

Article

# Design of SBS-Modified Bitumen Stabilizer Powder Based on the Vulcanization Mechanism

Wengang Zhang <sup>1,\*</sup> , Longting Ding <sup>2</sup> and Zhirong Jia <sup>1,\*</sup><sup>1</sup> School of Civil and Architectural Engineering, Shandong University of Technology, Zibo 255049, China<sup>2</sup> Highway College of Chang'an University, Xi'an 710064, China; 6675342@163.com

\* Correspondence: ziwuzizwg@sdut.edu.cn (W.Z.); jiazhr@126.com (Z.J.); Tel.: +86-15288931932 (W.Z.)

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**Abstract:** In order to improve the problem of the bad thermal storage stability of Styrene-Butadiene-Styrene Block Copolymer Modified Bitumen (SBS-modified bitumen), the vulcanization reaction was selected as the basic mechanism for the research and development of the stabilizer. Sulfur, tetramethylthiuram disulfide (TMTD), zinc oxide, butylated hydroxytoluene (BHT), kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) and carbon-white ( $\text{SiO}_2$ ) were used as raw materials, and 32 kinds of components with different contents of raw materials were designed. The 48-h segregation softening point and other modified bitumen technical indicators, such as ductility, penetration, penetration index, viscosity, and so on, were tested and analyzed. The fluorescence microscope test was also conducted to explore the crosslinking situation based on the vulcanization reaction. The results show that the component with good performance of the SBS-modified bitumen stabilizer powder was S:TMTD:ZnO:BHT:  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  = 60:16:4:20:1250 or S:TMTD:ZnO:BHT: $\text{SiO}_2$  = 60:16:4:20:625. The optimum content of stabilizer powder was 0.9% (S/modified bitumen). The stabilizer was dry powder and can be directly put into bitumen. It can cross-link SBS and especially has an effect on preventing SBS segregation. The technical performance of SBS-modified bitumen with stabilizer powder, such as hot temperature performance, low temperature performance, anti-aging performance and thermal storage stability, all meet the relevant specifications.

**Keywords:** SBS-modified bitumen; stabilizer; thermal storage stability; vulcanization reaction; 48-h segregation softening point difference

## 1. Introduction

The traditional base bitumen suffers from several common defects such as temperature sensitivity, low temperature brittleness, easy flow at high temperature, poor anti-aging performance, low equivalent softening point and other shortcomings. These seriously affect the durability and service life of roads. In order to overcome the shortcomings of the bitumen material, Styrene-Butadiene-Styrene Block Copolymer (SBS), Styrene-Butadiene-Rubber (SBR), Polyethylene (PE), Ethyl-Vinyl-Acetate (EVA) and other polymer modifiers were used to modify the base bitumen. These also have also become the main ways to improve the performance of bitumen [1–5]. Practical application showed that SBS was obviously superior to other polymer modifiers in improving the low temperature toughness and the temperature sensitivity of the bitumen. As a commonly-used modifier, the SBS has outstanding performance. It can increase the softening point and low temperature ductility significantly. Besides, it can also greatly improve the temperature sensitivity. After modification, the elastic recovery rate of bitumen was particularly large. Compared to linear SBS, radial SBS has better performance in improving thermal storage stability and low temperature ductility, but the defects in thermal storage stability of SBS-modified bitumen remain. This creates serious problems for the construction technicians and the performance advantages of SBS-modified asphalt pavement [6,7].

Segregation of polymer-modified bitumen limits its application in engineering practice to a large extent. In order to fully utilize the advantages of polymer-modified bitumen in road construction and widen the application of SBS-modified bitumen, the problem of thermal storage stability must be well solved. However, at present, the thermal storage performance of SBS-modified bitumen in the market is still not satisfactory. Most contractors usually use an extra stirring device to overcome the segregation problem produced in the bitumen transportation and storage process [8,9].

In recent years, due to economic reasons, the financial support of research and development of the SBS-modified bitumen stabilizer has decreased. As a result, there have been few achievements in the research and development of stabilizers. Liu Qianju [10] from South China University of Technology pointed out that by adding the stabilizer, a stable interface adsorption layer was formed between the polymer phase and base bitumen phase. Thus, affinity between the two phases increases, which improves the thermal storage stability. Yang Yang [11] developed a new SBS-modified bitumen stabilizer by using active calcium carbonate, sulfur powder and *N*-octadecylamine polyethenoxy ether as the main raw materials. It can improve the thermal storage stability of SBS-modified bitumen by forming a network structure between bitumen and SBS. Sulfur, stearic acid, vulcanization accelerator tetramethylthiuram disulfide (TMTD) and light stabilizers were also used as the main raw materials to develop a new stabilizer that can promote the compatibility between SBS and base bitumen by Shuangrui et al. [12]. This can improve the thermal storage stability of SBS-modified bitumen. Sulfur, morpholine disulfide and other substances were used by Jinyu et al. [13] as components to prepare stabilizer. The results show that this cannot only improve the thermal storage stability of SBS-modified bitumen, but also improve the performance of the bitumen mixing material to some extent. Aguirre de Carcer et al. [14] focused on the stability of SBS-/sulfur-modified bitumen at high temperature. With the help of sulfur, the fluctuation of the softening point and viscosity became small. The rheological properties and storage stability of bitumen/SBS/montmorillonite composites were studied by Sadeghpour Galooyak et al. [15]. The presence of montmorillonite improves the storage stability of polymer-modified bitumen significantly without adverse effects on its other properties of. Sienkiewicz et al. [16] considered that the storage stability of the polymer-modified bitumen can be improved by using various types of modifiers that form the bonds between the components of these binders. Some experimental studies have been done by Amini et al. [17], and the results show that using nano-composites can improve the storage stability at high temperature. Goli et al. [18] studied the influence of carbon nanotubes on the storage stability of SBS-modified bitumen binders, and the results showed that adding carbon nanotubes to the SBS-modified binder can improve the stability. Storage stability of bitumen binder modified with recycled plastic was studied by Al-Abdul Wahhab et al. [19]. The results showed that for a recycled high-density polyethylene content below 4% and a recycled low-density polyethylene content below 6%, either SBS or Polybilt (PB) will bring good storage stability. However, the development of the aforementioned stabilizers was prohibitive due to the over complex production process, the strict preparation environment requirement and the high cost of raw materials.

The main objective of this paper was to propose a novel design of a stabilizer, which has a simple production process and lower economic cost. Based on the mechanism of the vulcanization reaction, the selection of the raw materials and corresponding content can be properly determined. The laboratory experiments were also conducted in this paper to analyze the performance of the proposed SBS-modified bitumen. "Technical Specification of Construction of Highway Asphalt Pavement (JTG F40-2004, China)" [20] was adopted in this paper as a reference.

## **2. The Mechanism of Stabilizer Components to Improve the Thermal Storage Stability of SBS-Modified Bitumen**

### *2.1. Vulcanization Mechanism*

Sulfur can decompose and generate sulfur free radicals at a certain temperature and in a certain time, and the sulfur free radicals have high oxidizability. Therefore, in a certain condition,

hydrogen atoms in the bitumen polymer chain can be captured by the generated sulfur radicals during sulfur decomposition. Sulfur free radical and hydrogen atoms can generate hydrogen sulfide in the form of gas. Free radicals were generated at the hydrogen atom-losing site of the bitumen polymer chain. Free radicals in adjacent polymer chains can be coupled with each other in cross-link form, and free radicals can also be coupled with sulfur free radicals in bridging form, which can be coupled with O<sub>2</sub> in the form of thio-alcohol, sulfoxide, thioether or sulfone. Sulfur free radicals and the bitumen polymer chain can react with each other. Firstly, sulfur free radicals capture the benzyl carbon in bitumen and hydrogen atoms in the allyl carbon, then hydrogen atoms in the benzene ring [2,21,22]. It will be possible to further produce the following crosslinking reaction in Figure 1.

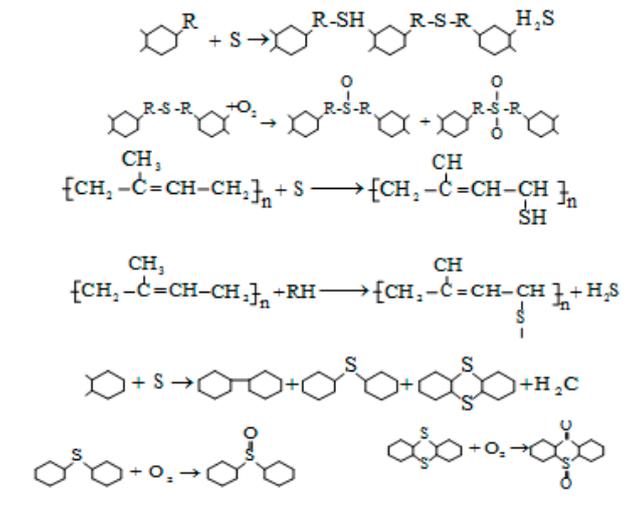


Figure 1. Vulcanization reaction mechanism [23].

The vulcanization reaction process includes an induction period, a hot vulcanization period, an optimum cure period and an over vulcanization period as shown in Figure 2. Vulcanization speed was different in different periods, and the torque of rubber mass will be reversed if the vulcanization time is too long.

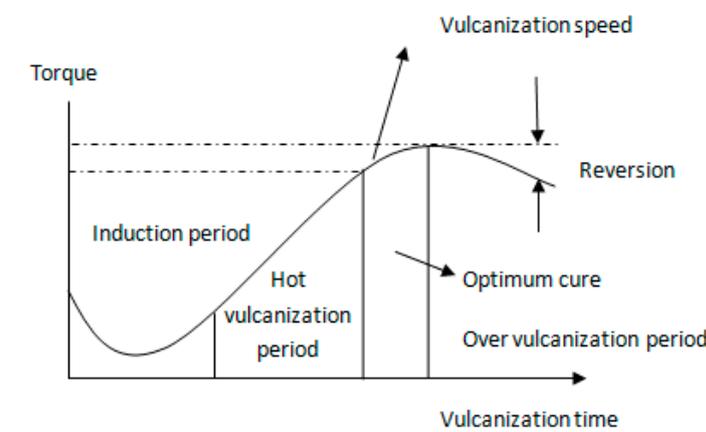
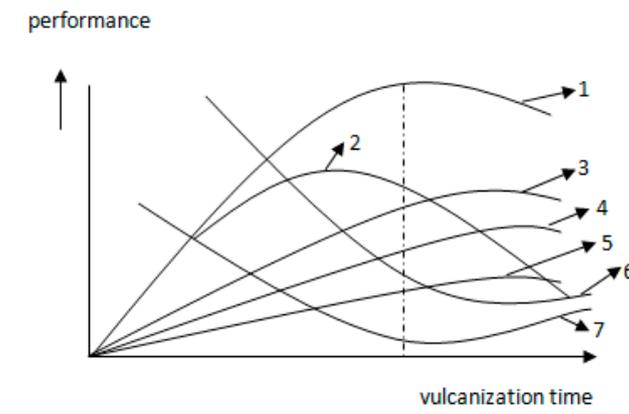


Figure 2. Vulcanization reaction process [24].

Rubber mass performance for different times of vulcanization reaction process was different as shown in Figure 3; tensile strength, tear strength, resilience, hardness, 300% stretching strength,

elongation and permanent deformation of rubber mass changed with the vulcanization time increase. There was also an optimum vulcanization time by considering the performance above.



**Figure 3.** Rubber mass performance for different times of the vulcanization reaction process [25]. 1, Tensile strength; 2, tear strength; 3, resilience; 4, hardness; 5, 300% stretching strength; 6, elongation; 7, permanent deformation.

## 2.2. Other Components' Mechanism of Action

Some other materials were beneficial to the vulcanization reaction or the improvement of the storage stability of polymer-modified bitumen, as follows.

- (1) Vulcanization accelerators [26]: Vulcanization accelerators are additives that can accelerate vulcanization reactions, cut down the vulcanizing time, reduce the vulcanizing temperature, reduce the amount of vulcanizer and improve the physical or mechanical properties of the vulcanized rubber, such as tetramethylthiuram disulfide.
- (2) Vulcanization activator: The vulcanization activator can increase the activity of accelerators, improve the vulcanizing speed and vulcanizing efficiency and improve the properties of vulcanized rubber [27–29], such as zinc oxide.
- (3) Other active ingredients that can improve one or several modified bitumen technical performances, for example, antioxidant butylated hydroxytoluene (BHT): This can improve the oxidation resistance of bitumen. Kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) can reduce the density difference between bitumen and SBS, which leads to modified bitumen to achieve stabilization [30]. In addition, there were also some reports on the same effect of carbon-white ( $\text{SiO}_2$ ) on the thermal storage stability of bitumen [31,32].

## 3. Test Design of the Stabilizer Component

### 3.1. Test Design

The corresponding tests of the component of SBS-modified bitumen stabilizer were designed based on the basic principle of the vulcanization reaction and the particularity of bitumen: sulfur, vulcanization accelerator, vulcanization activator, antioxidant and other active ingredients.

For the convenience of testing, the experimental raw material samples were labeled with English letters in lower case, and the definition was as follows: a, sulfur; b, tetramethylthiuram disulfide; c, zinc oxide; d, butylated hydroxytoluene. SBS-modified bitumen was prepared by using different Component No. stabilizers (stabilizer content was 0.1% of bitumen quality), and the 48-h segregation softening point was tested and analyzed. Then, the median of each component range was calculated. The details of the experimental design are shown in Table 1.

**Table 1.** Stabilizer component test design.

Component No.	A:B:C:D = a:b:c:d	Remarks	Component No.	A:B:C:D = a:b:c:d	Remarks
1	30:16:4:20	Determine a = the content of S	13	a:b:0:20	Determine c = the content of ZnO
2	40:16:4:20		14	a:b:3:20	
3	50:16:4:20		15	a:b:6:20	
4	60:16:4:20		16	a:b:9:20	
5	70:16:4:20		17	a:b:12:20	
6	80:16:4:20		18	a:b:15:20	
7	a:0:4:20	Determine b = the content of TMTD	19	a:b:c:0	Determine d = the content of BHT
8	a:10:4:20		20	a:b:c:5	
9	a:20:4:20		21	a:b:c:15	
10	a:30:4:20		22	a:b:c:20	
11	a:40:4:20		23	a:b:c:30	
12	a:50:4:20		24	a:b:c:40	

TMTD, tetramethylthiuram disulfide; BHT, butylated hydroxytoluene.

According to the components in Table 1, firstly, Component Nos. 1–4 were tested, and the value of a (the content of S) was determined based on the test results and analysis. Secondly, Component Nos. 7–12 were tested, and the value of b (the content of TMTD) was determined based on the test results and analysis. Thirdly, Component Nos. 13–18 were tested, and the value of c (the content of ZnO) was determined based on the test results and analysis. Lastly, Component Nos. 19–20 were tested, and the value of d (the content of BHT) was determined based on the test results and analysis. a:b:c:d comprised the basic components of the stabilizer.

### 3.2. Raw Materials

Sulfur, tetramethylthiuram disulfide, zinc oxide, butylated hydroxytoluene, kaolin and carbon-white were used as raw materials, and the specific technical indicators are shown below.

- (1) Base bitumen: The 70<sup>#</sup> base bitumen used in this paper was refined by Qilu Petrochemical (Zibo, China), and the technical indicators are shown in Table 2.

**Table 2.** The 70<sup>#</sup> bitumen technical indicators.

Test	Unit	Measured Value	Test Items	Unit	Measured Value
60 °C dynamic viscosity	Pa·s	195.3	Saturate	%	16.3
15 °C ductility	cm	65.8	Aromatic	%	39.5
10 °C ductility	cm	45.1	Asphaltene	%	13.1
Softening point	°C	49.5	Resin	%	31.1
15 °C density	g/cm <sup>3</sup>	1.001	25 °C penetration	0.1 mm	65.3
RTFOT		Penetration ratio		%	64.5
		Loss of quality		%	0.6
		10 °C residue ductility		cm	8
		15 °C residue ductility		cm	18

In Table 2, “Technical Specification of Construction of Highway Asphalt Pavement (JTG F40-2004, China)” [20] and “Standard Test Methods of Bitumen and Bituminous mixtures for Highway Engineering (JTG E20-2011)” [33] were adopted as the codes for the test.

- (2) Other raw materials: Sulfur in this paper was produced from Tianjin Damao Chemical Reagent Factory (Tianjin, China) with an analytical reagent more than 99.5% purity. Tetramethylthiuram disulfide was produced by Shanghai QingXi Chemical Technology Co., Ltd. (Shanghai, China). Zinc oxide was produced by Tianjin FuChen Chemical Reagent Factory (Tianjin, China). Kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) was produced by Guangzhou YiFeng Chemical Technology Co., Ltd. (Guangzhou, China). Carbon-white was produced by the Shandong Jiquan Biological Technology Co., Ltd. (Jinan, China). The technical indicators of the raw materials above are shown in Table 3.

**Table 3.** Technical indicators of S, TMTD, BHT, ZnO, carbon-white and kaolin.

	S	TMTD	BHT	ZnO	Carbon-White	Kaolin
Molecular formula	S	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> S <sub>4</sub>	C <sub>15</sub> H <sub>24</sub> O	ZnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O
Density	2.3600 g/cm <sup>3</sup>	1.43 g/cm <sup>3</sup>	1.048 g/cm <sup>3</sup>	5.6060 g/cm <sup>3</sup>	2.2–2.6 g/cm <sup>3</sup>	2.5 g/cm <sup>3</sup>
Molecular weight	32.07 g/mol	204.14 g/mol	220.36 g/mol	81.39 g/mol	60.08 g/mol	87–88 g/mol
Characteristics	Can be dissolved in benzene, inflammable substance.	Can be dissolved in alcohol, benzene, with smell.	Can be dissolved in ethyl alcohol, benzene, ether.	White or pale yellow powder.	White powder.	White powder, can be slightly soluble in hydrochloric acid and acetic acid.

### 3.3. SBS-Modified Bitumen Preparation Process

Due to the large amount of experiments, the test error caused by the different preparation processes of modified bitumen should be avoided during the experiment. Therefore, the same modification process was adopted for the modified bitumen in different samples. The preparation process of samples of the SBS-modified bitumen is shown as follows. Firstly, put some base bitumen with SBS modifier and compatibilizer together into a container. Secondly, shear the mixture at a shear rate of 4500 r/min for 30 min at a temperature of  $175 \pm 5$  °C, and add the right amount of stabilizer during the shearing process. Lastly, keep the SBS-modified bitumen at a temperature of  $175 \pm 5$  °C for 3 h and keep stirring constantly after shearing is completed.

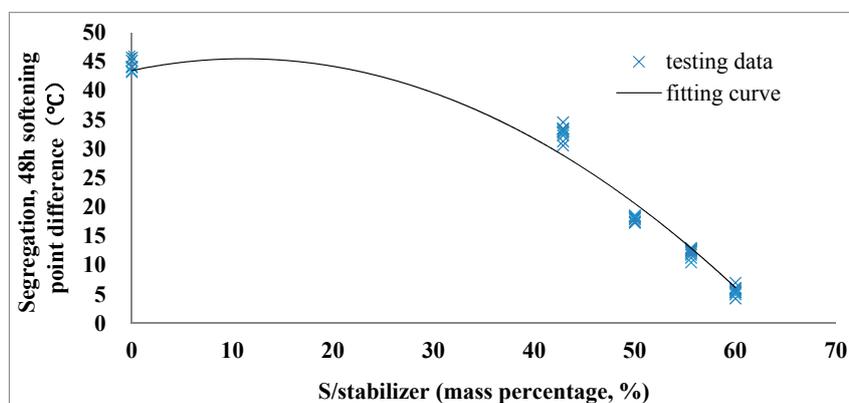
## 4. Analysis of Test Results of the Basic Component of the Stabilizer

### 4.1. Basic Component Analysis of the Stabilizer

The basic components include S, TMTD, ZnO and BHT. The basic component analysis of the stabilizer is described as below.

#### 4.1.1. The S Content of Basic Components

The SBS samples with different contents of S were prepared based on the aforementioned procedure and used in the 48-h segregation softening point test (a measured quantity of polymer-modified bitumen in a sealed aluminum tube was conditioned in a vertical position for 48 h at a temperature of  $163 \pm 5$  °C. At the end of the conditioning period, the top and bottom portions were separated and subjected to further testing to determine the degree of separation. The softening point was the test used for this purpose in this article.). Component Nos. 1, 2, 3, 4 did not show the gelation phenomenon; Component Number 5 showed an obvious gelation phenomenon after shearing for 20 min; component number 6 showed a serious gelation phenomenon after shearing for 10 min. The test results are shown in Figure 4 below.

**Figure 4.** The 48-h segregation softening point with different S content.

As shown in Figure 4, the 48-h segregation softening points' difference of modified bitumen decreases gradually with the increasing content of S compared to lower content of S. With the further increase of the content of S, the gelation phenomenon occurs in the bitumen modification process. The higher the content of S is, the earlier the gelation phenomenon occurs and the more serious the gelation phenomenon. This phenomenon can be explained by the vulcanization reaction process shown in Figure 2. It can be called over vulcanization or a high degree of vulcanization. With respect to the comprehensive test phenomenon, test results and economic factors, the content of S in Component No. 4 was the optimum content, which determines  $a = 60$ .

#### 4.1.2. The TMTD Content of Basic Components

The SBS samples with different contents of TMTD were prepared based on the aforementioned procedure and used in the 48-h segregation softening point test. Component Nos. 7, 8, 9 and 10 did not show the gelation phenomenon; Component Number 11 showed the gelation phenomenon; and component number 12 showed an obvious gelation phenomenon. The test results are shown in Figure 5.

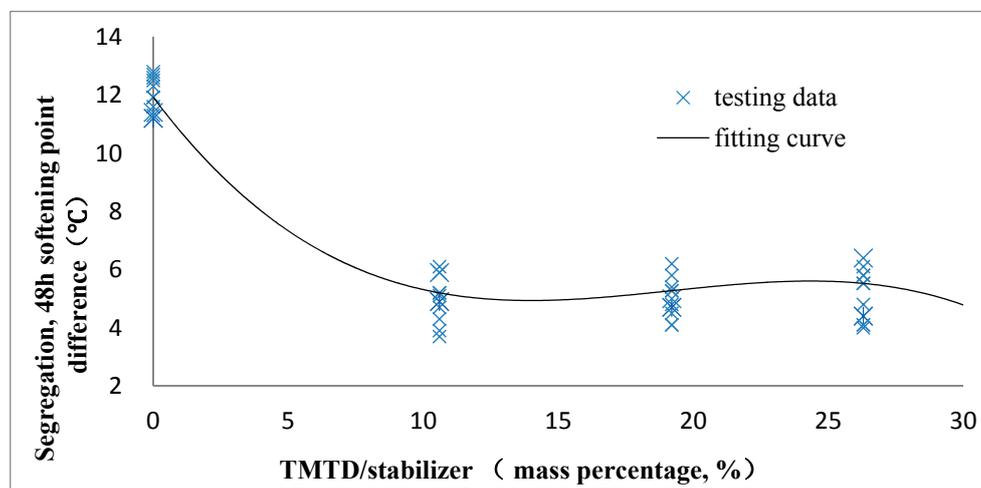


Figure 5. The 48-h segregation softening point with different TMTD content.

As can be seen from Figure 5, the 48-h segregation softening points' difference of the modified bitumen constantly decreased with the increasing content of TMTD. Due to the certain cross-linking effect that TMTD itself has, the gelation phenomenon appeared during the modification while the TMTD content continued increased: the higher the content was, the earlier the gelation phenomenon occurred and the more serious the degree of gelation was. The reason was that TMTD can be used as a vulcanizing agent, which can provide 13% self-quality as S, and the higher the TMTD content is, the deeper the vulcanization reaction degree is. In the content range of no cross-linking occurring, TMTD had a bit of improvement on the segregation softening point difference when the content was more than 15%. Considering the test phenomenon, test results and economic factors, it was determined that  $b = 16$ .

#### 4.1.3. The ZnO Content of Basic Components

The SBS samples with different contents of ZnO were prepared based on the aforementioned procedure and used in the 48-h segregation softening point test. There was no gelation phenomenon in Component Numbers 13, 14, 15, 16, 17 and 18, and the test results are shown in Figure 6.

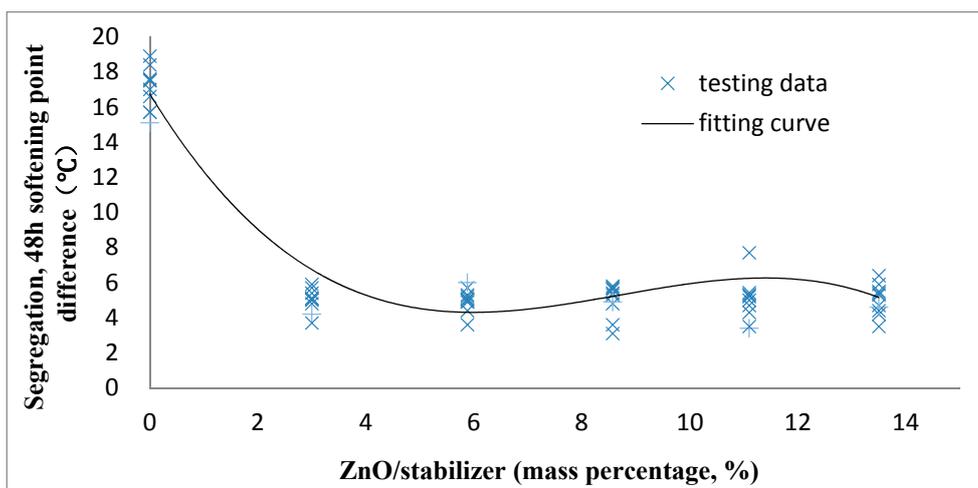


Figure 6. The 48-h segregation softening point difference with different ZnO content.

As can be seen from Figure 6, the 48-h segregation softening points' difference of modified bitumen decrease with the increasing content of ZnO. This can be ascribed to the activity of ZnO. However, with the continued increase of ZnO content, its activity was almost unchanged due to the effect of S and TMTD content. The reason was that with the incorporation of ZnO, the quantity of crosslinking agent in SBS-modified bitumen will increase, and TMTD will self-methyl decompose, which can promote cross-linking between macromolecules. The above phenomena can enhance the efficiency of the vulcanization reaction. Considering the test phenomenon, test results and economic factors, it was determined that  $c = 4$ .

#### 4.1.4. The BHT Content of Basic Components

According to the test design above, SBS was prepared. The content of BHT was different in each Component No. There was no gelation phenomenon observed in Component Nos. 19, 20, 21, 22, 23 and 24, and the 48-h segregation softening point test and Rolling Thin Film Oven Test (RTFOT) were carried out. The results are shown in Figure 7 and Table 4.

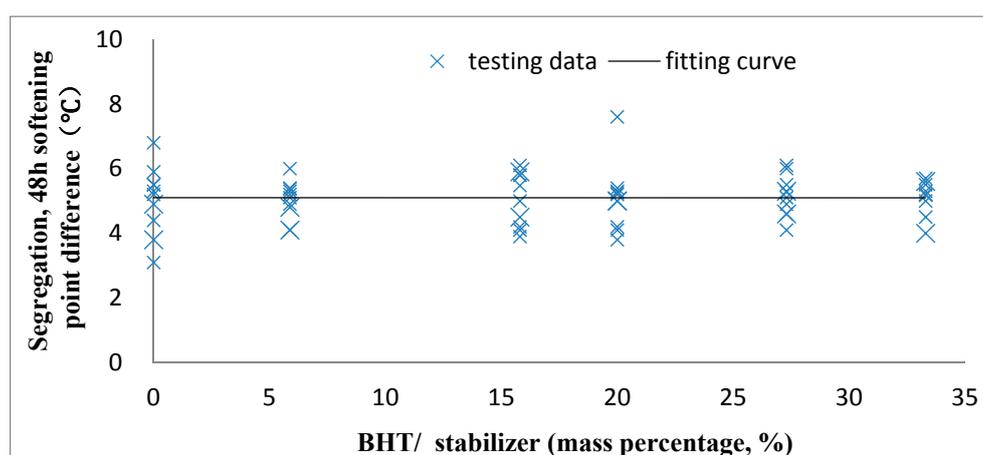


Figure 7. The 48-h segregation softening point difference with different BHT content.

As can be seen from Figure 7, with the increase of BHT content, the 48-h segregation softening point difference of modified bitumen was almost unchanged, which shows that BHT has little effect on the thermal storage stability of bitumen. However, BHT being an antioxidant, its ability of oxidation

resistance may be useful to bitumen. Table 4 shows the anti-aging performance of SBS-modified bitumen with different BTH content.

**Table 4.** The anti-aging performance of SBS-modified bitumen with different BTH content.

Component No.	RTFOT		
	Loss on Heating (%)	Penetration Ratio (%)	Residue Ductility at 5 °C (cm)
19	0.38	69.3	16.6
20	0.30	72.5	17.7
21	0.21	75.7	19.4
22	0.14	78.3	20.5
23	0.13	78.2	20.3
24	0.13	78.5	20.4

RTFOT, Rolling Thin Film Oven Test.

Table 4 shows that with the increase of BHT content, the loss on heating of SBS-modified bitumen after the rolling thin film oven test gradually decreased, the percent of residual penetration increased and the residual ductility at 5 °C slightly increased. However, the performance improvement effect was no longer obvious after the content of BHT was greater than 20%. BHT can provide H to the free radical of SBS-modified bitumen. The resistance to oxidation of SBS-modified bitumen will be increased in this way. This can also be explained by means of Chemical Reactions 1 and 2 [25] below.



In this reaction AH is the antioxidant, R· the free radical, A· the antioxidant free radicals and RH the polymer molecules

It can also be explained by means of Chemical Reaction 2 below.



In this reaction AH is the antioxidant, ROO· the free radical peroxidation, A· the antioxidant free radicals and ROOH the hydroperoxide.

Considering the test phenomenon, test results and economic factors, it was determined that  $d = 20$ .

From this, we can determine that the basic components of the stabilizer powder were S:TMTD:ZnO:BHT = 60:16:4:20.

#### 4.2. Analysis of Stabilizer Content in Bitumen

In order to explore the reasonable content of stabilizer powder in SBS-modified bitumen, SBS-modified bitumen was prepared respectively with the stabilizer contents of 0%, 0.05%, 0.1%, 0.15%, 0.2%, 0.25%, 0.3% (percentage by mass of modified bitumen, and S:TMTD:ZnO:BHT = 60:16:4:20). Gelation did not occur. When the content of the stabilizers was less than 2%, slight gelation occurred at a content of 0.2%, significant gelation at a content of 0.25% and serious gelation at a content of 0.3%. The test results re shown in Table 5 and Figure 8.

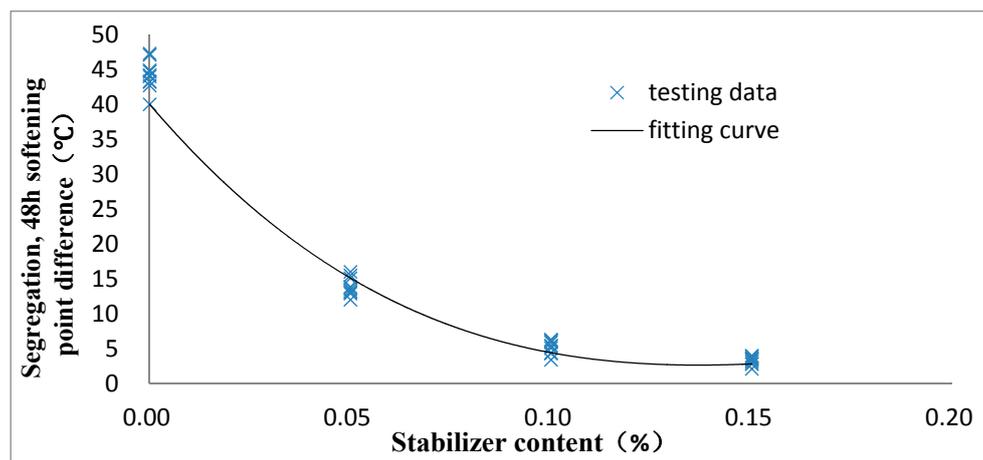
In Table 5, “Technical Specification of Construction of Highway Asphalt Pavement (JTG F40-2004, China)” [20] and “Standard Test Methods of Bitumen and Bituminous mixtures for Highway Engineering (JTG E20-2011)” [33] were the referenced standards.

It can be seen from the test results shown in Table 5 that with the stabilizers’ constant increase, the anti-aging properties of SBS-modified bitumen were continuously improved, the penetration of SBS modified bitumen decreased, the penetration index remained unchanged, the softening point continuously increased, Brookfield viscosity at 135 °C increased, the solubility slightly reduced (this may be related to the insolubles in the stabilizer) and elastic recovery no longer changed. When the

content of stabilizer exceeds 0.2% (including 0.2%), the gelation phenomenon of bitumen occurs. With the content increasing, the gelation phenomenon becomes more and more serious.

**Table 5.** The performance of modified bitumen with different stabilizer content.

Content, %	RTFOT			Penetration, 0.1 mm, 25 °C	Penetration Index PI
	Loss on Heating, %	Penetration Percentage, %	Residue Ductility at 5 °C		
0	1.1	62.6	11.3	64.6	0.2
0.05	0.41	74.3	16.1	62.3	0.2
0.1	0.15	78.3	20.5	58.5	0.1
0.15	0.08	79.2	21.0	55.3	0.1
>0.2	Gelation occurs				
Content, %	Ductility at 5 °C, cm	Softening Point °C	Brookfield viscosity at 135 °C, Pa·S	Solubility, %	Resilient at 25 °C, %
0	27.7	65.5	1.621	99.5	86.5
0.05	28.3	70.1	1.827	99.5	85.6
0.1	28.4	75.2	1.911	99.4	88.4
0.15	29.6	78.4	1.972	99.3	87.7
>0.2	Gelation occurs				



**Figure 8.** The relationship between stabilizer content and the 48-h segregation softening point difference of SBS-modified bitumen.

Figure 8 shows that the 48-h segregation softening points' difference of modified bitumen decreased with the increasing content of stabilizer content. However, even when the stabilizer content reached 0.15%, the 48-h segregation softening points' difference was no lower than 2 °C. From the analysis of the segregation softening point data and the performance of SBS-modified bitumen, the best content of the basic components of the stabilizer was 0.15%. If the content of S were taken as the reference, the optimum content of the stabilizer (expressed as the mass percentage of S content) was 0.09%.

### 5. Optimization Design of the Stabilizer Component

In this paper, kaolin ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ) and carbon-white ( $SiO_2$ ) were selected as auxiliary components to improve the performance of the stabilizer, and the design component test is shown in Table 6 below.

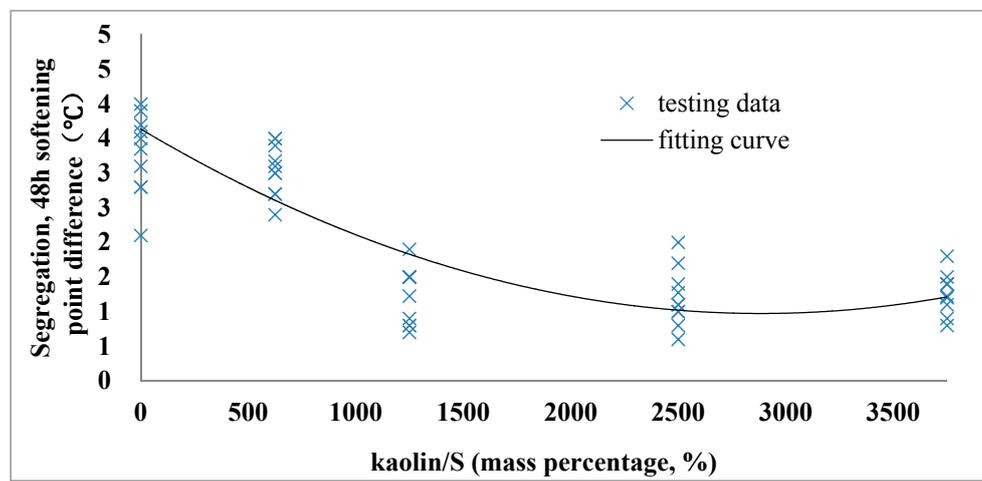
**Table 6.** The composition with kaolin or carbon-white stabilizer.

Component No.	S:TMTD:ZnO:BHT: Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O	Component No.	S:TMTD:ZnO:BHT:SiO <sub>2</sub>
25	60:16:4:20:500	29	60:16:4:20:500
26	60:16:4:20:1000	30	60:16:4:20:1000
27	60:16:4:20:2000	31	60:16:4:20:2000
28	60:16:4:20:3000	32	60:16:4:20:3000

According to the above components, the different stabilizers prepared, the amount of stabilizer (in terms of the amount of S bitumen percentage) being 0.09% control stabilizer content, prepared SBS-modified bitumen and relevant tests according to the research need to be selected.

### 5.1. Kaolin Content

SBS-modified bitumen was prepared according to the test design, and the content of stabilizer (expressed as S content) was 0.09%. No gelation phenomenon occurred in the preparation process, and the 48-h segregation softening point difference was analyzed as Figure 9 shows.



**Figure 9.** The relationship between kaolin content and the 48-h segregation softening point difference of SBS-modified bitumen.

As can be seen from Figure 9, with the increase of kaolin content, the 48-h segregation softening point difference of SBS-modified bitumen gradually decreases. When the content of kaolin (relative to S) reaches 1250%, the modified bitumen has almost reached the smallest of the 48-h segregation softening point difference; with the kaolin content continuing to increase, the 48-h segregation softening point difference seems to no longer decrease. The reason was that kaolin can reduce the density difference between bitumen and SBS, which leads to the modified bitumen achieving stabilization. Considering the result of the 48-h segregation softening point difference test, it was determined that the proper content of kaolin (relative to S) was 1250%.

It can be seen from Table 7 above that the incorporation of kaolin has a certain degree of enhancement on the softening point, the Brookfield viscosity at 135 °C and the penetration percentage after RTFOT, but the enhancement was not significant in the range of the test content. With the kaolin content increase, the ductility decreases slightly after RTFOT, and the ductility at 5 °C decreases obviously. From the viewpoint of low temperature and anti-aging performance, the content of kaolin should be controlled.

**Table 7.** Performance of SBS-modified bitumen with different kaolin content.

Component No.	RTFOT			Penetration, 0.1 mm, 25 °C	Penetration Index PI
	Loss on Heating, %	Penetration Percentage, %	Residue Ductility at 5 °C		
4	0.08	79.2	21.0	55.3	0.1
25	0.11	77.2	18.9	54.4	0.1
26	0.11	77.9	18.8	54.3	0.1
27	0.11	78.5	18.4	54.5	0.1
28	0.10	78.7	17.5	54.1	0.1

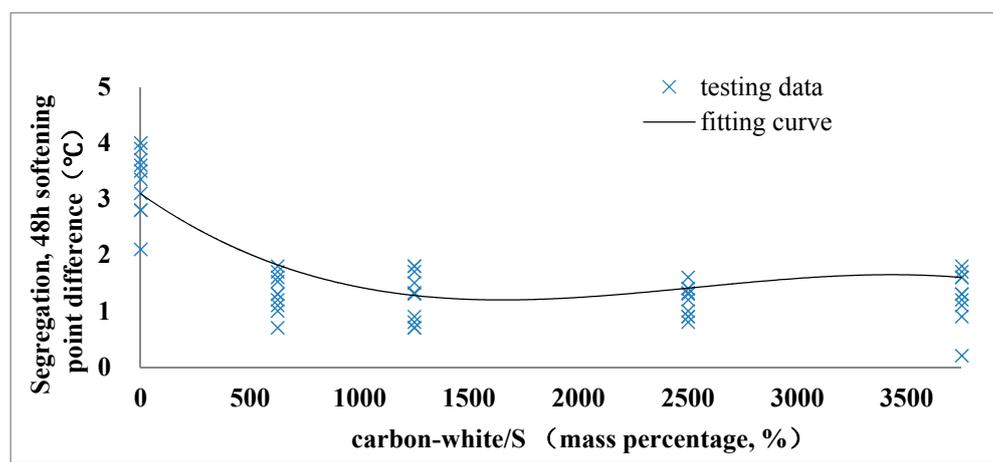
  

Component No.	Ductility at 5 °C, cm	Softening Point °C	Brookfield viscosity at 135 °C, Pa·S	Solubility, %	Resilient at 25 °C, %
4	29.6	78.4	1.972	99.3	87.7
25	29.5	79.7	1.984	99.4	87.4
26	28.7	80.5	2.046	99.3	86.7
27	27.8	81.5	2.107	99.2	87.3
28	26.6	81.3	2.157	98.9	86.4

“Technical Specification of Construction of Highway Asphalt Pavement (JTG F40-2004, China)” [20] regulates that the 48-h segregation softening point difference should be no more than 2 °C; according to the testing data, when the content of kaolin is up to 1250%, the 48-h segregation softening point difference of SBS-modified bitumen was less than 2 °C, and considering the test phenomenon, test results and economic factors, it was determined that the proper content of kaolin (relative to S) was 1250%.

### 5.2. Carbon-White Content

SBS bitumen was prepared according to the experimental design above, and the content of the stabilizer was 0.09% (expressed as S content). No gelation phenomenon occurred during the preparation process, and the 48-h segregation softening point difference test was carried out. The test results are shown in Figure 10.



**Figure 10.** The relationship between carbon-white content and 48-h segregation softening point difference of SBS-modified bitumen.

As can be seen from Figure 10, the 48-h segregation softening point difference of SBS-modified bitumen decreased about 2 °C with the incorporation of carbon-white, but there was no significant difference after the content of carbon-white exceeded 625%, so from the perspective of improving the thermal storage stability of bitumen, the content of carbon-white (relative to S) was 625%.

Table 8 shows the performance of SBS-modified bitumen with different carbon-white content.

**Table 8.** Performance of SBS-modified bitumen with different carbon-white content.

Component No.	RTFOT			Penetration, 0.1 mm, 25 °C	Penetration Index PI
	Loss on Heating, %	Penetration Percentage, %	Residue Ductility at 5 °C		
4	0.08	79.2	21.0	55.3	0.1
29	0.10	77.2	19.7	55.0	0.1
30	0.09	78.3	19.5	54.4	0.1
31	0.12	78.5	18.7	54.2	0.1
32	0.09	79.4	18.2	53.6	0.1

Component No.	Ductility at 5 °C, cm	Softening Point °C	Brookfield viscosity at 135 °C, Pa·S	Solubility, %	Resilient at 25 °C, %
4	29.6	78.3	1.973	99.3	87.7
29	29.0	79.1	1.983	99.1	87.5
30	28.2	79.3	1.990	99.1	87.2
31	27.5	79.8	1.936	99.1	87.4
32	26.3	80.2	1.998	98.8	87.3

As can be seen from Table 8 above, the incorporation of carbon-white improves the softening point, the Brookfield viscosity at 135 °C and the penetration percentage after RTFOT. However, the enhancement was not significant in the experimental range; the improvement of the modified bitumen properties above was limited; with the increase of carbon-white content, the ductility after RTFOT decreased slightly; and the ductility at 5 °C decreases obviously. From the perspective of low temperature performance, the carbon-white content should be controlled.

“Technical Specification of Construction of Highway Asphalt Pavement (JTG F40-2004, China)” regulates that the 48-h segregation softening point difference should be no more than 2 °C; according to the testing data, when the content of carbon-white was up to 625%, the 48-h segregation softening point difference of SBS-modified bitumen was less than 2 °C. Based on the economic factors and the technical performance of SBS-modified bitumen, especially the response to heat storage stability, it was suggested that the proper content of carbon-white (relative to S) be 625%.

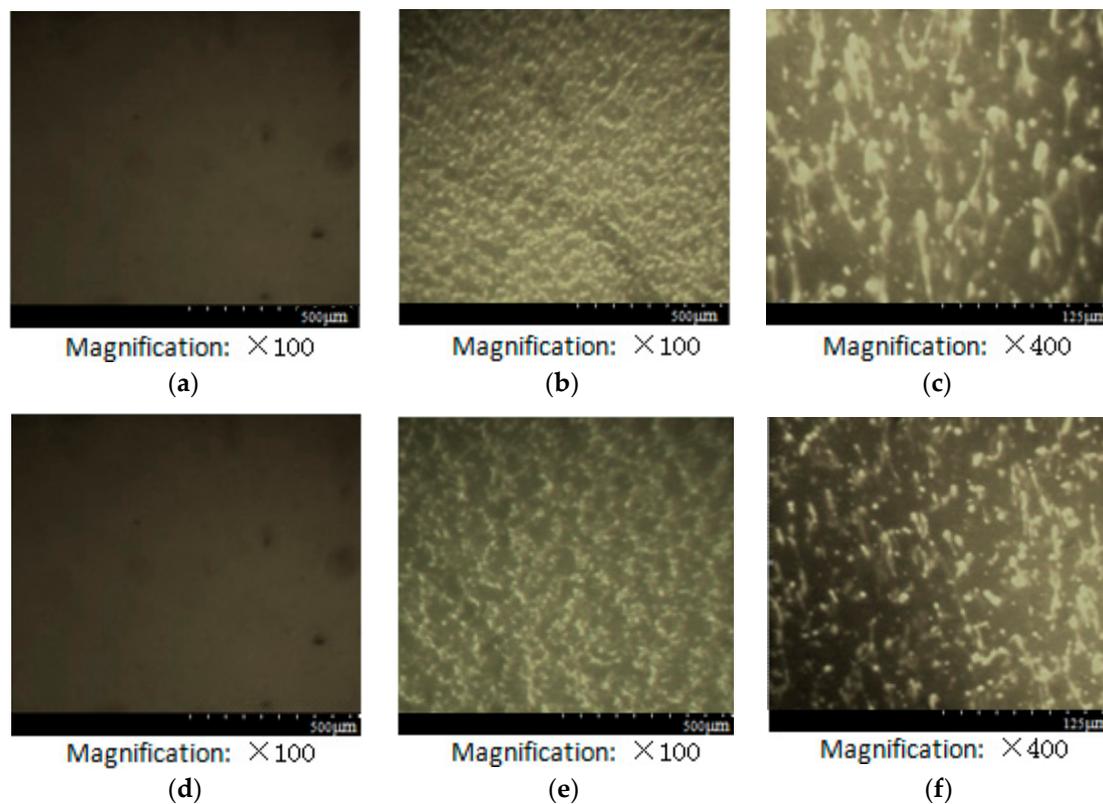
In conclusion, the components of SBS-modified bitumen stabilizer powder were S:TMTD:ZnO:BHT: Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O = 60:16:4:20:1250 or S:TMTD:ZnO:BHT:SiO<sub>2</sub> = 60:16:4:20:625, and SBS-modified bitumen has good performance, especially for the thermal storage stability.

## 6. Microcosmic Test

A fluorescence microscope was used in this paper to observe the SBS bitumen from a microcosmic view after vulcanization reaction. The principle of the fluorescence microscope is described as follows. Fluorescence will occur in a short period of time after materials are excited. Most of the polymer materials can emit fluorescence light directly after high energy luminescent beam irradiation, and a red shift interval will occur between the high energy luminescent beam and fluorescence after excitation, then the wavelength of fluorescence will become longer as visible light. Bitumen cannot produce fluorescence in the blue light region, while the yellow-green fluorescence comes from SBS. The fluorescence microscope worked on the principle above.

Before the fluorescence microscope test, SBS-modified bitumen was prepared respectively with different stabilizers (S:TMTD:ZnO:BHT: Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O = 60:16:4:20:1250, S:TMTD:ZnO:BHT:SiO<sub>2</sub> = 60:16:4:20:625), and the stabilizer contents were both 0.09% (bitumen mass percentage, expressed as S content), while SBS content was 4% (bitumen mass percentage). SBS bitumen was put into the oven at a temperature of 163 °C for 48 h, sampling the upper 1/3 and the lower 1/3, respectively. Then, different SBS-modified bitumen was dropped on the glass, respectively, and the cover glass was pushed from one side to another lightly without air bubbles. The glass with bitumen was put under

the fluorescence microscope, and it was observed with a 100 and a 400 amplified factor, as shown in the Figure 11.



**Figure 11.** Fluorescence microscope test (stabilizer was S:TMTD:ZnO:BHT:Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O = 60:16:4:20:1250). (a) Base bitumen; (b) top portions (SBS bitumen); (c) top portions (SBS bitumen); (d) base bitumen; (e) bottom portions (SBS bitumen); (f) bottom portions (SBS bitumen).

In Figure 11, black represents bitumen, while white represents SBS. SBS in modified bitumen of the upper 1/3 was almost as much as the lower 1/3, which can be seen from Figure 11b,e. It shows that the stabilizer plays a good role in preventing SBS segregation. SBS was cross-linked, as shown in Figure 11c or Figure 11f, which was caused by the vulcanization reaction. The degree of vulcanization in SBS-modified bitumen was almost the same in the upper 1/3 and the lower 1/3. The same phenomenon occurred when using the stabilizer S:TMTD:ZnO:BHT:Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O = 60:16:4:20:1250.

According to the phenomenon that the stabilizer developed based on the vulcanization reaction in this research can allow SBS to be cross-linked, it especially has the effect of preventing SBS segregation.

## 7. Conclusions

In this paper, S, TMTD, ZnO, BHT, Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O and SiO<sub>2</sub> were used as raw materials to obtain SBS-modified bitumen stabilizer powder. The following conclusions can be drawn on the basis of the results and analysis.

- (1) The vulcanization reaction was the main mechanism by which stabilizers improved the thermal storage stability of SBS-modified bitumen. Sulfur, vulcanization accelerator, vulcanization activator, antioxidant, other active ingredients was the basic design idea, and the basic components of the stabilizer were S:TMTD:ZnO:BHT = 60:16:4:20. The presence of the basic components of the stabilizer improves the storage stability and aging resistance of SBS-modified bitumen significantly. It can also improve the softening point and viscosity and reduce the penetration.

- (2)  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SiO}_2$  can further improve the storage stability of SBS-modified bitumen significantly. However, they also reduce the low temperature property at the same time. The proper formula of SBS-modified bitumen stabilizer was S:TMTD:ZnO:BHT: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  = 60:16:4:20:1250 or S:TMTD:ZnO:BHT: $\text{SiO}_2$  = 60:16:4:20:625; the optimum content was 0.9% (bitumen mass percentage, expressed as S content).
- (3) The stabilizers developed in this paper were a dry powder, which can be directly put into bitumen easily, and the performance of SBS-modified bitumen with these stabilizers can meet the requirement of “Technical Specification of Construction of Highway Asphalt Pavement” (JTG F40-2004, China) [20].

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**Author Contributions:** W.Z. conceived of and designed the experiments. L.D. performed the experiments. W.Z. analyzed the data. Z.J. contributed reagents/materials/analysis tools. W.Z. wrote the paper.

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