 5 that the favourable properties of the block copolymer-blends of the invention are also clearly maintained with other bitumen grades.

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Table 5

Block co- polymer of Ex. No.	Viscosity at 180°C (Pas)		Flow Resistance Temperature (°C)		Cold Bend Temperature (°C)			
	20s <sup>-1</sup>	100s <sup>-1</sup>	Initial	Aged	Initial	Aged		
6	2	2	95	85	10	-25	-10	15
8	2	1	95	85	10	-25	-10	15
C8	1.5	1.5	95	80	15	-35	0	35

**The claims defining the invention are as follows:**

1. A bituminous composition which comprises a bituminous component and a block copolymer comprising at least one block of a conjugated diene and at least one block of a monovinylaromatic hydrocarbon, wherein the block copolymer has a vinyl content of at least 25% by weight based on the total diene content and a diblock content of 25 wt% or less, and any diblock copolymer present has an apparent molecular weight which is in the range of from 100,000 to 170,000.
2. A bituminous composition as claimed in claim 1, wherein the block copolymer composition has a vinyl content in the range of from 35 to 65% by weight.
- 10 3. A bituminous composition claimed in claim 2, wherein the block copolymer has a vinyl content in the range of from 45 to 55% by weight.
4. A bituminous composition as claimed in any one of claims 1 to 3, wherein any diblock copolymer present has an apparent molecular weight in the range of from 110,000 to 150,000.
- 15 5. A bituminous composition as claimed in claim 4, wherein any diblock copolymer present has an apparent molecular weight in the range of from 115,000 to 125,000.
6. A bituminous composition as claimed in any one of claims 1 to 5, wherein the block copolymer is present in an amount in the range of from 6 to 15% by weight, based  
20 on total bituminous composition.
7. The use of block copolymer as claimed in any one of claims 1 to 6, as a modifier for bitumen whereby the modified bituminous composition has a viscosity at 180°C of in the range of from 1 to 8 Pas coupled with a change of flow resistance temperature and of cold bend temperature over 6 months in the UEAtc laboratory ageing  
25 test of 25°C or less, and 10°C or less respectively.
8. A method for improving the service life of a bituminous composition modified with an elastomer which comprises utilising as the elastomer a block copolymer as claimed in claim 7.
9. Block copolymer as claimed in any one of claims 1 to 5.

10. A bituminous composition, substantially as hereinbefore described with reference to any one of the Examples but excluding the Comparative Examples.

11. A method for improving the service life of a bituminous composition modified with an elastomer, substantially as hereinbefore described with reference to any one of the  
5 Examples but excluding the Comparative Examples.

**Dated 24 March, 1999**  
**Shell Internationale Research Maatschappij B.V.**

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