Formulating and Performance of Quick Drying Fog Seal Material

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Abstract: A new fog seal material was formulated with asphalt rejuvenator, alcohol and co-solvent. The new material provides a quick drying performance and could be used for airport runways and elevated highways. Properties of the rejuvenator used in the fog seal materials were analyzed firstly by several instruments, and its functional groups were calculated. Then, the functional groups were used in the group-contribution method and Hansen solubility parameters theory to screen out a suitable co-solvent, which should have a better solubility in alcohol. Experimental results showed that the co-solvent *N*-Methyl-2-Pyrrolidone could greatly improve the solubility of the rejuvenator in alcohol. Ternary phase diagram was used to optimize the formula of the fog seal material. At last, the prepared material was evaluated and showed good performances of fast drying, stability and regeneration of aged asphalt.

Keywords: Fog seal, functional groups, group contribution method, ternary solubility, fast drying.

1. INTRODUCTION

Fog seal technology is an application of a specially formulated emulsion to an existing asphalt road surface. The conventional emulsions used in fog seal applications mainly contain water, emulsifying agents, and rejuvenator materials. Rejuvenator materials are often heavy byproducts of petroleum refining industry. They are always in suspension until demulsification happened when the water in the emulsion starts to evaporate. Rejuvenator materials could permeate and restore the properties of asphalt so that the flexibility and cohesiveness of binder is improved [1].

Asphalt pavement is subjected to traffic loads and ages. Oxidation is the main reasons that asphalt concrete pavement gradually fades in color from the deep black color. Besides, temperature change, rain, and friction also lead to chemical and physical changes of the asphalt binder [2]. In chemical part, resins and aromatics are gradually oxidized into heavy components in asphalt. This results in the drop of cohesiveness of the binder, and the penetration and softening point of asphalt will also be worsen. Asphalt pavement becomes fissile and brittle, and cracking and raveling of asphalt pavements happened. Rejuvenator in fog seal materials contains oils, and provides resins and aromatics components back into the asphalt binder. This will reduce the viscosity of aged asphalt and the cohesive failure of the asphalt. The flexibility of binder could also be improved. The restored asphalt will expend to some extent, and fill some small voids in the pavement. An effective rejuvenator must penetrate well into the pavement surface so that the properties of aged hardened asphalt could be well restored [3].

The conventional fog seal emulsions are formulated by water, emulsifying agents and rejuvenator. However, the operating time of fog seal emulsions for some special roads, such as airport runways and elevated highways, are not long enough for the evaporation of the water in the emulsion. Short evaporation time often leads to slippery surface and traffic accidents. Therefore, it is necessary to develop a fast drying fog seal material for these special roads [4, 5].

This work formulates and assesses a quick drying fog seal material by using alcohol as the main solvent. As the solubility of rejuvenator in alcohol is limited, a co-solvent should be developed and blended with alcohol for improving the solubility of rejuvenator. At first, the properties of the rejuvenator were analyzed, and its molecular model was simulated. Then, the molecular model was used in the group-contribution method and Hansen solubility parameters theory to screen out a suitable co-solvent. After that, ternary phase diagram was used to optimize the formula of the fog seal material. At last, the prepared new fog seal material was evaluated.

2. EXPERIMENT

2.1. Materials

The fresh asphalt was supplied by Sinopec and its properties were shown in Table **1**. The fresh asphalt was aged in a rolling thin film oven at 163℃ for 5h for obtaining aged asphalt. Rejuvenator was composed by a deasphalted oil and a heavy aromatic oil with a mass

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E-ISSN: 2409-787X/17

Table 1: Basic Properties of Raw Materials

Properties		Fresh asphalt	Aged asphalt	Deasphalted Oil	Heavy aromatic Oil
SARA/wt%	Saturate	9.33	8.39	42.73	5.78
	Aromatic	50.21	46.88	48.54	87.46
	Resin	31.6	33.84	7.41	6.12
	Asphaltene	8.86	10.92	1.32	0.64
Penetration (25°C)/mm		69.4	46.35	—	—
Softening point/°C		46.0	54.8	—	—
Ductility (15°C)/cm		>150.0	12.1	—	—
Density (25°C)/g·cm^{-3}		—	—	0.9779	0.9892
Flash point/°C		—	—	215	219

ratio of 2:1 [6]. The basic properties of the aged asphalt and rejuvenator were shown in Table **1**.

Solvents used in this work are *N*-butyl alcohol, ethyl acetate, 1, 4-dioxane, butyl acetate, dimethyl sulfoxide, *N*, *N*-dimethyl formamide, cyclohexanol, *N*, *N*-dimethylacetamide, o-cresol, *N*-methyl pyrrolidone, ethylene glycol carbonate, sulfolane, etc. All of them were analytical pure and purchased form Sinopharm Chemical Reagent.

2.2. Experimental

2.2.1. Analysis and Characterization Methods

^{13}C-NMR analyses was carried out on NMR equipment (AVANCE DMX400, BRUKER). The field strength was 400MHz; the resolution was 0.2; scan frequency was 125MHz.

IR spectra analyses was conducted on a FT-IR Spectrometer (Nicolet 6700, Thermo Fisher Scientific). The scanning wave number range was 4000-500cm^{-1}; spectrum resolution was 4cm^{-1}.

Elemental analyses (EA) was carried out on an element analyzer (Vario EL III, Elementar).

Molecular weight of the sample was test by WATERS Waters1515 (American), the solvent is THF, the test temperature was 308.15K.

Simulated distillation analyses was tested by a GC-14A gas chromatograph with a CDMC-12 work station, WH-500B simulated distillation software and gas supply system, the solvent was carbon disulfide.

2.2.2. Co-Solvent Preselected Method

The functional groups of the rejuvenator were simulated according to the above analysis results. The group-contribution method and Hansen solubility parameter were used for the selection of the co-solvent [7]. Hansen solubility parameter(δ) is divided into three forces: dispersion force (δ_d), polar force (δ_p) and hydrogen bond force (δ_h), shown in equation (1) [8, 9], and F_d, F_p, E_h are group contribution value of the three forces respectively. *Ro* is experimentally-determined radius of the solubility sphere and could be calculated by equation (2). The distance of solvent (*Ra*) could be calculated by equation (3). *RED* in equation (4) is defined as the difficult of solubility, and a value of less than 1.0 indicates high affinity.

$$\delta_d = \sum_n^i F_{di} / V; \delta_p = \left(\sum_n^i F_{pi}^2\right)^{1/2} / V; \delta_h = \left(\sum_n^i E_{hi} / V\right)^{1/2} \quad (1)$$

$$Ro = \left(4.(\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2\right)^{1/2} \quad (2)$$

$$Ra = \left(4.(\delta_{d2} - \delta_{d1})^2 \middle| (\delta_{p2} - \delta_{p1})^2 \middle| (\delta_{h2} - \delta_{h1})^2\right)^{1/2} \quad (3)$$

$$RED = Ra / Ro \quad (4)$$

δ_d; δ_p; δ_h Dispersion force; Polar force; Hydrogen bond force;

Ro Experimentally-determined radius of the solubility sphere;

Ra Distance of solvent;

RED The difficult of solubility.

2.2.3. Ternary Solubility Diagram

The test was carried out in a 250cm^3 flask. Asphalt rejuvenator and alcohol were charged into the flask with different rejuvenator to alcohol ratio. Then, the flask was placed in a thermostatic water bath. The co-solvents were addicted in the mixture. The mixture solution in the flask were stirred with a magnetic stirrer about 15min at 323.15K. The effect of co-solvents on the solubility of asphalt rejuvenator and alcohol was studied by calculating the co-solvent consumption. The ternary solubility diagram was carried out by varying the ratio of asphalt rejuvenator, alcohol and co-solvent.

2.2.4. Evaluation of the Quick Drying Fog Seal Material

Stability performance of the fog seal material was tested according to the standard of JTG/T 0656-1993. Regeneration performance was carried out according to the JTG/T 4509-1998 standard [10]. The volatility performance of various samples were tested by a self-developed method. At first, a 3g sample was mixed with 50g clean and dry limestone. Then, the mixed sample was dried at room temperature for 4h, and dissolved in carbon disulfide for 12h. After that, the carbon disulfide solution was tested by the simulation distillation. The fresh rejuvenator and co-solvent were also tested for blank comparison.

3. RESULTS AND DISCUSSION

3.1. Formulation of the Quick Drying Fog Seal Material

3.1.1. Rejuvenator Functional Groups

Figure **1** shows the ^{13}C-NMR analysis of the asphalt rejuvenator. The proportion of aromatic carbon and saturated carbon could be analyzed and calculated according a Chinese standard SH/T 0793-2007. The obtained spectrum could be separated into two regions. One region was in the range of 0ppm-45ppm, which was the characteristic region of saturates [11]. Another region of the chemical shift in the range of 120ppm-140ppm was aromatics. A shift peak around 76ppm was solvent [12]. The aromaticity (f_A) of asphalt rejuvenator was calculated and the value was 0.3067.

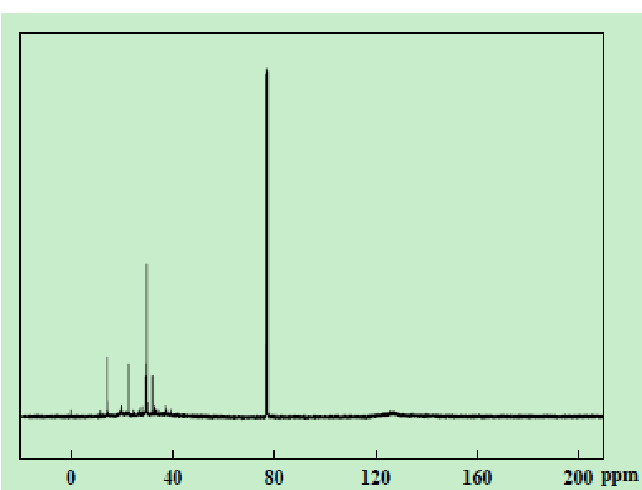

Figure 1: ^{13}C-NMR spectrum of asphalt rejuvenator.

Figure **2** shows the FTIR spectrum of the rejuvenator. Peaks ranging from 2878cm^{-1} to 2950cm^{-1} were C-H of cycloalkanes and alkanes stretching vibration absorption. The strong absorption at 1460cm^{-1} and 1402cm^{-1} were caused by the asymmetry of C-CH_3 and the symmetry of -CH_2-. It indicated that methyl and methylene exist in asphalt rejuvenator. The IR absorption at 1602cm^{-1} was attributed to stretching vibration of aromatic ring carbon, which proved the existence of aromatic compound. The absorption at 879cm^{-1} was related to the replacement of aromatic ring carbon hydrogen, indicating that hydrogen on the aromatic ring was replaced. The absorption peak at 820cm^{-1} was connected to the aldehyde group. The absorption peak at 757cm^{-1} was the vibration of the pyridine ring [13].

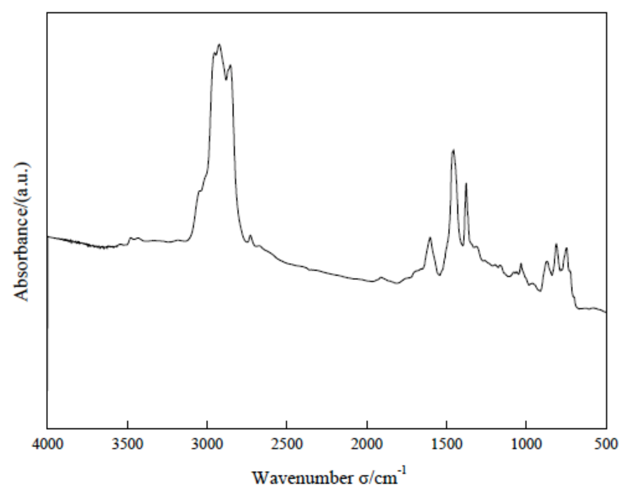

Figure 2: FTIR spectrum of asphalt rejuvenator.

Table **2** shows the element analysis and GPC analysis result of asphalt rejuvenator. The functional groups of the rejuvenator could be determined according to the element analysis, GPC analysis, ^{13}C-NMR and FTIR analysis [14, 15]. Table **3** presented the Hansen properties of functional groups of the rejuvenator. The functional groups could present some properties of rejuvenator, and be used to express the solubility of the rejuvenator. As a result, the distance of solvent (*Ra*) could be calculated which was 56.77.

Table 2: Element Data of Asphalt Rejuvenator

Properties	Mw	C, wt.%	H, wt.%	N, wt.%	S, wt.%	O, wt.%
	438	87.09	10.32	0.38	0.01	2.2

3.1.2. Selection of the Co-Solvent

The three forces parameters of the rejuvenator and some candidate co-solvents were calculated and showed in Table **3**. According to Hansen solubility parameter method, *RED* is defined as the difficult of solubility. The *RED* values of Dimethyl Sulfoxide, *N*-Methyl-2-Pyrrolidone (NMP) and sulfolane were shown in Table **4**, and indicated that the above three solvents have high affinity with the rejuvenator. Among them, 1, 4-dioxane and sulfolane could not improve the solubility of rejuvenator and alcohol obviously. *N*-Methyl-2-Pyrrolidone was selected for co-solvent of asphalt rejuvenator.

Table 3: Hansen Properties of Functional Groups

Groups	V, $cm^3 \cdot mol^{-1}$	Hansen		
		F_d	F_p	E_h
$-CH_3$	33.5	420	0	0
$-CH_2-$	16.10	270	0	0
-CH<	-1.0	80	0	0
>CH<	-19.2	-70	0	0
>C=	13.5	400	0	0
Aldehyde	22.3	470	800	4500
Phenyl	33.4	1140	110	0
-CN	24.0	430	1100	2500

Table 4: Solubility Parameters of Asphalt Rejuvenator and Preselected Co-Solvent

Properties	δ_d	δ_p	δ_h	*RED*
Rejuvenator functional groups	25.61	17.12	17.49	0
Ethyl Acetate	15.8	5.3	7.2	0.366
1,4-Dioxane	19.0	1.8	7.4	0.398
N-Butyl Acetate	15.8	3.7	6.3	0.463
Cyclohexanol	17.4	4.1	13.5	0.350
N, *N*-Dimethyl Acetamide	16.8	11.5	10.2	0.350
Dimethyl Sulfoxide	18.4	16.4	10.2	0.285
N-Methyl-2-Pyrrolidone	18	12.3	7.2	0.335
Sulfolane	20.3	18.2	10.9	0.211

3.1.3. Ternary Solubility Diagram

The ternary solubility diagram of rejuventor, alcohol and NMP was shown in Figure **3**. It contains a miscible phase region A and a 2-phase region B, and the region A was larger than B obviously. Thus NMP could be found as a good co-solvent for rejuvenator in alcohol. In the miscible region, rejuvenator could dissolve well in the solution of alcohol and NMP. The 2-phase region contains a phase rich in rejuvenator/NMP in equilibrium with an alcohol-rich phase, the rejuventor dissolved in the co-solvent and could mix with alcohol well. The mass fraction of asphalt rejuvenator should not less than 30% for regeneration performance. In order to reduce the cost of raw materials and improve the quick-dry property, the quick drying fog seal material was optimized, and it has 12 wt.% co-solvent, 30 wt.% asphalt rejuvenator and 58 wt.% alcohol.

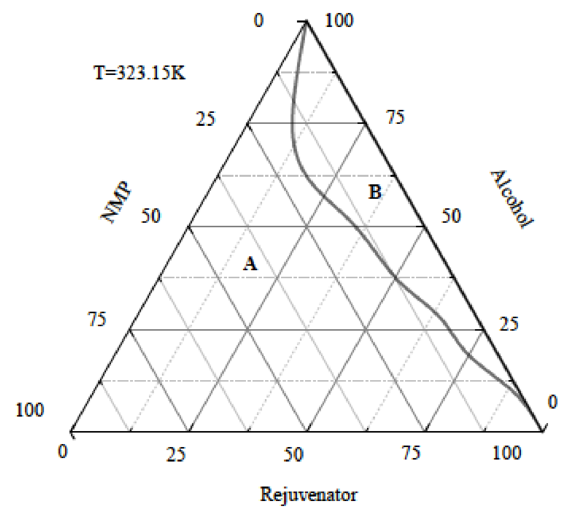

Figure 3: Schematic phase diagram of ternarymixture, A-miscible phaser, B-2-phase region.

3.2. Performance Evaluation

3.2.1. Stability

From a practical point of view, measurement of stability is one of the most important properties of the fog seal material. The standard bottle test method of asphalt emulsion was employed in the test. The stability of the material is generally related to the ease of rejuvenator separation with time. Rejuvenator solution can be rated on its stability by the amount of rejuvenator separated in a given period of time. A comparison of solid contents of the top solution and the bottom solution of the test pipe in five days was shown in Table **4**. Samples with different mass ratio of rejuvenator from 30% to 60% were compared. Results showed that the rejuvenator contents of the two solutions were very close, which means that the stability of the fog seal material could satisfy long-term storage, and performs well with different ratio of rejuvenator.

Table 5: The Stability of different Ratio of AQDFSM in 5 Days

	30%	40%	50%	60%
Top	29.3%	39.4%	49.9%	59.8%
Bottom	30.8%	40.1%	50.0%	60.2%

3.2.2. Regeneration Performance

Oil contents in rejuvenator solution could soften the existing binder, thus improving the flexibility of the binder, which reduces the likelihood of cohesive failure. If the conventional emulsions do not penetrate the surface well, they may create a slippery surface after they break. Therefore, the permeability of fog seal is a very important issue for the road application at the same time.

The prepared rejuvenator solution could penetrate well in the aged asphalt, and the penetration of the aged asphalt changed from top to bottom. The penetrations of aged asphalt, fresh asphalt and recycled asphalt were shown in Figure **4**. With permeation of the prepared rejuvenator solution along with time, penetration of asphalt recovered to be closed to fresh asphalt. It could be found in Figure **4** that the penetration of the recycled asphalt could almost recovered to the level of the value of fresh asphalt.

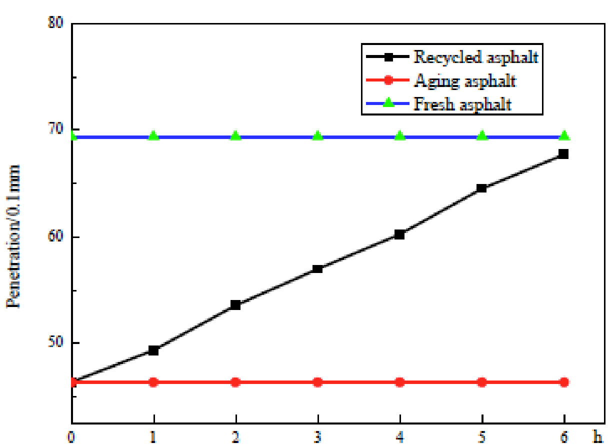

Figure 4: The changes of penetration along with generation time.

3.2.3. Volatility Performance

Figure **5** was the simulation distillations of NMP, rejuvenator and the prepared solution. The prepared solution, containing 30 wt.% rejuvenator, 58 wt.% alcohol and 12 wt.% co-solvent, was mixed with clean and dry limestone with a mass ratio of 1:20. Then, they were dried at room temperature for 4h and dissolved in carbon disulfide for 12h. The solution was tested by gas chromatography simulation distillation. Rejuvenator and co-solvent were tested for blank comparison. From Figure **5**, the result showed that the sample did not have NMP after 4h. This means the co-solvent could completely volatilize with alcohol after 4h.

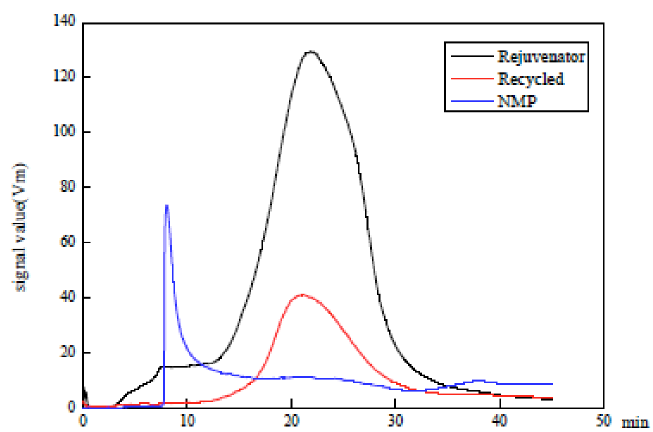

Figure 5: Simulation distillations of various samples.

CONCLUSION

A new fog seal material was formulated with asphalt rejuvenator, alcohol and co-solvent. Element analysis, ^{13}C-NMR, FTIR, and GPC were used for determining the functional groups of the asphalt rejuvenator. The calculated functional groups were used for screening a suitable co-solvent for increasing the solubility of the rejuvenator in alcohol. Results showed that NMP could greatly improve the solubility of the rejuvenator in alcohol. Ternary phase diagram was used to optimize the formula of the fog seal material, and the optimal formula has 30 wt.% rejuvenator, 12 wt.% NMP and 58 wt.% alcohol. The prepared material was also evaluated, and showed good performances of fast drying, stability and regeneration of aged asphalt.

FUND

Guangzhou Science and Technology Project Contract No: 201604020126

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Received on 21-12-2016 Accepted on 20-03-2017 Published on 03-04-2017

DOI: http://dx.doi.org/10.15377/2409-787X.2017.04.01.1