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(54) Title: POLYMER-MODIFIED ASPHALT COMPOSITION

(57) Abstract: A polymer-modified asphalt composition is disclosed. The composition comprises base asphalt, a thermoplastic elastomer, and a polycyclic diterpene of carbon number 20 and having a carboxyl group. The thermoplastic elastomer is a mixture of a first styrene-based thermoplastic elastomer and a second styrene-based thermoplastic elastomer. The composition has been shown to reduce the softening point while maintaining a high rut resistance (DS value) after production and without curing.



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POLYMER-MODIFIED ASPHALT COMPOSITION

Field of the Invention

This invention relates to a polymer-modified asphalt composition which is primarily useful in road paving. In particular the composition allows for development of the desired strength without carrying out curing.

Background of the Invention

Conventionally, asphalt has been used in a broad range of applications such as road paving. Polymer-modified asphalt uses a thermoplastic elastomer, e.g. styrene-butadiene-styrene block copolymer (SBS), as a strengthening agent and is generally used in heavy traffic road surfaces. Kenichi Uesaka in Study For Material Characterization and Manufacture Method Of The High Viscous Modified Asphalt Used For Porous Pavement, Journal of Pavement Engineering, Japan Society of Civil Engineers, Vol. 9 (pages 87-94) December 2004, describes a typical production plant for polymer-modified asphalt. The polymer-modified asphalt undergoes a maturing process wherein it is cured at a temperature of 160-180°C for 1 to 3 days after completion of the blend manufacturing process. The polymer-modified asphalt is then stored in a storage tank. The maturing process achieves evenly dispersed polymer in asphalt and is considered to be a necessary process in the preparation of polymer-modified asphalt.

The maturing process has been a limitation in the production of polymer-modified asphalt. As this maturing process must be maintained for 1 to 3 days at 160-180°C in a large maturing tank, large-scale capital investment is required and the burden on the environment has become

a problem as it is energy intensive. In addition, if the demand for polymer-modified asphalt for road surfaces is high and there is rapid, large-scale demand for polymer-modified asphalt, the supply would be delayed since a period of 1 to 3 days is required for the maturing process and there is the problem that road surface construction would be delayed.

The present inventors have sought to provide a polymer-modified asphalt composition in which the softening point can be lowered whilst maintaining a high rut resistance (DS value) without post-production curing in order to shorten the lead time from asphalt production to delivery on site. The inventors have conducted intensive studies and focused on lowering the softening point whilst maintaining a high rut resistance (DS value) without post-production curing by optimising the styrene-based thermoplastic elastomer that is added to the polymer-modified asphalt.

Summary of the Invention

Accordingly the present invention provides a polymer-modified asphalt composition characterised by containing base asphalt, from 3 to 6wt% of a thermoplastic elastomer which is a mixture of a first styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of from 3,000 to 6,000mPa•s at 25°C and a second styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of from 500 to 2,500mPa•s at 25°C, and from 0.3 to 2wt% of a polycyclic diterpene of carbon number 20 and having a carboxyl group, wherein the content by percentage of the first styrene thermoplastic elastomer in the thermoplastic elastomer is 60-80wt%.

The inventors have shown that, by mixing a first styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of 3,000-6,000mPa•s at 25°C and a second styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of 500-2,500mPa•s at 25°C at a predetermined ratio, superior properties could be demonstrated experimentally not only for the softening point but also for the DS value without curing.

Therefore, if demand for asphalt at a location is particularly high, it is immediately shipped after blending without curing and can be delivered to site so it is possible to prevent a delay in road surface construction.

Detailed Description of the Invention

The polymer-modified asphalt composition which applies to the invention is explained below with reference to the details of each constituent component and to the reasons for the limits on the numerical values.

Base Asphalt

The base asphalt of the invention may be straight asphalt (refer to JIS K 2207), blown asphalt (refer to JIS K 2207), semi-blown asphalt (refer to 'Asphalt Pavement Standards', Japan Road Association, 13th January 1997, p51, Table 3.3.4), solvent-deasphalted asphalt (refer to 'New Petroleum Dictionary', the Petroleum Society, 1982, p308) or mixtures thereof, and each type of asphalt to which aromatic heavy mineral oil has been added may be used. In particular, as base asphalt used in the invention, asphalt to which aromatic heavy mineral oil has been added to straight asphalt and solvent-deasphalted asphalt are preferred.

Each of the penetration grades of asphalt of the invention are investigated and suitably up to the equivalent of straight asphalt 60/80-100/120 may be used.

5 Generally speaking, the lower the penetration grade the higher the mechanical strength represented by the DS value, however, the low-temperature properties represented by the bending workload and bending stiffness worsen.

10 As solvent-deasphalted asphalt, propane-deasphalted asphalt using propane or propane and butane is preferred. The mixing ratio of straight asphalt and solvent-deasphalted asphalt is, for example, 60-80 and is adjusted according to the desired penetration.

15 Aromatic heavy mineral oil, as stipulated in Petroleum Based Solvent Extracted Oil and JIS K6200, is a solvent extracted oil when brightstock (heavy lubricating oil) is obtained, that is, an extract obtained by solvent extraction using a polar solvent such as furfural of aromatic hydrocarbon process oil containing at least
20 35wt% hydrocarbons and the like and, further, solvent de-asphalted oil obtained by de-asphalting using propane and the like vacuum distilled residual oil from crude oil. In the invention, it is preferable to add extract as an aromatic heavy mineral oil.

25 The role of the extract in the invention is to increase the solubility of thermoplastic elastomer in asphalt. To avoid separation in storage, a lot of thermoplastic elastomer is added and the amount of extract which needs to be added increases. Moreover, if
30 more extract than needed is added to the thermoplastic elastomer, the strength decreases.

The amount of extract added to the overall asphalt composition is determined in consideration of a complex

modulus indicating penetration, softening point, storage stability, strength and dynamic stability (DS value) in the wheel tracking test, as well as the Cantabor loss rate indicating low temperature properties but, in the range investigated in the invention, the amount of extract present in the overall asphalt composition is preferably 4-12wt%.

Thermoplastic Elastomer

The styrene-based thermoplastic elastomer used in the polymer-modified asphalt composition of the invention contains a mixture of a first styrene-based thermoplastic elastomer and a second styrene-based thermoplastic elastomer.

The first styrene-based thermoplastic elastomer has a 25% toluene solution viscosity at 25°C in the range of from 3000 to 6000mPa•s. Examples of the first styrene-based thermoplastic elastomer are not particularly limited as long as they satisfy the viscosity criterion, and mention can be made of a styrene-butadiene-styrene block copolymer (SBS), a styrene-butadiene-styrene block copolymer in which the SBS butadiene block double-bonded part is completely hydrogenated (SEBS), and a butadiene/butylene-styrene block copolymer in which the SBS butadiene block double bonded part has been selectively partially hydrogenated (SBBS) and, in addition, a styrene-isoprene-styrene block copolymer (SIS) and a styrene-ethylene/propylene-styrene block copolymer in which the SIS butadiene block double bonded part has been completely hydrogenated (SEPS). Among these, the use of SBS is preferable.

The first styrene-based thermoplastic elastomer has a 25% toluene solution viscosity at 25°C in the range of from 3000 to 6000mPa•s and it is of a higher molecular

weight than the second styrene-based thermoplastic elastomer. If the 25% toluene solution viscosity of the first styrene-based thermoplastic elastomer is less than 3000mPa•s, the difference in molecular weight between it and the lower molecular weight second styrene-based thermoplastic elastomer becomes small if the molecular weight is too low. As a result, the first styrene-based thermoplastic elastomer and the second styrene-based thermoplastic elastomer show an interaction and this is not preferred as the desired modification effect is not obtained. However, if the 25% toluene solution viscosity at 25°C of the first styrene-based thermoplastic elastomer is more than 6000mPa•s, the viscosity of the polymer-modified asphalt composition markedly increases if the molecular weight is too high and is not preferred as compacting becomes difficult when mixing aggregate at low temperature.

Furthermore, the first styrene-based thermoplastic elastomer can more suitably exhibit the effects mentioned above in the preferred 25% toluene solution viscosity in the range of from 4000 to 5000mPa•s at 25°C.

The second styrene-based thermoplastic elastomer has a 25% toluene solution viscosity at 25°C in the range of from 500 to 2500mPa•s. Examples of the second styrene-based thermoplastic elastomer are not particularly limited as long as they satisfy the viscosity criterion, and mention can be made of a styrene-butadiene-styrene block copolymer (SBS), a styrene-butadiene-styrene block copolymer in which the SBS butadiene block double-bonded part is completely hydrogenated (SEBS), and a butadiene/butylene-styrene block copolymer in which the SBS butadiene block double bonded part has been selectively partially hydrogenated (SBBS) and, in

addition, a styrene-isoprene-styrene block copolymer (SIS) and a styrene-ethylene/propylene-styrene block copolymer in which the SIS butadiene block double bonded part has been completely hydrogenated (SEPS). Among these, the use of SBS is preferable.

As the second styrene-based thermoplastic elastomer has a 25% toluene solution viscosity at 25°C in the range of from 500 to 2500mPa•s, it is of a higher molecular weight than the first styrene-based thermoplastic elastomer. If the 25% toluene solution viscosity of this second styrene-based thermoplastic elastomer is less than 500mPa•s at 25°C, it is not preferred as the desired modification effect is not obtained as the molecular weight becomes too low. However, if the 25% toluene solution viscosity of this second styrene-based thermoplastic elastomer is more than 2500mPa•s at 25°C, the difference in molecular weight between it and the higher molecular weight first styrene-based thermoplastic elastomer becomes small. As a result, the first styrene-based thermoplastic elastomer and the second styrene-based thermoplastic elastomer show an interaction and this is not preferred as the desired modification effect is not obtained.

Furthermore, the second styrene-based thermoplastic elastomer can more suitably exhibit the effects mentioned above in the preferred 25% toluene solution viscosity in the range of from 1000 to 2000mPa•s at 25°C.

As described above, by combining two types of styrene-based thermoplastic elastomer in the invention comprising a first styrene-based thermoplastic elastomer having a high 25% toluene solution viscosity at 25°C and a second styrene-based thermoplastic elastomer having a low 25% toluene solution viscosity at 25°C, it is

possible to lower the softening point compared to conventional polymer-modified asphalt. In addition to this, sufficient strength can develop without post-production curing due to an interaction between a first
5 styrene-based thermoplastic elastomer and a second styrene-based thermoplastic elastomer, rut resistance (DS value) is high and can be maintained.

When the total amount of thermoplastic elastomer is shown by the sum of the amounts of a first styrene-based
10 thermoplastic elastomer and a second styrene-based thermoplastic elastomer, the content by percentage of a first styrene-based thermoplastic elastomer in the overall thermoplastic elastomer needs to be from 60 to 80wt% and preferably from 73 to 80wt%.

15 In addition, if the total amount of thermoplastic elastomer in a polymer-modified asphalt composition overall is less than 3wt%, the performance mentioned above cannot be sufficiently exhibited. Further, if the total amount of thermoplastic elastomer in a polymer-
20 modified asphalt composition exceeds 6wt% overall, the above effects are saturated and, by increasing the amount of expensive thermoplastic elastomer added, the raw material cost markedly increases and this presents problems. That is, even if the amount of thermoplastic
25 elastomer added exceeds 6wt%, the mechanical properties of the asphalt composition will not be improved significantly beyond this yet it will be disadvantageous as regards raw material costs.

Therefore, the amount of thermoplastic elastomer
30 needs to be from 3 to 6wt% compared to the total amount of polymer-modified asphalt composition. To suitably exhibit the above effects further, the amount of thermoplastic elastomer is preferably from 4 to 5wt%.

Polycyclic Diterpene of Carbon Number 20 and having a Carboxyl Group

A polycyclic diterpene (resin acid) of carbon number 20 and having a carboxyl group, for example, may include
5 abietic acid, dehydroabietic acid, neoabietic acid, pimaric acid, isopimaric acid and palustric acid although not limited to these, and includes any resin acid falling under the definition of a polycyclic diterpene of carbon number 20 and having a carboxyl group. This polycyclic
10 diterpene of carbon number 20 and having a carboxyl group generally includes rosin. Here, gum rosin, wood rosin and tall oil rosin may be used as rosins. Depending on differences in place of origin, raw material and method of extraction, these rosins can be classified as gum
15 rosins or wood rosins and they may be obtained as the residual component of steam distillation of pine resin. Rosin is typically a mixture containing abietic acid, palustric acid, neoabietic acid, dehydroabietic acid, pimaric acid, sandaracopimaric acid, isopimaric acid and
20 so on. Rosin normally softens at about 80°C and melts at 90 to 100°C. Various resin acids such as abietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, palustric acid, neoabietic acid and laevopimaric acid are contained within the rosin, but
25 these resin acids may also be refined and used individually.

The invention will be explained in the following using gum rosin as an example of the polycyclic diterpene (resin acid) of carbon number 20 and having a carboxyl
30 group. Impurities are removed from this gum rosin by filtering raw tapped pine resin, after which the rosin is obtained by distillation, and separating out the terpene oil in the low boiling point component. In general, this

gum rosin contains 20-40wt% abietic acid, 15-25wt% of neoabietic acid, 20-30wt% palustric acid, 3-8wt% pimaric acid, 10-20wt% isopimaric acid and 3-8wt% dehydroabietic acid.

5 Also, instead of using the rosin as is, it is also possible to use one or more acids selected from among abietic acid, dehydroabietic acid, neoabietic acid, pimaric acid, isopimaric acid and palustric acid.

10 The polycyclic diterpene (resin acid) of carbon number 20 and having a carboxyl group is present at from 0.3 to 2wt% relative to the total weight of the polymer-modified asphalt composition. For example, if the amount of this resin acid is less than 0.3wt%, the addition of polycyclic diterpene of carbon number 20 and having a
15 carboxyl group to the butadiene block in SBS is insufficient and it is not possible to improve the stability of the asphalt composition as a final product. In contrast, if the amount of resin acid exceeds 2wt%, stability will not be improved significantly beyond this
20 and by increasing the amount of expensive resin acid added, the raw material cost markedly increases and this presents problems. That is, even if the amount of resin acid added exceeds 2wt%, the stability will not be improved significantly beyond this yet it will be
25 disadvantageous as regards raw material costs.

 Also, it is preferable if the polycyclic diterpene (resin acid) of carbon number 20 and having a carboxyl group is present within the range of from 0.3 to 1wt% relative to the total weight of polymer-modified asphalt
30 composition. By making the upper limit of the amount of resin acid 1wt%, it is possible to bring about an improvement in the stability of the asphalt composition while keeping the increase in raw material costs

extremely low, and so it is possible to improve the effect on expenditure.

The test methods, examples and comparative examples mentioned in the invention will be described in more detail below but the invention is not limited to these examples. In addition, if the following examples give units in % only, it is assumed to indicate wt%.

In the invention, tests of properties comprising parameters of penetration (25°C), softening point and viscosity (180°C) were carried out as tests to confirm binder properties in samples obtained for an experimental study as shown in Tables 1A and 1B. In addition, the DS value was measured as a test to confirm the mechanical strength indicated by rut resistance of mixtures comprising polymer-modified asphalt composition and aggregate. Detailed test methods will be described below.

Table 1A

Binder ratio	Raw material	Reference example 1 (before curing)	Reference example 2 (after curing)	Comparative example 1	Comparative example 2	Comparative example 3	Example 1	Example 2	Standard and target criteria
		38.5	38.5	38.5	38.3	38.3	38.3	38.3	-
Binder ratio	Straight asphalt	10	10	10	10	10	10	10	-
	Extract								-
	Propane deasphalted asphalt	46.9	46.9	46.9	46.65	46.65	46.6 ₅	46.6 ₅	-
	SBS1 (31, 4500)	4.3	4.3	3.2	0	2.15	2.7	3	-
	SBS2 (30, 1700)			1.1	4.3	2.15	1.6	1.3	
	SBS3 (31, 1150)								
Binder properties	SBS4 (45, 170)								-
	Ratio of 1 st elastomer in SBS	100	100	75	0	50	63	70	
	Dimeric acid	0.3	0.3	0.3					-
	Antistripping agent				0.75	0.75	0.75	0.75	-
	Rosin								-
	Raw material total	100	100	100	100	100	100	100	-
Mixture properties	Penetration (1/10mm)	47	47	46	47	47	47	47	40 or more
	Softening point °C	76.0	64.5	77.5	57.0	56.0	57.5	62.5	56.0-70.0
	180°C viscosity mPa•s	233	208	219	182	192	196	199	-
DS value times/mm		4846	6000	4846	3706	4846	6000	6000	6000 or more

*: (styrene content %, 25% toluene solution viscosity at 25°C mPa•s)

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Table 1B

	Raw material	Example 3	Example 4	Comparative example 4	Comparative example 5	Comparative example 6	Example 5	Example 6	Standard and target criteria
Binder ratio	Straight asphalt	38.3	38.3	38.3	38.3	38.3	38.3	38.3	-
	Extract	10	10	10	10	10	10	10	-
	Propane deasphalted asphalt	46.65	46.65	46.65	46.65	46.65	46.65	46.65	-
	SBS1 (31, 4500)	3.2	3.3	3.6	4.1	4.3	3.3	3.3	-
	SBS2 (30, 1700)	1.1	1	0.7	0.2	0	0	0	-
	SBS3 (31, 1150)						1	0	-
	SBS4 (45, 170)						0	1	-
	Ratio of 1 st elastomer in SBS	75	77	84	95	100	77	77	-
Antistripping agent	Dimeric acid								-
	Rosin	0.75	0.75	0.75	0.75	0.75	0.75	0.75	-
	Raw material total	100	100	100	100	100	100	100	-
	Penetration (1/10mm)	47	46	46	46	46	46	45	40 or more
Binder properties	Softening point °C	65.0	65.5	77.5	79.5	80.5	63.0	61.5	56.0-70.0
	180°C viscosity mPa•s	199	203	212	217	231	204	190	-
Mixture properties	DS value times/mm	6000	6300	5727	4846	4345	6300	6000	6000 or more

*: (styrene content %, 25% toluene solution viscosity at 25°C mPa•s)

Penetration (25°C) was measured using JIS K2207 'Petroleum Asphalt - Penetration Test Method'. A value of 40 (0.1mm) or more is preferred.

Softening point was measured using JIS K2207
5 'Petroleum Asphalt - Softening Point Test Method'. A value of 56.0-70.0 (°C) or more is preferred.

Viscosity was measured under the conditions of JPI-5S-54-99 'Asphalt - Method for Testing Viscosity using a Rotating Viscometer' with a measurement temperature of
10 180°C and measurements were undertaken at 20 spindle rotations/minute using an SC4-21 spindle.

For the DS value (dynamic stability), each polymer-modified asphalt composition and a combination with aggregate shown in Table 2 was used, the asphalt content
15 of the mixture was 5.0wt%, test pieces in sheet form measuring 30cm vertically, 30cm horizontally and with a depth of 5cm were used and tests were carried according to the 'Wheel Tracking Test Method' in the 'Handbook of Methods of Evaluating and Testing Pavement' (Japan Road
20 Association). Japanese roads have been experimentally verified to reach a temperature of 60°C in summer. Under these conditions, when cars pass over them, flow deformation and rutting occur. A wheel tracking test is a test designed to confirm experimentally the degree to
25 which this rutting occurs and is a test carried out in order to evaluate the dynamic stability which is an indicator of flow resistance properties in paving materials. Specifically, a tyre upon which a specified load has been applied is run backwards and forwards over
30 the experimental sample (test piece) for 1 hour in a constant temperature tank maintained at 60°C, and the amount of deformation is measured.

The DS value (times/mm) was determined using the amount of deformation (mm) in 15 minutes from 45-60 minutes after the start of the test and the number of tyre passes in 15 minutes from 45-60 minutes after the start of the test using the following equation:

$$\text{DS value (times/mm)} = (\text{number of tyre passes in the period from 45 min to 60 min (times)} / (\text{amount of deformation (mm) in the period from 45 min to 60 min}))$$

The higher the DS value, the stronger the asphalt which means a paving material which is resistant to rutting can be provided. In the Handbook of Methods of Evaluating and Testing Pavement, if the DS value becomes 6000 times/mm or more it is reported as an DS value of 6000 times/mm or more but, to obtain a higher road surface strength, actually obtained DS values are used in this invention. Moreover, the DS value is 6000 times/mm or more and preferably 6300 times/mm or more.

Table 2

Production Site

Material name	Quality	Production site
Crushed stone No. 6	Hard sand	Miyamacho, Hachioji City, Tokyo
Fine sand	Washed sand	Tsuruoka, Fuji City, Tokyo
Stone powder	Limestone powder	Mizuhocho, Nishitama gun, Tokyo

Material Test Results for Fine Aggregate and Stone Powder

Classification	(mm)	Crushed stone No. 6	Fine sand	Stone powder	Standard value
Passing wt% fraction	19	100			
	13.2	93.7			
	4.75	3.8	100		
	2.36		98.9		
	0.6		92.1	100	
	0.3		50.8	100	
	0.15		46	93.1	
	0.075		1.4	82.2	

Specific gravity	dry surface	2.665	2.581		
	volume	2.651	2.518		
	apparent	2.688	2.688		2.50 or more
Water absorption	(%)	0.53	2.52		3.0 or less
Abrasion loss	(%)	11.8			30 or less
Wastage	(%)	4.4	2.5		12 or less
Content of soft particles	(%)	3.7			5 or less
Long, thin stone	(%)	4.3			25 or less
Peeling area ratio	(%)	8.7			15 or less
Plasticity index	(%)		NP		
Water	(%)			0.12	

Selected Combination

Crushed stone No. 6	85
Fine sand	10
Stone powder	5

To verify the effect of the modified asphalt according to application of the invention, examples, comparative example and reference examples using SBS as a styrene-based thermoplastic elastomer were prepared.

5 Samples comprising straight asphalt, extract, propane-deasphalted asphalt, SBS, and antistripping agent (dimeric acid, rosin) at the blending ratios shown in Tables 1A and 1B (Examples 1-6, comparative examples 1-6 and reference examples 1-2) were prepared.

10 The properties of straight asphalt used in these examples and comparative examples are typical properties and are a penetration of 67 (1/10mm), a softening point of 48.0°C and a 15°C density of 1036kg/m³. The properties of propane-deasphalted asphalt are typical properties and
15 are a penetration of 12 (1/10mm), a softening point of

63.5°C and a 15°C density of 1062kg/m³. In addition, typical properties of the extract used are a kinematic viscosity of 556mm²/s at 60°C and a 15°C density of 977.2kg/m³.

5 The SBS used in this verification is shown in Tables 1A and 1B. There are four types of SBS with different styrene content and 25% toluene solution viscosity at 25°C. Among a total of four types of SBS shown in Tables 1A and 1B, SBS in the first row is a first styrene-based
10 thermoplastic elastomer having a styrene content of 31wt% and a 25% toluene solution viscosity of 4500mPa•s at 25°C. The second to fourth rows from the top show SBS2-SBS4 and are second styrene-based thermoplastic elastomers. SBS2 has a styrene content of 30wt% and a 25%
15 toluene solution viscosity of 1700mPa•s at 25°C, SBS3 has a styrene content of 31wt% and a 25% toluene solution viscosity of 1150mPa•s at 25°C and SBS4 has a styrene content of 45wt% and a 25% toluene solution viscosity of 170mPa•s at 25°C.

20 The 25% toluene solution viscosity at 25°C can be, for example, measured using a Brookfield (BL) viscometer as noted in Japanese unexamined patent JP2008-31267.

 As an antistripping agent, in order to exhibit stripping prevention and compatibility between aggregate,
25 disproportionated gum rosin having an acid value of 156 (mgKOH/g: JIS K 0070), a softening point of 77.0°C (JIS K 2207) is used in examples 1-6 and comparative examples 2-6. Impurities are removed from this gum rosin by filtering raw tapped pine resin, after which the rosin is
30 obtained by distillation and separating out the terpene oil in the low boiling point component. Generally, this gum rosin contains 20-40wt% abietic acid, 15-25wt% neoabietic acid, 20-30wt% palustric acid, 3-8wt% pimelic

acid, 10-20wt% isopimaric acid and 3-8wt% dehydroabiatic acid. In the invention, if this gum rosin is added, the amount is 0.5wt% to total amount of composition. In addition, dimeric acid is used in reference examples 1-2 and in comparative example 1.

Straight asphalt, propane-deasphalted asphalt, extract and antistripping agent are mixed at the blending ratios shown in examples 1-6, comparative examples 1-6 and reference examples 1-2 in Tables 1A and 1B and SBS and antistripping agent are added after maintaining the mixture at 195°C. Stirring is conducted at 3500 rpm for 3 hours using a homomixer. In this case the production amount is 1.8kg. The prepared asphalt and aggregate are then mixed at 170°C, a predetermined test piece is prepared and is subjected to testing.

Reference examples 1 and 2 both showed experimental results of conventional asphalt compositions. In these reference examples 1 and 2, the thermoplastic elastomer is composed of one type SBS1 only and it is present at 4.3wt%. In addition, a dimeric acid is used as an antistripping agent. Incidentally, reference example 1 shows the properties before curing and the properties when curing is carried out over a period of 1-2 days are shown in reference example 2. The softening point exceeds 70°C prior to curing as shown in reference example 1, and although the DS value falls below 6000 times/mm, in reference example 2 the softening point is 70°C or more and the DS value becomes 6000 or more after curing.

The properties before curing for examples 1-6 and comparative examples 1-6 are shown compared to reference examples 1 and 2. That is, curing was not carried out in any of examples 1-6 and comparative examples 1-6 and the properties were measured immediately after mixing.

Comparative example 1 is a thermoplastic elastomer composed of a mixture of SBS 1 and SBS2 and the ratio of SBS1 to the overall thermoplastic elastomer is 75wt%. In addition, a dimeric acid is used as an antistripping agent. The softening point exceeds 70°C in this comparative example 1 and, as the DS value is 4846 (times/mm), it falls below 6000 (times/mm).

As comparative example 2 is composed a thermoplastic elastomer comprising SBS 2 only, the ratio of SBS1 to the overall thermoplastic elastomer is 0wt%. In addition, rosin is used as an antistripping agent. As the softening point in comparative example 2 was 57.0°C, it has been shown that it can be adjusted to 70°C or lower and, as a result, it has been shown that the viscosity can be lowered. However, as the DS value was 3706 (times/mm), it fell below 6000 (times/mm).

Comparative example 3 is a thermoplastic elastomer composed of a mixture of SBS 1 and SBS2 and the ratio of SBS1 to the overall thermoplastic elastomer is 50wt%. In addition, rosin is used as an antistripping agent. As the softening point in comparative example 3 was 56.0°C, it has been shown that it can be adjusted to 70°C or lower and, as a result, it has also been shown that the viscosity can be lowered. However, as the DS value was 4846 (times/mm), it fell below 6000 (times/mm).

Comparative example 4 is a thermoplastic elastomer composed of a mixture of SBS 1 and SBS2 and the ratio of SBS1 to the overall thermoplastic elastomer is 84wt%. In addition, rosin is used as an antistripping agent. The softening point in comparative example 4 was 75.5°C and exceeded 70°C. As the DS value was 5727 (times/mm), it fell below 6000 (times/mm).

Comparative example 5 is a thermoplastic elastomer composed of a mixture of SBS 1 and SBS2 and the ratio of SBS1 to the overall thermoplastic elastomer is 95wt%. In addition, rosin is used as an antistripping agent. The softening point in comparative example 5 was 79.5°C and exceeded 70°C. In addition, as the DS value was 4846 (times/mm), it fell below 6000 (times/mm).

Comparative example 6 is a thermoplastic elastomer composed of a mixture of SBS1 only and the ratio of SBS1 to the overall thermoplastic elastomer is 100wt%. In addition, rosin is used as an antistripping agent. The softening point in comparative example 6 was 80.5°C and exceeded 70°C. As the DS value was 4345 (times/mm), it fell below 6000 (times/mm).

In examples 1-6, the amount of thermoplastic elastomer, the content by percentage of first styrene-based thermoplastic elastomer in the above thermoplastic elastomer, and the type of antistripping agent are combined in any range specified in the present invention.

In particular, in examples 1-4 the thermoplastic elastomer is composed of a mixture of SBS1 and SBS2. The ratio of SBS1 to thermoplastic elastomer overall from example 1 over the next 3 samples was 63wt%, 70wt%, 75wt% and 77wt% and gradually increased. In addition, rosin is used as an antistripping agent. Accordingly, the DS value in examples 1-4 was 6000 (times/mm) or more. That is, a notable difference in effect between comparative example 3 having a ratio of SBS1 to thermoplastic elastomer overall of 50wt% and example 1 having a ratio of SBS1 to thermoplastic elastomer overall of 63wt%, in particular, is shown in the DS value. Therefore, by having a ratio of SBS1 (1st styrene-based thermoplastic elastomer) to thermoplastic elastomer overall of 60wt% or more, it has

been shown that superior properties for both the DS value and softening point could be demonstrated experimentally.

A notable difference in effect between comparative example 4 having a ratio of SBS1 to thermoplastic elastomer overall of 84wt% and example 4 having a ratio of SBS1 to thermoplastic elastomer overall of 77wt%, in particular, is shown in the DS value and softening point. Therefore, by having a ratio of SBS1 (first styrene-based thermoplastic elastomer) to thermoplastic elastomer overall of 80wt% or lower, it has been shown that superior properties for both the DS value and softening point could be demonstrated experimentally.

In particular, according to the tendency from example 4 and comparative examples 4-6, the tendency for the DS value to drop in proportion to the increase in ratio of SBS1 (first styrene-based thermoplastic elastomer) in thermoplastic elastomer overall at 77wt%, 84wt%, 95wt% and 100wt% was newly found, and among them it is said that a rate of 80wt% was experimentally found to be the threshold at which the predetermined DS value could be obtained.

In connection with this, example 5 is a thermoplastic elastomer composed of a mixture of SBS1 and SBS3 and the ratio of SBS1 to the overall thermoplastic elastomer is 77wt%. In addition, rosin is used as an antistripping agent. In example 5, as the softening point is 63.0°C, it is possible to suppress this to 70°C or below and the DS value becomes 6000 (times/mm) or more. Therefore, it has been shown that superior properties for both the DS value and softening point could be demonstrated experimentally. In particular, SBS3 having a 25% toluene solution viscosity at 25°C of 1150mPa•s as a 2nd styrene-based thermoplastic elastomer is used in

example 5 and, although it has a lower molecular weight than SBS2, it has been shown that identical superior properties could be demonstrated experimentally.

5 Example 6 is a thermoplastic elastomer composed of a mixture of SBS1 and SBS4 and the ratio of SBS1 to the overall thermoplastic elastomer is 77wt%. In addition, rosin is used as an antistripping agent. In example 6, as the softening point is 61.5°C, it is possible to suppress this to 70°C or below and the DS value becomes 6000
10 (times/mm) or more. Therefore, it has been shown that superior properties for both the DS value and softening point could be demonstrated experimentally. In particular, SBS4 having a 25% toluene solution viscosity at 25°C of 170mPa•s as a second styrene-based
15 thermoplastic elastomer is used in example 6 and, although it has a lower molecular weight than SBS2, it has been shown that identical superior properties could be demonstrated experimentally.

In this way, according to the present invention, by
20 mixing a first styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of 3,000-6,000mPa•s at 25°C and a second styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of 500-2,500mPa•s at 25°C at a
25 predetermined ratio, it has been shown that superior properties could be demonstrated experimentally not only for the softening point but also the DS value without curing. Therefore, if demand for asphalt at a location is particularly high, it is immediately shipped after
30 blending without curing and can be delivered to site so it is possible to prevent a delay in road surface construction.

C L A I M S

1. A polymer-modified asphalt composition characterised by comprising base asphalt, from 3 to 6wt% of a thermoplastic elastomer which is a mixture of a first styrene-based thermoplastic elastomer having a 25%
5 toluene solution viscosity in the range of from 3,000 to 6,000mPa•s at 25°C and a second styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of from 500 to 2,500mPa•s at 25°C, and from 0.3 to 2wt% of a polycyclic diterpene of carbon
10 number 20 and having a carboxyl group, wherein the content by percentage of the first styrene thermoplastic elastomer in the above thermoplastic elastomer is from 60 to 80wt%.
2. A polymer-modified asphalt composition according to
15 claim 1 characterised by comprising the first styrene-based thermoplastic elastomer having a 25% toluene solution viscosity in the range of from 4,000 to 5,000mPa•s at 25°C and the second styrene-based thermoplastic elastomer having a 25% toluene solution
20 viscosity in the range of from 1,000 to 2,000mPa•s at 25°C, wherein the content by percentage of the first styrene-based thermoplastic elastomer in the thermoplastic elastomer is from 73 to 80wt%.
3. A polymer-modified asphalt composition according to
25 claim 1 or claim 2 comprising the thermoplastic elastomer at from 4 to 5wt%.
4. A polymer-modified asphalt composition according to any preceding claim, wherein the first styrene-based thermoplastic elastomer is styrene-butadiene-styrene and

the second styrene-based thermoplastic elastomer is
styrene-butadiene-styrene.

5. A polymer-modified asphalt composition according to
any preceding claim, wherein the polycyclic diterpene of
5 carbon number 20 and having a carboxyl group is rosin.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/077505

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L95/00
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)

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)

EP0-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.
A	JP 2012 116897 A (SHOWA SHELL SEKIYU) 21 June 2012 (2012-06-21) abstract table 3	1-5
A	----- WO 2010/125167 A1 (SHELL INT RESEARCH [NL]; SEO AKIRA [JP]) 4 November 2010 (2010-11-04) claims; examples -----	1-5

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/077505

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2012116897 A	21-06-2012	NONE	

WO 2010125167 A1	04-11-2010	JP 2010260939 A	18-11-2010
		WO 2010125167 A1	04-11-2010
