Enhancing Reological Properties of liquid Asphalt

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Abstract

The purpose of this study is to improve the specifications of cut back asphalt (S125) in order to use in the treatment of holes, potholes and cracks of roads. Different methods were carried out to enhance physical and mechanical properties and to get better construction behavior. These treatments are:-

First: The vacuum distillation of S125 cut back asphalt was employed to remove oil, vacuum gas oil and vacuum residue as a rapid curing. FTIR spectra of the four fractions of S125 were recorded. It was observed a low penetration and high softening point for the vacuum residue.

Second: extraction method using ethanol as a solvent was employed to extract light component that could be in the S125 cut back asphalt. The results indicated that the softening point was highly increased and the penetration as well as ductility was decreased to minimized level.

Third: Some Polymers were used as cross linking agent such as melamine and phenol formaldehyde resins.

Fourth: The unsaturated monomers were polymerized free radically to increase the solidification of S125.

Fifth: The hydrated white cement was used as additive to the S125 cutback asphalt at different ratios to improve the properties. This method was observed as a suitable and economic method, and easy employed compared to others and the best rheological behaviors were given in this method. Also the vacuum distillation method gave high improvements in rheological properties for asphalt residue.

Keywords: Liquid asphalt, Modification, Cut back S125.

Introduction

Asphalt is a viscose bituminous material obtained mainly from either nature sources or from petroleum refining and ranges in color from brown to dark [1, 2]. The structure of asphalt is typically composed of 80 wt% of carbon, 10 wt% of hydrogen and 6 wt% of sulfur as well as traces of nitrogen, oxygen and metals [3]. The percentages of these elements form the major building materials of asphalt body which are namely classified as asphaltenes and maltenes according to the solubility in hexane or heptane [4]. Furthermore, asphaltene fraction has high molecular weight and insoluble compared with the maltenes that have lower molecular weight and much soluble in these solvents [5]. Moreover, asphaltenes are mostly consisted of condensed, aromatic and hetero-atoms groups. In other words, the presence of hetero-atoms is influential of making these molecules to be potentially polar functions and alternatively changed their characteristics. Maltenes, on the other hand, are composed of two fractions, oils and resins [6]. Oil fraction of maltenes represents the liquid part of asphalt, whereas resins are the dispersed colloidal fraction in the oily constituents. When asphalt cement is blended with one of petroleum distillates or emulsified with water, liquid asphalt as a result is produced. There are many applications of liquid asphalt binder in paving industry due to remarkable binding properties.

Moreover, prime coat, seal coat, soil stabilization and surface dressing as well as grouting are particularly some of these applications. Liquid asphalt binder can be specifically divided into two types namely cut back and emulsified asphalt. There is another type of asphalt that considered as a modern binder called foamed or expanded asphalt [7, 8]. Cut back asphalt is produced from blending asphalt cement with a petroleum solvent. Generally, in some applications that need low temperature such as tack coats, slurry seals and cog seals, cut back asphalt is more preferred to use due to effectively having reduced binder viscosity. Furthermore, when cut back asphalt is applied, the solvent part starts to evaporate on surface that in which applied leaving behind original asphalt (asphalt cement). Therefore, according to the speed of solvent evaporation, three types of cut back asphalts, rapid curing (RC), medium curing (MC) and slow curing (SC), can be observed [9]. Particularly, rapid curing cut back asphalt is produced from mixing asphalt cement with a high volatile solvent such as naphtha or gasoline. However, medium curing can be obtained from mixing asphalt cement with a solvent of low volatility such as kerosene. On the other hand, slow curing cut back asphalt is a combination of asphalt cement and a solvent of much less volatility such as gas oil. In the process of modifying asphaltic binder, specific rheological properties are required to meet the physical and chemical changes that occur during different conditions of applied environment. Thus, different polymers have been used to improve the performance of asphalt over more than five decades [9-14]. During the manufacturing process of configuration using polymers as modifier for asphalt, dispersion and reaction are the limited steps of determining the final structure of binder and its properties as well. For example crumb rubber (CR) was used to improve the performance of asphalt [15]. They found that by increasing the percentage of crumb rubber, the softening point was increased, whereas the penetration and ductility of asphalt were decreased. Others have investigated the effect of adding sulfur to the asphaltic binder for improving rheological properties. They pointed that the penetration of asphalt was noticeably increased compared with the increase of penetration and ductility. Moreover, the optimum percentage of sulfur was 5% and the penetration was increased by 33% and the softening point by 70% while the ductility kept remaining (100^{+}) [16].

The pavement asphalt 40/50 penetration grade used in Iraq is exclusively made in the north and middle refineries. In general, crude oil that produced from Kirkuk (north of Baghdad) has at least 40% as residue compared with the Basra (south of Baghdad) crude oil that has 30% as a fraction of bitumen. Unlike these fractions of residue, the crude oil produced from Qiara (north east of Baghdad) can produce between (70-90) % fractions as residue. Kisik refinery (north east of Baghdad) is one of the refineries that mainly use crude oil of Kirkuk as feed stock. Thus, there is a huge amount of residue as a result after refining process has been performed. S125 (cutback) is one of the liquid asphalt that produce in large quantities in this refinery. Furthermore, S125 is mainly used as a tack coat in the road paving industry [17].

The focus of this research is to modify liquid asphalt (cutback S125) using different methods (physical and chemical) in order to use it as a remedy in the road pavement industry. Additionally, the objective of the present study is to improve the rheological properties of liquid asphalt using different methods to obtain the lowest cost with best result.

Experimental

Materials

All materials and chemicals were purchased from Fluka and Aldrich companies, without any purification. White cement was obtained from Iraqi market, acrylic acid, acrylonitrile, acryl amide were purchased from BDH. Melamine and phenol formaldehyde resins were obtained from Aldrich.

Apparatus

Vacuum pump, air compressor , pressure gauge, flow meter , vacuum gauge ,water pump , vacuum volumetric flask, condenser (QVF) ,heater, mixer, heating coil ,volumetric flask ,valve, control panel**. Penetration test** was carried out before and after treatment according to ASTM D5 using PNR10 Pentro meter made by petro Test Company. **Ductility test** was used ductility instrument made by Petro Test Company according to ASTM DDA3. **Softening point test**was used softening instrument as ring and ball apparatus that has the model RB 365G made by SI Company, and followed the ASTM D36.

First method

Vacuum distillation was carried out under 60mm/Hg using 977 gm of S125 asphalt. This amount of asphalt was added to the treatment vessel, the temperature was raised gradually to 320 ^{o}C by direct heating using mental heater. Four fractions were obtained in different ranges of temperatures and the specifications are listed in the Table (1)

Table (1) Rheological behavior changes of asphalt from vacuum distillation for 1

No.	Softening point (C^{o})	Penetration (mm)
1	81	8.6
2	88	5.3
3	91	2,8
4	98	24

Second method

Precipitation method was used to purify S125 asphalt from its hydrocarbon solvent. 100gm of S125 was charged to a vessel and 20 ml of benzene was added to dissolve the S125. Then the liquid part was poured slowly into a 100 ml of ethanol with stirring. The procedure was repeated four times, and the contained oil was removed from S125 by ethanol. The test results of extracted asphalt were listed in Table (2) which shows the behavior before and after treatment.

Table (2) Rheological behavior changes of extracted asphalt after precipitation.

Asphalt type	Softening point (°C)	Penetration (mm)	Ductility (cm)
S125 asphalt	34	294	100
Extracted asphalt	50.8	76.2	90

Third method

Chemical additives were used as cross linking agents such as melamine, phenolic resins with formaldehyde in different weight ratios. 100 gm of liquid asphalt was heated to 40 C° and different ratios of 5, 10, 15, 20% of melamine –formaldehyde or phenol formaldehyde resins were added to the asphalt with stirring for 2hrs. Then the mixture was cooled down and tested. Table (3) shows the changes of rheological behaviors of the treated S125.

Table (3). Different ratios of chemical additives used to the S125 asphalt and the changes of rheological properties.

	Melamine-formaldehyde			Phenol formaldehyde		
Wt%	softening point (°C)	Penetration (mm)	Ductility cm	softening point °C	Penetration mm	Ductility cm
No. | softening Point 1 2 3 4 5%	42	290	100	44	283	100
10%	46	281	95	46.6	272	100
15%	52	255	90	53	267	95
20%	54	210	85	59	160	90

Fourth method

Vinylic monomers were added to the S125 asphalt and polymerization the mixture was prepared. Specifically, 5% as weight percentage of monomers (acrylic acid, acrylonitrite, acrylamide) was added to the asphalt with 0.05% of dibenzoyl peroxide as initiator and a 10 ml of chloroform as a solvent. The free radical polymerization was carried out at (90 -95 ^{0}C) under stirring for 1 hr. The mixture was then heated and the solvent was evaporated, the product was cooled and tested. Table (4) shows the rheological properties of the modified asphalt with 5% weight ratio.

Table (4) Rheological properties of polymers modified asphalt.

5% weight	Softening point (^oC)	Penetration (mm)
Acrylic acid	46	97
Acrylonitrite	60	85.3
Acrylamide	63.7	79

Fifth method

The hydrated white cement was used as an additive binding material and different weights ratio were added to the liquid asphalt. The mixture was heated under stirring for 1hr and then cooled down and tested as shown in Table (5).

Table (5) Changes in the rheological behavior of S125 asphalt before and after addition of white cement.

Wt ratio %	Penetration (mm)	Softening point (^oC)
0	294	34
10	200	39
20	180	40
30	170	45
40	160	47
50	150	49
55	127	89

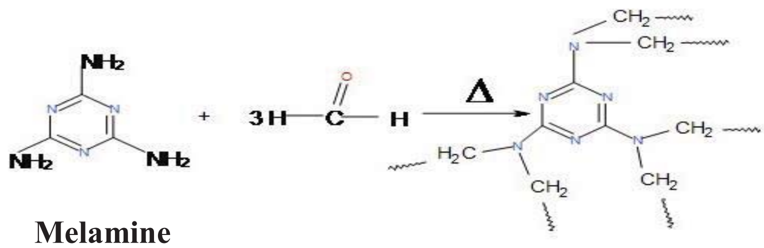
Result and Discussion

In this work, all treatments have been carried out to improve physical and rheological properties of liquid asphalt S125. These improvements have included the following: Firstly, It was used to distillate liquid asphalt (S125) at pressure of 60 mm Hg at different ranges of temperatures. Four fractions were collected in vacuum volumetric flask. Different temperatures have been recorded as it is shown in Table (6).

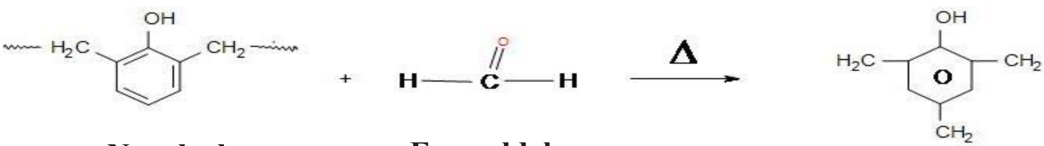
Table (6) The temperatures range, weight and volume of produced oil fractions from vacuum distillation for 977gm of S125 at 60 mmHg

Samples	Temperature (^oC)	Weight of cut (gm)	Volume of cut (ml)
1	55-278	127	145
2	278-300	70	78
3	300-310	66	68
4	310-320	59	60

The asphalt cement was obtained as a solid material from vacuum distillation and was analyzed through measuring penetration, softening point and ductility. According to the Table (1), the decreasing in the penetrations was observed to (8.8-2.4 mm). The change in the ductility was reduced to zero. On the other hand, the softening points were increased from 37 to 98 ^oC which means that a high enhancement was occurred. Ductility of asphalt is the ability to remain coherent under large strain when stretched in tension. It is expressed as the distance in centimeters to which a standard briquette can be elongated before the threads formed breaks under the specified condition. Ductility depends on the nature of the binder. It was observed that the ductility decreased with increasing melting point due to the hardness and this causes the decreasing in penetration which obtained to 2.4mm. This is due to the asphalt binder as a matrix of structure that has less ductility at harder grades. The vacuum distillation was carried out under 60 mm Hg. Four fractions were isolated as shown in Table (5). At the first step, the fraction (a) was distillated at temperatures of (155-278 ^oC) and it was determined as gasoline. The second fraction was obtained in the range of temperatures (278-300 ^oC) and it was determined as kerosene as it was expected. The third fraction was separated at temperatures of 300-310 ^oC and it was determined as light gasoil. The fourth fraction was isolated as heavy gas oil at range of temperatures of 310-320 ^oC. The change in penetration of asphalt before and after distillation for the four fractions of asphalt cement was changed from (294-2.4 mm). This enhancement in the penetration grade gave indication about availability of light components in the main body of asphalt. Moreover, during the vacuum distillation, oil fractions were removed to decrease the penetration degree of asphalt. The FTIR of four fractions as isolated oil, and the FTIR spectrum of produced asphalt cement. All absorptions indicated the hydrocarbon structure included the –CH aliphatic which appeared at 2980 cm-^{1}, and CH-aromatic that was observed at 3080 cm^{-1}. The other absorptions were observed at 3080 cm^1 indicated the CH-unsaturated group that could be treated by cross linking agents in the other methods were carried out in this study. The vacuum distillation was carried out in four steps and the remained asphalt was measured in every step .The increasing in softening point and decreasing in penetration was observed. Secondly, purification of liquid asphalt from its solvent by dissolving S125 with benzene and re-precipitation with ethanol for several times was carried out to extract the oil. The black product of asphalt was obtained from this method and can be improved mostly with more extraction. Table (2) shows the improvements in the softening point. It was increased from (34 ^{o}C) of liquid asphalt to (50.8 ^{o}C) and the penetration was decreased from (294 to 76.2 mm). The number of extracted times could give the required properties Table (3) shows the improvements on characteristics of asphalt using different ratios of weight percentage of melamine or phenol formaldehyde (Novolack) resin. The increasing in softening point of asphalt was observed and decreasing in penetration was obtained). This method, melamine formaldehyde or phenol formaldehyde were used as cross linked agent through the asphalt matrix. The formaldehyde could be used as hexamine or paraformaldehyde. The following equations were illustrated the reactions:-



Melamine

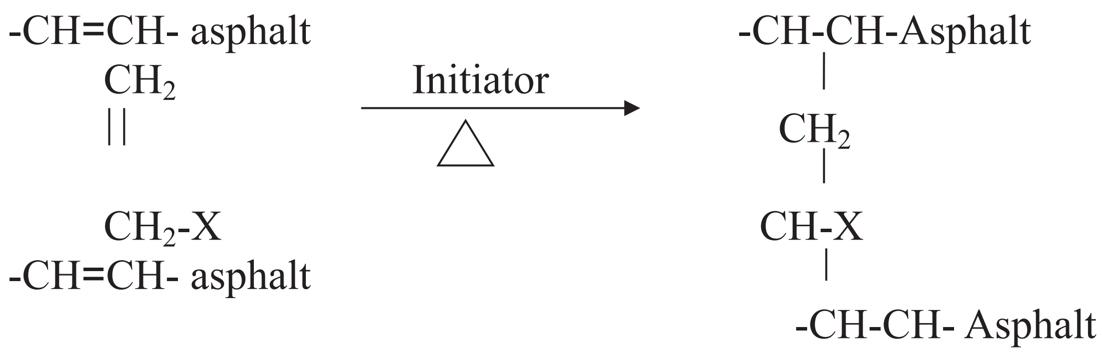


Novolack

Formaldehy

Phenol formaldehyde resin

The cross linked polymers acts as a thermally stable polymer with high improvement in rheological properties. Thirdly, different unsaturated monomers were used as cross linking agent for some unsaturated groups through the asphalt material. Free radical polymerization of the used monomers using dibenzoyl peroxide as an initiator was observed. The following polymerization was described as below:



Cross linked polymer through asphalt matrix X=-COOH of acrylic acid, - CN acrylionitrite,-$CONH_2$ of acryl amide

Table (4) shows the decreasing in softening point and decreasing in penetration. The increasing in wt% ratio of monomer gave higher results in 5wt% and lower results in penetration.

Fourthly, white cement in different weight ratios was used. The increase of softening points was observed due to increasing in wt% of white cement. The change was from (34) to (89^oC) indicated the enhancement while the penetration was decreased from (294mm) to (127mm) with 55% of white cement to S125 as shown in and (816). The 55% of white cement gave the best results compared with the other wt% as shown in Table (5).

Conclusion

The vacuum distillation gave the best results, with high changes in softening point and penetration. The white cement also gave a good changes and low cost which could use as a economically suitable enhancer. All the other methods appeared good results even though but they were used in other chemical applications. The four fractions of isolated oils from vacuum distillation could be used industrially also we recommended in our suggestions that the solid asphalt which was obtained from this method could use for future investments and it could applied in different uses such as flame coat and for anti-corrosion treatments of oil pipes.

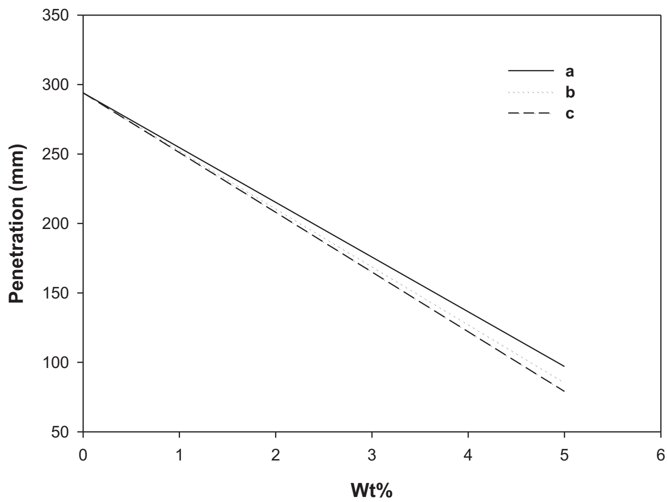


Fig. (1) Penetration verses weight % of (a) Acrylic acid (b) Acrylonitrite (c) Acrylamide.

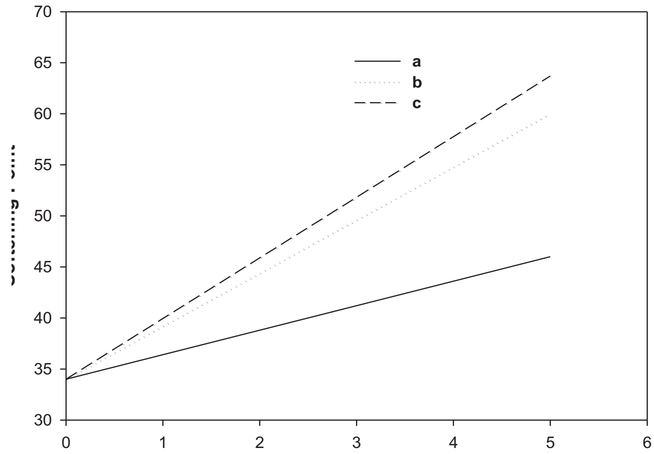


Fig. (2)Softening point verses weight % of (a) Acrylic acid (b) Acrylonitrite (c) Acrylamide.

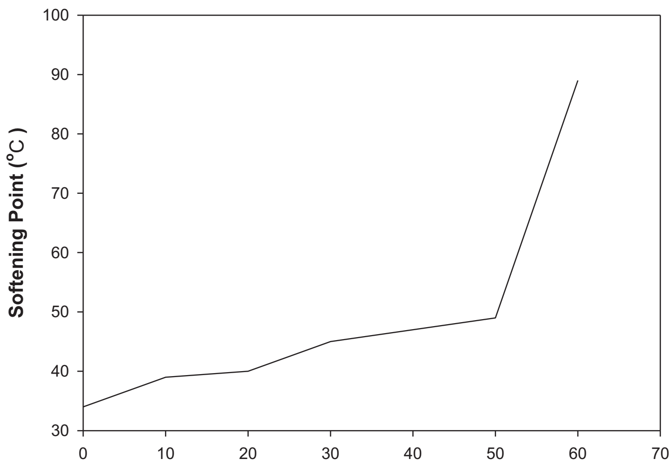


Fig. (3) Softening point verses white cement additive to S125.

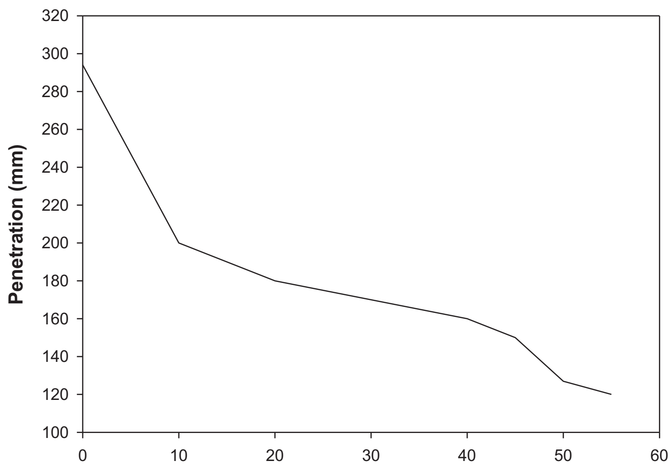


Fig. (4) Penetration verses white cement additive to S125.

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