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Enhanced of Maltenes - Asphalt Blends Specifications via Thermal Catalytic Processes

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Abstract: In this article the effects of using maltenes, which have been pre-separated recently from paraffinic base asphalt to modify asphalt pavement in variety of percentages has been investigated. Further modification has been performed by applying chlorine gas using ultra violet and ferric chloride as catalyst at certain temperature in order to increase the homogeneity and performance of paving asphalt. Characterization of asphalt blends has been performed according to ASTM standards. The results showed that addition of 1% of maltenes increases the softening point for the blends from catalytic chlorination, which reflects the benefit of this treatment. The penetration index for blends obtained by catalytic chlorination has also improved compared to unchlorinated samples and to those obtained from treating the asphalt with maltenes alone. Finally the specific gravity of catalytic chlorinated blends increased, thus indicating the influence of chlorination on the improvements of asphalt blends.

Keywords: Asphalt; Modified Asphalt; Chlorination; Maltenes; Asphalt Blends.

1- Introduction

Asphalt, a black or brown highly viscous liquid or semisolid material present in most crude oils and in some natural deposits, is a complex mixture of organic compounds containing up to 150 carbon atoms, mainly aromatic, naphthenic and aliphatic. In addition, it may also contain small amounts of organic acids, bases, heterocyclic compounds nitrogen, oxygen, and sulfur and some metals. Its composition may typically contains (83-86)% carbon, (9-10)% hydrogen, (1-5)% sulfur, less than 1% each of nitrogen and oxygen, and minor amounts of metals such as vanadium and nickel [1,2,3]. It is a thermoplastic material; it softens when heated and hardens on cooling. Within a certain temperature range, asphalt is viscoelastic; it exhibits the mechanical characteristics of viscous flow and elastic deformation [1, 4]. Asphalt is the residue of mixed-base and asphalt-base crude oils. It cannot be distilled even under the highest vacuum, because the temperatures required to do this promote formation of coke. It is useful anywhere where waterproofing, insulation, or chemical resistance problems are encountered. It is used in the lining of water reservoirs, canals, and the upstream side of large dams to prevent water seepage and erosion [4]. Asphalt is used in diverse industries such as cable jointing compound, cold sticker compound for sticking, roofing felt over metallic surfaces, timber, battery sealing compound, for making printing inks, in automobiles for undercoating, as a base for paint and lacquers, manufacture of floor covering, and a wide variety of waterproofing and damp-proofing applications. Different end uses of asphalt require different properties and different manufacturing methods.

Asphalt modification is driven by the fact that neat asphalt is a thermoplastic material with relatively poor thermo-mechanical properties because it is fragile at low temperatures (< -10°C) and soft at high temperatures (>60°C). The thermo-mechanical properties of asphalt are essentially dependent on its composition [7]. Asphalt can be considered a colloidal solution in which asphaltenes are held in suspension in a mixture of oil and resins. Asphaltenes are insoluble in oil, but the polar nature of resin molecules keeps asphaltenes in a colloidal suspension. It is usually divided into fractions that differ in structure, molecular weight and solubility properties: saturates aromatics, resins and asphaltenes, known as SARA. The first three together are usually referred to as maltenes [5]. The fractions are classified as asphaltenes or maltenes according to their solubility in n-hexane or n-heptane. Asphaltenes are high-molecular compounds and thus

insoluble in these solvents. Maltenes, in contrast, have a much lower molecular weight compared with asphaltenes and are soluble in these solvents. Both asphaltenes and maltenes are surface active components, with a hydrophobic structure containing some hydrophilic functional groups [1, 5]. The complexity, aromaticity, heteroatom content, and molecular weight increase in the order S < A < R < As [6].
The performance of bitumen has been improved through the utilization of additives such as virgin polymers (SBS, SBR, EVA, etc.), and waste polymers (plastic from agriculture, crumb tire rubber, etc.). However, the mixing process may have a significant effect on the technical properties of the resulting blend, as well as on the costs of the whole operation [8]. Carbon black and sulfur have been used for modification of the asphalt. There were two reasons for considering the use of sulfur in asphalt mixes: (1) to improve the mix quality and (2) to reduce the cost. The latter depends mainly on the relative costs of sulfur and asphalt, but energy saving is also important [9, 10, 11]. Chlorine has also been used for modification of asphalt [12]. The advantages of such treatment is to decrease the effect of the oxidation on the road pavement. Another study gave hard and brittle products which are not suitable for the application [13].

Most of difficulties in the modification of asphalt come from the incompatibility and phase separation [11].
In this work, we therefore choose maltenes to modify asphalt for reasons such as

- the solvation and the dispersion of maltenes within asphalt are easier and extremely higher than those for polymers.
- minimize the cost for the process.
- increase the compatibility of the asphalt blends.
- improve the performance of paving asphalt.

2- Experimental

2.1. Materials

2.1.1 Binders

Two straight-run asphalts of different origin were used. One is from the Qaiyarah Refinery, in Qaiyarah - Iraq, and the other from Baiji Refinery. These asphalts are referred to as the Qaiyarah and Baiji Asphalts and their characteristics are shown in Table 1.

Table 1: Basic Characteristic of Qaiyarah and Baiji Asphalts

Properties	Qaiyarah Asphalt	Baiji Asphalt
Penetration at 25°C 100 g, 5 seconds, 0.1 mm	62	55
Softening point °C (Ring and Ball)	50	44
Ductility / 25 °C, 5 cm/min, cm	100	100
Specific Gravity	1.0495	1.040

2.1.2. Maltenes

The maltenes used in this work were obtained by subjecting Baiji Asphalt to selective solubilization process using petroleum ether (60-80) ^{o}C.

2.1.3. Chlorine Gas

Chlorine gas was obtained from Water and Processing Foundation, Mosul, Iraq.

2.1.4. Petroleum Ether (60-80) ^{o} C

Petroleum ether was supplied from BDH and used without further purification.

2.1.4. Anhydrous Ferric Chloride

Anhydrous ferric chloride was supplied from BDH and used as received.

2.2. General procedure

2.2.1. Separation of Maltenes

5 g of Baiji Asphalt and 200 ml of Petroleum Ether were placed in a conical flask. The flask was shaken until all the maltenes were dissolved. The mixture was left for 3 h to ensure complete precipitation of the asphaltenes. The solution of solvent and maltenes was filtered using a Whatman No. 42 filter paper. The flask was rinsed with solvent to ensure that all dissolved maltenes were transferred through the filter. The residue was washed with solvent until the filtrate was colorless. The filtrate was collected in a pre-weighed round-bottom flask. The solvent was then removed from the solution by distillation till the mixture becomes sticky. The sticky mixture was then transferred and left overnight at 25^{o} C to ensure the complete dryness. The dried maltenes was weighed, and reported as weight percent maltenes.

2.2.2. Preparation of Blends Bases

Different blend bases of Qaiyarah Asphalt were modified using the pre-separated maltenes from Baiji Asphalt as described in 2.2.1., in various percentages. First 300 g of Qaiyarah Asphalt was melted, then 1% of maltenes was added to the melt and mixed physically in a closed system using mechanical stirrer and the temperature was maintained in the range of 125-130^{o} C for 3 h. At the end of run the softening point and penetrability of the product was determined. This procedure was repeated using 3%, 5% and 8% of maltenes addition. The prepared blends are referred as QBB.

2.2.3. Chlorination of Blends

Thermal chlorination of QBB was performed by melting known amount of sample (150 g obtained from 2.2.2.) and introducing dry chlorine into the melt at constant rate through a glass tube in a closed system. The temperature was regulated in the range of 160±1^{o} C. The chlorination was carried out for 3 h, after which the chlorine supply was discontinued and the contents heated at same temperature for 15 min to expel out any unreacted chlorine and HCl. The softening point and penetrability of samples were determined at the end of the run. This method was conducted using ultra violet and ferric chloride as catalyst. The samples prepared using ultraviolet and ferric chloride catalysts are referred to as QBBUV and QBBFC respectively.

2.2.4. Detection Method

After blending the samples were characterized according to ASTM standards as follows:

1- Softening point (ring and ball test): This test was performed according to the method of ASTM, D 36 – 95.
2- Penetrability: This test was performed according to the method of ASTM, D 5 – 97.
3- Ductility: This test was performed according to the method of ASTM, D 113 – 99.
4- Specific Gravity: This test was performed according to the method of ASTM, D 70 – 03.

3. Results and Discussion

3.1. Physical Properties

All properties obtained from pre-modification with maltenes(QBB) and chlorination samples(QBBFC & QBBUV) are recorded in the Tables 2,3 and 4.

Table 2 Specification obtained of QBB Asphalts

Sample	Maltenes %	Softening Point (°C)	Penetrability 0.1mm.5s.25°C	Ductility cm.25°C	Specific Gravity	Penetration Index	PTS
1	0	50	62	100	1.0495	0.6396	0.0441
2	1	49	65	100	1.0093	-0.8257	0.0454
3	3	48	66	100	1	-1.0581	0.0471
4	5	45	71	100	1.0194	-1.7355	0.0526
5	8	44	75	100	1.0097	-1.9028	0.0541

3.2.1. Softening point

The softening points according to ASTM D36-95 (ring and ball test) of the samples are reported in Tables 2, 3 and 4. Figure 1 reports the behavior of all blends. It is seen that the softening points for the QBB blends decrease with addition of maltenes and this is as expected. For the QBBUV and QBBFC blends, it is seen that the softening points increase due to the chlorination compared to that for the original and for those of QBB blends. This can be explained in terms of the ratio of the maltenes and asphaltenes contents in the bitumen. When the maltenes oil content of the bitumen is high, the molecules of the bitumen components move freely and consequently the system is fluid. This explanation can be applied on the QBB blends. As far as the effect of heat in the presence of chlorine is concern, the added chlorine reacts with certain amount of maltenes molecules, leading the system of maltenes oils to coagulate and condense. [13].

Table 3: Specification obtained of QBBUV Aasphalts

Sample	Maltenes %	Softening Point (°C)	Penetrability 0.1mm.5s.25°C	Ductility cm.25°C	Specific Gravity	Penetration Index	PTS
1	0	50	62	100	1.0495	0.6396	0.0441
2	1	114	1	3	1.0515	1.4068	0.0326
3	3	84	9	15	1.0537	1.3208	0.033
4	5	57	34	75	1.0549	-0.461	0.0429
5	8	80	16	19	1.0591	1.7878	0.0309

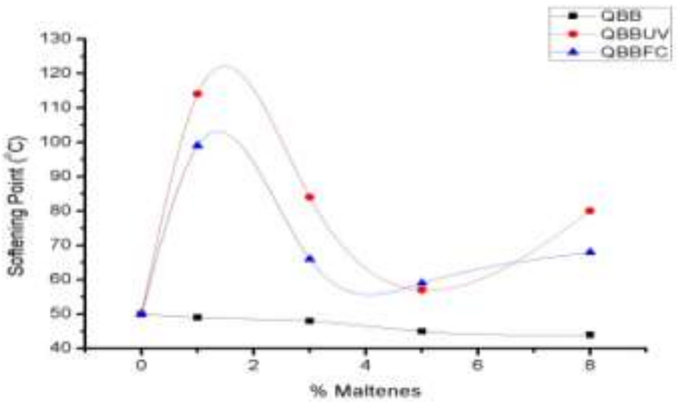

Figure.1: Influence of Maltenes addition on Softening Point of base and Modified Asphalts

Table 4: Specification obtained of QBBFC Aasphalts

Sample	Maltenes %	Softening Point (°C)	Penetrability 0.1mm.5s.25°C	Ductility cm.25°C	Specific Gravity	Penetration Index	PTS
1	1	99	10	7	1.0518	3.1291	0.0257
2	3	66	25	18	1.0531	0.5820	0.0367
3	5	59	32	25	1.0544	-0.1800	0.0411
4	8	68	21	12	1.0611	0.5634	0.0368

3.2.2. Penetrability

The results for the penetrability of the samples are reported in Tables 2, 3 and 4. The consistency of samples based on the penetrability within 5 s of a standard needle into the material under a load of 100 g at 25°C (ASTM D 5-97) is indicated in Figure 2. It is seen that the penetrability of QBB samples increases with increasing maltenes addition. An increase in penetrability means that the consistency of bitumen increases as a result of the interactions between the maltenes and the components of the asphalt. This increase in the penetrability could be due to the increase of paraffinic contents of asphalt. In both QBBUV and QBBFC blends, the penetrability decreases. This is can be explained because of the increase of light constituent present in the blends which allows chlorination to take effect and thus increases the viscosity making the mixtures harder. At this point we can express the QBB samples are more elastic (gel) asphalt, while QBBUV and QBBFC are the more viscous (sol) asphalt [6, 13, 15].

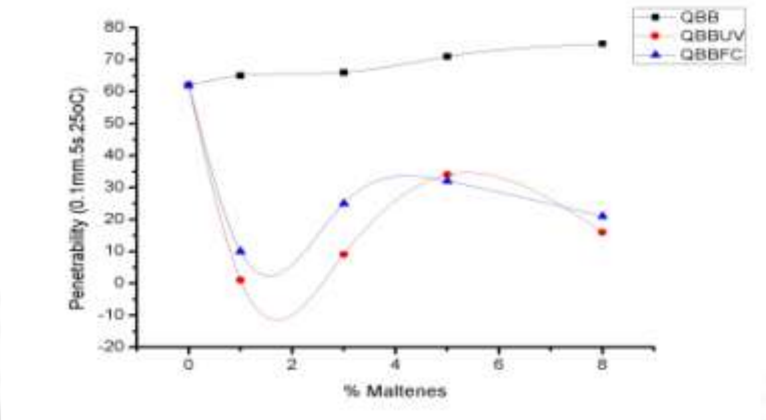

Figure 2: **Effect of maltenes addition on penetrability of base and modified asphalts**

3.2.3. Penetration Index and Penetration Temperature Susceptibility

The penetration index relationship and the penetration temperature susceptibility are calculated to investigate the influence of maltenes addition and the chlorination on temperature susceptibility of asphalt. Penetration index, PI, is defined as the change in the consistency parameter as a function of temperature. A classical approach related to PI calculation is shown in the following equation:

$$PI = (20 - 500A) / (1 + 50A) \ldots\ldots(1)$$

Where A is the temperature susceptibility which is the slope of the straight line plot between the logarithm of penetration (abbreviated as pen) and temperature.

$$A = (\text{Log pen at } T - \text{Log } 800) / (T - T_{R\&B)}) \ldots\ldots(2)$$

Where T is the penetration testing temperature and $T_{R\&B}$ is ring and ball softening point [17].

Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation. The obtained data of PTS and PI prove that the modified asphalts are less sensitive to temperature than the base asphalt resulting in less cracking at low temperature and also it reflects higher dispersion of asphalt contents [13, 16]. As seen in Figure 4, both QBBUV and QBBFC samples exhibit less temperature susceptibility compared to QBB with increasing maltenes content.in figure 3,show QBBFC modified samples yield higher PI values compared to QBBUV modified samples especially at (5%) addition .

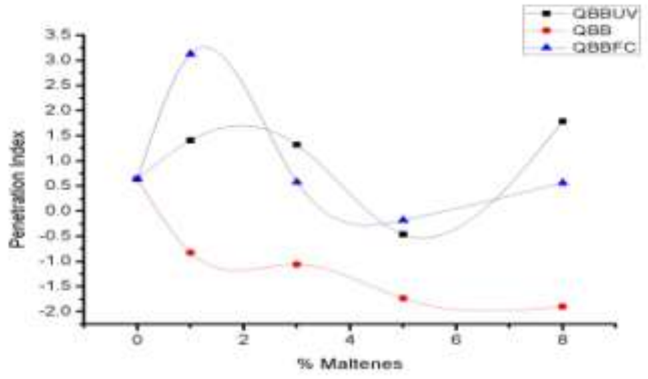

Figure.3: **Penetration Index of Base and Modified Asphalts**

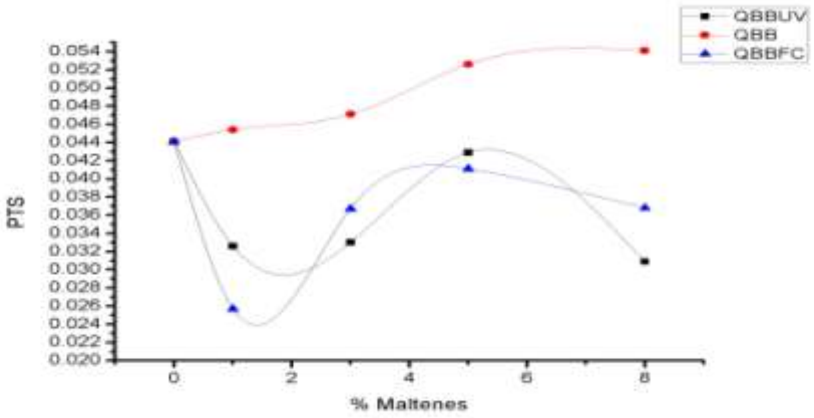

Figure.4: Temperature Susceptibility of Base and Modified Asphalts

3.2.4. Ductility

The ductility of samples according to (ASTM D 113-99) is reported in Table 2, 3 and 4. Figure 5 reports the ductility behavior of all blends. For QBB the addition of maltenes has no influence on the ductilities as it dilutes the asphalt constituent. The ductility for both QBBUV and QBBFC blends decrease severely in the first sample (1% w/w maltenes) compared to QBB blends. With the increase of maltenes addition (3% and 5% w/w), the ductility increases both QBBUV and QBBFC blends. As the addition increases further, ductility decreases for the both last samples. Our explanation is, in the first sample the chlorination takes more effect than dilution (due to maltenes addition) while in the next two samples the dilution starts to take effect more than chlorination but still less than that in QBB blends. In the last one the chlorination returns to take effect more against dilution but still less than that in QBB blends.

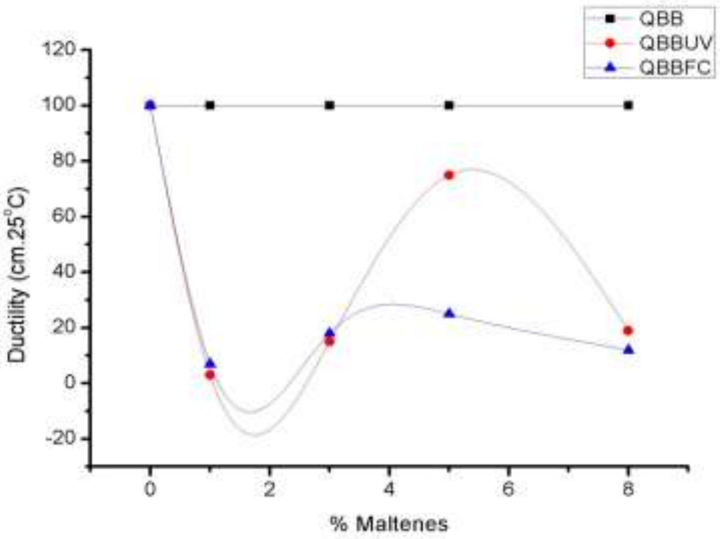

Figure.5: Effect of Maltenes Addition on Ductility of base and Modified Asphalts

3.2.5. Specific Gravity

According to ASTM D 71-52 the specific gravity can be expressed as the ratio of the weight of a given volume of materials at 25^{o} C to that of an equal volume of water at the same temperature and it reflects the ability of asphalt to absorb water. Thus this specification is important for the performance in construction. The result records in Figure 6 and Tables 2, 3, 4. For QBB blends the results show that the addition of maltenes decreases the specific gravity for the first two additions due the dilution of the component and shows irregularity for the next addition and the specific gravity increases but is still less than the original and finally, the last addition decreases again. For the QBBUV and QBBFC blends the results show linear increase in the specific gravity. This is can be explained as above which is due to influence of chlorination.

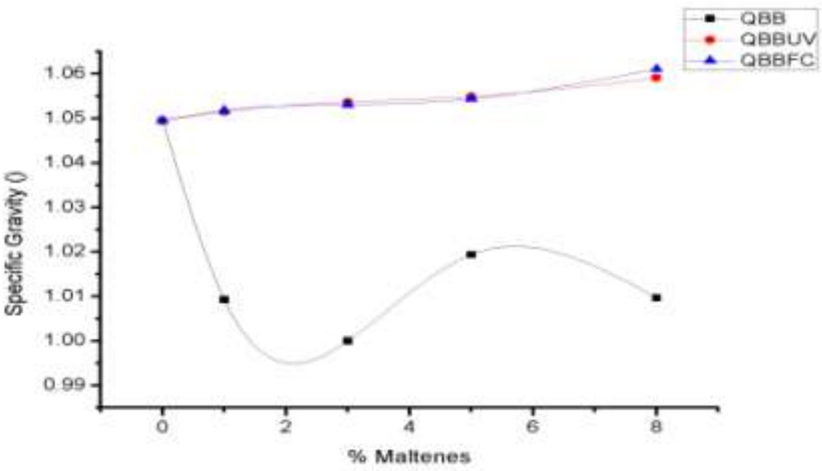

Figure.6 Specific Gravity of Base and Modified Asphalts

4. Conclusion

- The addition of maltenes gives improvement in the penetrability and ductility implying that the modified blends are less sensitive to temperature and that the dispersion of the asphalt constituent has increased.
- The catalytic chlorination gives improvement in the softening point and the penetration index and this improvement can have potential for use roofing applications.
- Both addition of maltenes and chlorination of the samples improved the specific gravity for the modified samples which reflects the benefits of using chlorine gas for the modification.

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References

[1]. S. Parkash, Petroleum Fuel Manufacturing Handbook, McGraw-Hill Companies, USA, p. 101(2010).
[2]. G. V. Chilingarian, T. F. Yen, Bitumens, Asphalts and Tar Sands, Elsevier Scientific Publishing Company, Amsterdam, p. 157(1978).
[3]. Speight, James G., The Chemistry and Technology of Petroleum, Marcel Dekker, Inc., New York, 3rd Ed., p. 810(1999).
[4]. L. Alvarez, M. Elena Diaz, F. J. Montes , M. A. Galan, Fuel, 89: 691-702(2010).
[5]. F.J. Navarro , P. Partal , M. Garcı´a-Morales , M.J. Martı´n-Alfonso , F. Martı´nez-Boza , C. Gallegos , J.C.M. Bordado , A.C. Diogo, J. Ind. Eng. Chem., 15, 458–464(2009).
[6]. P. Gonzalez-Aguirre, et.al., J. App. Poly. Sci.,112, 3, 1330-1344(2009).
[7]. Y. Yildirim, Cons. Build. Mat., 21, 66-72(2007).
[8]. A. Chaala , C. Roy, A. Ait-Kadi, Fuel, 75,13, 1575-1583(1996).
[9]. X. Bourrat, A. Oberlin, J.C. Escalier, Fuel, 66, 4, 542-550(1987).
[10]. T. F. Yen & G. V. Chilingarian, Asphaltene and Asphalts, Elsevier Science B.V., 1st ed., 2000, pp: 511.

[11]. D. Urban, K. Takamura, Polymer Dispersions and Their Industrial Applications, Wiley-VCH Verlag GmbH, Weinheim, p.309-311(2002).
[12]. S. R. Patwardhan, Fuel, 58, May, 375-378(1979).
[13]. F. C. Sanderson, Transportation Research Board, USA, 1-12(1956).
[14]. Wiley Critical Contents, Petroleum Technology, John Wiley & Sons, Inc., and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, p.187-189(2007).
[15]. G.R. Morrison, J.K. Lee, S.A.M. Hesl, J. Appl. Poly. Sci., 54, p.231-40(1994).
[16]. Y. H. Huang, Pavement Analysis and Design, Pearson Education Inc., Pearson Printice Hall, USA, 2nd Ed., p. 301-302(2004).