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Comparative Study on the Stability of SBS Modified Asphalt with M Resin Replacing Sulfur

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Abstract: In order to compare the difference between M resin and sulfur modified asphalt stabilizer, two stabilizers were prepared according to the mass ratio of sulfur is 75%, tetramethylthiuram disulfide is 20%, and zinc oxide is 5%. The resin is equivalently incorporated in such a way that the sulfur mass remains unchanged. The softening point, penetration, 5 ℃ ductility, and 48-hour softening point difference index of the modified asphalt were measured in five cases: 0%, 0.05%, 0.10%, 0.15%, and 0.2%. The change law of each index, and the physical dispersion state of SBS modified asphalt was compared by fluorescence microscope. The test results show that with the increase of the amount of the two stabilizers, the softening point of the modified asphalt increases, the penetration degree decreases, the softening point difference at 48 hours decreases, and the ductility at 5 ℃ increases first and then decreases; M resin-based stabilizers and The optimal blending amount of sulfur-based stabilizers is 0.15%; under the optimal blending amount, compared with sulfur-based stabilizers, the M resin base has a reduced softening point of modified asphalt of 0.6 ℃ and an increase in penetration index of 2.2 (0.1 mm), the ductility at 5 ℃ is reduced by 0.7 cm, and the softening point difference at 48h is increased by 1.4 ℃. The sulfur-based stabilizer is slightly better than the M resin-based stabilizer, but the difference is not large. Microscopic analysis also proves the effectiveness of the two stabilizers. It is feasible that M resin replaces sulfur to prepare modified asphalt stabilizer.

Key words: M resin; sulfur; SBS modified asphalt; stabilizer; thermal storage stability

1. INTRODUCTION

M resin is a by-product produced during the preparation of rubber accelerator M by a high-pressure method. M resin is yellow viscous at normal temperature, has no fluidity, and is a hazardous solid waste containing sulfur.

M resin is difficult to handle. Liu Anhua et al. Used M resin, phenol, and formaldehyde as raw materials to copolymerize them into thermoplastic resins[1]; Yin Zhigang et al. Mixed M resin with sulfur through high temperature and high pressure to generate accelerator M[2]. Limited by processing cost and technology, M resin is often simply burned, which emits harmful gases such as sulfur dioxide, nitrogen oxides, and hydrogen sulfide, causing air pollution.

Modified asphalt is obtained by adding a certain amount of modifiers such as ethylene-butadiene-styrene block copolymer (SBS) to the matrix asphalt, and its road performance is significantly improved than the matrix asphalt. However, SBS has poor compatibility with matrix asphalt and cannot be stably dispersed. To this end, it is necessary to incorporate sulfur-containing stabilizers to improve thermal storage stability[3-4]. Due to the high sulfur content of M resin, the total content of elemental sulfur and compound sulfur is about 20% -38%. Therefore, an attempt was made to replace the M resin equivalently with sulfur to prepare a stabilizer. By comparing with the traditional stabili zer, the stability of the resin Effect, to explore new ways of using M resin waste.

2.MATERIALS

The A-grade 70 # Qilu road petroleum asphalt was selected in this experiment. The basic indicators are shown in Table 1. In the test, SBS with a star and linear ratio of 1: 1 was used as the modifier. The materials used in the test met the requirements of JTGF40-2004 "Technical Specifications for Highway Asphalt Pavements".

Table 1 Asphalt technical index test results

Test items	unit	results	requirements	method
Penetration 25 ℃	0.1mm	69	60～80	T0604-2011
Penetration Index PI	一一	-1.1	-1.5～+1.0	T0604-2011
Softening Point	℃	48.6	≥46	T0606-2011
Ductility 10 ℃, 5cm / min	cm	40	≥20	T0605-2011
Ductility 5 ℃, 5cm / min	cm	＞150	≥100	T0605-2011
density	g/cm3	1.033	实测值	T0603-2011
60 ℃ dynamic viscosity	Pa•S	218	≥180	T0620-2011
Flash point	℃	296	≥260	T0611-2011
Wax content	%	1.6	≤2.2	T0615-2011
Solubility	%	99.94	≥99	T0607-2011
Film oven quality change	%	-0.07	≯±0.8	T0609-2011

The M resin (A) selected for the test was provided by Shandong Shangshun Chemical Co., Ltd. as a vulcanizing cross-linking agent in the stabilizer; the sulfur used in the test comparison was produced by Tianjin Damao Chemical Reagent Factory with a purity higher than 99.5%; Shanghai Dibo Tetramethylthiuram disulfide (B) produced by Chemical Technology Co., Ltd. is used as a vulcanization crosslinking accelerator; zinc oxide (C) produced by Yantai Shuangshuang Chemical Co., Ltd. is used as a vulcanization crosslinking active agent. Among them, Shandong Shangshun Chemical Co., Ltd. commissioned Shanghai Microspectrum Technology Co., Ltd. to perform in-depth micro spectral analysis on the mixture M resin. The microspectral analysis test results are shown in Table 2[5].

Table 2 M resin microspectrum depth analysis results

Composition	Mass fraction%	Composition	Mass fraction%
water	7.68	Thioisocyanate	0.03
sulfur	18.79	Methylphenyl disulfide	0.89
Thiophenol	0.61	2-acetylbenzothiazole	0.21
Benzothiazole	35.55	2-aminobenzenethiol	0.03
aniline	3.51	4-methyl-5- (5-methyl-1H-pyrazol-3-yl) -1H- 1,2,3-triazole	0.07
2-methylbenzothiazole	0.80	Metronidazole	0.05
2-mercaptobenzothiazole	5.08	2,2'-bibenzothiazole	0.83
O-Toluene isothiocyanate	0.05	Triphenylguanidine	0.53
2-methylthiobenzothiazole	1.78	2- [3- (2-thienyl) phenyl] thiophene	1.38
2-hydroxybenzothiazole	0.15	2- (4-aminophenyl) -6-methylbenzothiazole	0.04
Diphenylamine	0.58	Biphenylurea	0.14
3-methyl-2 (3H) -benzothiazolthione	1.27	10-methylphenothiazine	0.09
Phenothiazine	1.04	Quinoline-8-thioamide	0.32
N-phenyl-1,3-benzothiazol-2-amine	17.23	Diphenyl disulfide	0.02
1-methyl-2-phenylbenzimidazole	0.05	Sodium sulfate	1.20

3. EXPERIMENTAL METHOD

3.1 Preparation of SBS modified asphalt

The process is as follows: (1) heating the matrix asphalt to 180 ℃ and maintaining the temperature constant; (2) weighing 4% of the mass of the matrix asphalt SBS modifier (star type: linear type = 1: 1) and adding to Heat to the flowing matrix asphalt, and then use a high-speed shearer to shear the SBS modifier into the asphalt at a shear rate of 5000 r / min for 30 minutes; (3) modify the SBS after the shearing is completed. The asphalt was developed in an oven at 180 ° C for 2 hours, during which indirect stirring was performed and two base stabilizers were added.

3.2 Experimental design to determine the effect of stabilizers

According to the previous research, two base stabilizers were prepared according to the mixing ratio of A (M resin (calculated as sulfur) / S): B (TMTD): C (ZnO) = 15: 4: 1, and two base stabilizers were prepared. SBS modified asphalt samples with the amount of 0%, 0.05%, 0.1%, 0.15%, 0.2% (modified asphalt mass fraction), and the softening point, penetration (25 ℃), and ductility (5 ℃) And 48h softening point index.

4. TEST RESULTS AND ANALYSIS

4.1 Analysis of conventional performance index test results of modified asphalt

In this section, conventional performance indicators s uch as penetration (25 ℃, 100 g, 5 s), softening point, an d ductility at 5 ℃ are tested and analyzed for the prepare d M resin-based and sulfur-based stabilizer modified aspha lt samples. The effectiveness of the M resin and the effec ts of the amounts of the two base stabilizers on the softe ning point, penetration, and ductility at 5 ° C were analyz ed. The test results are shown in Figures 1-3.

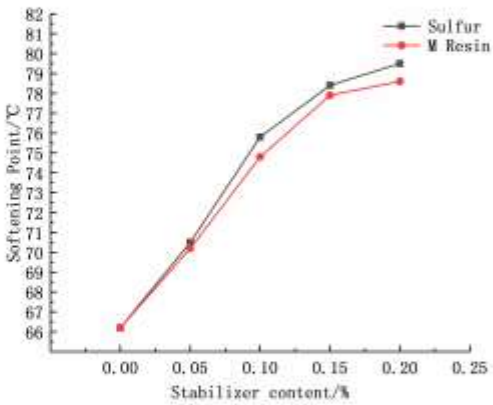

Fig.1 Softening Point Index

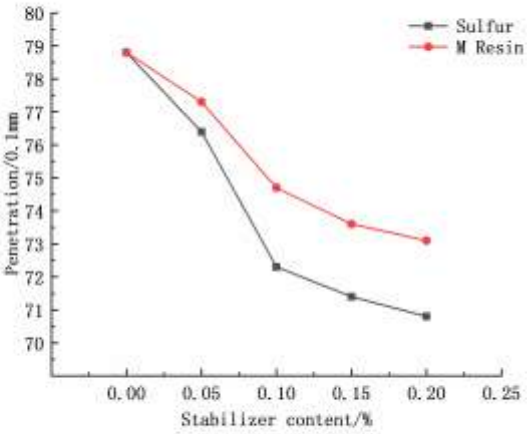

Fig.2 Penetration Index

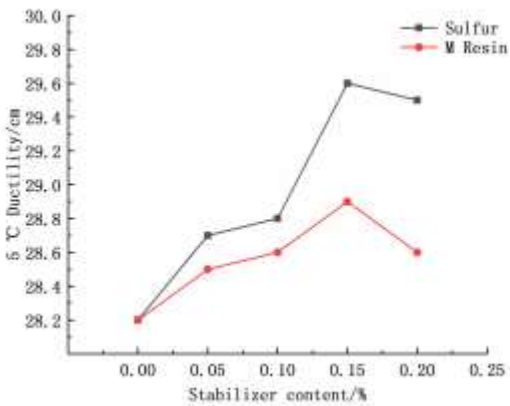

Fig.3 5℃ductility index

As shown in Figure 1, with the increase in the amou nt of M resin-based stabilizer and sulfur-based stabilizer, t he softening point shows an upward trend. Although the i ncrease range is different, it meets the requirements of reg ularity. After adding M resin-based and sulfur-based stabili zers, the softening point of the modified asphalt can reach above 70 ℃.

As shown in Figure 2, the penetration test results of modified asphalt with M resin-based and sulfur-based stabi lizers show that the penetration of modified asphalt decrea ses regularly with the increase in the amount of M resin-based stabilizer. It shows that with the addition of M resi n-based and sulfur-based stabilizers and the increase of the amount, the viscosity of the modified asphalt material co ntinues to increase. The penetration test results ranged fro m 70 to 80 (0.1 mm).

As shown in Figure 3, the ductility index at 5 ° C increases with the increase in the amount of the two base stabilizers from 0% to 0.15%. However, the modified asphalt had slight gelation and the ductility decreased when the content of the two base stabilizers reached 0.2%. The results of the ductility test ranged from 28 to 30 cm.

From the comparative analysis of Figures 1 to 3, it can be seen that when the stabilizer content is increased from 0% to 0.05%, the softening points of sulfur-based and M resin-based stabilizer-modified asphalt are increased by 4.3 ℃ and 3.9 ℃, respectively, and the penetration is reduced. 2.4 and 1.5 (0.1mm), the ductility at 5 ℃ increased by 0.5 cm and 0.3 cm respectively; when the blending amount was increased from 0.05% to 0.1%, the softening points of sulfur-based and M resin-based stabilizer modified asphalt were increased by 5.3 ℃ And 4.6 ℃, the penetration decreased by 4.1 and 2.6 (0.1mm), and the ductility at 5 ℃ increased by 0.1 cm and 0.1 cm, respectively; when the blending amount was increased from 0.1% to 0.15%, the sulfur and M resin-based stabilizers The softening point of modified asphalt was increased by 2.6 ℃ and 3.1 ℃, the penetration was decreased by 0.9 and 1.1 (0.1mm), and the ductility at 5 ℃ was increased by 0.8 cm and 0.3 cm, respectively. The reason for the analysis is that the addition of sulfur-based and M resin-based stabilizers improves the high-temperature performance of modified asphalt, and the softening point and viscosity value are gradually increased, but excessive stabilizers are not conducive to the stable diffusion of stabilizers in the asphalt and asphalt colloids. The structure is transformed into a gel type, which impairs its construction pumping ability. When the stabilizer content is too high, the low temperature crack resistance of asphalt is damaged to a certain extent. On the other hand, the plasticity and strength of the material are two relative indicators. When a higher amount of stabilizer is added to the blending system to increase the strength, the ductility value will decrease to a certain extent. Sulfur-based stabilizers improve the high-temperature performance of modified asphalt better than M resin-based stabilizers. At the same time, the viscosity and low-temperature properties of modified asphalt are stronger than M resin-based stabilizers. M resin is a mixture in which non-sulfur components are mixed between sulfur and polymer to affectthe progress of its cross-linking and vulcanization reaction.

4.2 Analysis of test results of thermal storage stability performance index of modified asphalt

The prepared modified asphalt samples containing M resin-based and sulfur-based stabilizers were tested, and the 48h softening point difference was used as an index to evaluate the thermal storage stability of the modified asphalt. The test data are shown in Tables 3, 4 and Figure 4.

Table 3 Softening point of modified asphalt with different content of M resin-based stabilizer at 48h

M resin-based stabilizer content /%	Separation -48h softening point difference / ℃			Note
	1	2	Mean	
0	35.6	34.0	34.8	No gelation
0.05	25.8	26.8	26.3	No gelation
0.1	13.8	12.4	13.1	No gelation
0.15	6.7	5.9	6.3	No gelation
0.2	-	-	-	Slight gelation

Table 4 Softening point of modified asphalt with different content of S stabilizer at 48h

M resin-based stabilizer content /%	Separation -48h softening point difference / ℃			Note
	1	2	Mean	
0	35.6	34.0	34.8	No gelation
0.05	25.2	25.6	25.4	No gelation
0.1	11.6	12.6	12.1	No gelation
0.15	4.2	5.6	4.9	No gelation
0.2	-	-	-	Slight gelation

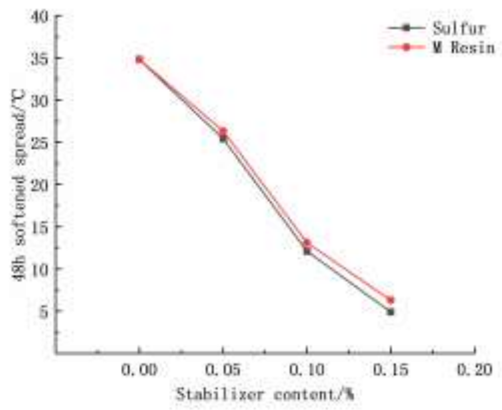

Fig.4 Index of softening spread in 48h

From the data in Tables 3 and 4, and Figure 4, it ca n be known that with the increase of the amount of M re sin-based and sulfur-based stabilizers, the softening point a t 48 hours gradually decreases, and its thermal storage sta bility is improved.

Tables 3 and 4 show that when the blending amount is from 0% to 0.05%, the 48h softening point difference o f the M resin-based stabilizer modified asphalt is reduced by 8.5 ℃, and the sulfur-based stabilizer modified bitume n is reduced by 9.4 ℃. When the blending amount is fro m 0.05% to 0.1%, the 48h softening point difference with the M resin-based stabilizer is reduced by 13.2 ° C, and t he 48h softening point difference with the sulfur-based sta bilizer is reduced by 13.3 ° C; The 48h softening point o f M resin-based stabilizer-modified asphalt was reduced by 6.8 ℃, and the 48h softening point of sulfur-based stabil izer-modified asphalt was reduced by 7.2 ℃. With the ad dition of the same amount of stabilizer, the M resin-based stabilizer reduced the softening point of modified asphalt a t 48h slightly less than the sulfur-based stabilizer, but the gap between the two was small. The reason for this is th at the sulfur content of the M resin-based stabilizer and t he sulfur-based stabilizer modified asphalt is the same, but because the M resin is a mixture, the addition of non-sul fur components may affect the sulfur modification. The di stribution in the asphalt blending system and the progress of the vulcanization reaction, the composition of the M re sin substance is more complicated. After researching the v arious components of the M resin, it was found that the mercaptobenzothiazole and sulfate can be used as vulcaniz ation accelerators It has a certain effect to promote the vu lcanization cross-linking reaction, which reduces the gap b etween the M resin-based stabilizer and the sulfur-based st abilizer on the thermal storage stability of the modified as phalt.

4.3 Evaluation of microstructure of modif ied asphalt

With the help of fluorescence microscopy, the distrib ution state of the polymer and the matrix asphalt can be observed and recorded, and the homogeneity of the polym er in the asphalt can be analyzed. The prepared modified asphalt samples without stabilizers, M resin-based stabilizer s, and sulfur-based stabilizers were photographed at a mag nification of 100 times under visible light using a fluoresc ence microscope, and the microscopic shapes are shown in Figures 5-7.

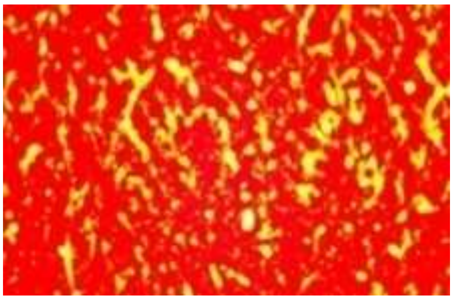

Fig.5 Microstructure of modified asphalt (without stabil izer)

Fig.6 Microstructure of modified asphalt (M resin-bas ed stabilizer)

Fig.7 Microstructure of SBS modified asphalt (with S stabilizer)

From the analysis of the fluorescence photos, it can be known that the SBS modifiers are combined and aggre gated with each other in the matrix asphalt by a high-speed shearing machine at a certain temperature. There is no significant difference in the microscope images obtained by adding M resin-based stabilizers and sulfur-based stabilizers under fluorescent irradiation. The polymer distribution is more uniform and better continuity than the microscopic images without stabilizers. . The reason is analyzed: the active ingredient in the stabilizer improves the degree of dispersion stability of SBS in asphalt.

5. CONCLUSION

（1）The addition of M resin-based stabilizer improves the softening point and thermal storage stability of the modified asphalt, reduces the penetration, increases the viscosity of the modified asphalt, and the ductility at 5 ℃ increases from 0% to 0.15%. During the change, it showed an upward trend, and the peak value was 0.15%. When the blending amount is 0.2%, the ductility index at 5 ℃ decreases, and the modified asphalt slightly gels, which reduces the pumping capacity.

（2）With the addition of the M resin-based stabilizer, SBS is uniformly distributed in the asphalt in the microstructure of the SBS modified asphalt, and the dispersion stability is improved. The SBS performance is effectively transferred to the asphalt, the modification effect is optimized, and the modified asphalt is improved. Performance.

（3）M resin has a higher sulfur content, and non-sulfur components such as mercaptobenzothiazole and sulfates can also promote the crosslinking and vulcanization reaction. According to the comparison of experimental data, M resin can replace the role of sulfur in stabilizers. Participate in the vulcanization cross-linking reaction process in modified asphalt, improve the performance of modified asphalt, and the optimal blending amount of stabilizer for M resin basic formulation is 0.15%.

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