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THE EFFECT OF BITUMEN AGEING TO FRACTIONAL COMPOSITION

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Abstract

Bitumen is manufactured from different crude oil sources also by various refining technologies, therefore, the impact of ageing is different. Bitumen is a complex chemical mixture consisting of a large number and diversity of organic compounds, mostly hydrocarbons, and varying in molecular mass, polarity and aromaticity. Various polar and non-polar fragments in bitumen interacting in-between form the certain structures which changes bitumen behaviour. Since bitumen is assigned as a colloidal system, consisting of high molecular weight asphaltene micelles dispersed in a lower molecular weight maltenes (saturates, aromatics, resins), the bitumen structure changes over time. Since ageing is one of the main factors effecting bitumen properties and asphalt pavement performance, it is essential to understand how the fractional composition of bitumen is affected by the long-term ageing simulation in the laboratory. The main purpose of this article is to analyse bitumen ageing process and influence to bitumen fractional composition (saturates, aromatics, resins, and asphaltenes), i.e. to show what happens to the bitumen fractional composition and colloidal stability when bitumen reaches a critical ageing point. The saturates, aromatics, resins, and asphaltenes were determined with the Thin Layer Chromatography with flame-ionisation detector (TLC/FID), the IATROSCAN MK-6s.

Keywords: bitumen, fraction composition, SARA, ageing, oxidation, colloidal stability

1 Introduction

Determination of detailed bitumen chemical composition has been a major challenge for many years since it varies every time depending on the crude oil source, the batch of crude oil as well as the refining technology [1, 2]. Crude oil is the base for lots of products which variety depends on the market demand. Since crude oil products include transportation fuels such as diesel, gasoline, fuel oils used for heating and electricity generation, synthetic fibres as well as many other products, bitumen, as the end distillation product, differs with each production process [3]. The increase in demand for petroleum products encourages scientists to take a deeper interest in the properties of bitumen. The knowledge of crude oil source and processing is essential because it helps to understand bitumen behaviour under different conditions [4]. In general, crude oil mainly contains hydrocarbons and small quantities of nitrogen, oxygen, and sulphur compounds as well as some metal components such as iron, nickel, copper and palladium [5, 6]. The chemical structure of different crude oil directly effects the refining technology and the bitumen quality. Naphthenic type of crude oil is one of the best option for bitumen production since it contains a large amount of naphthene, whereas paraffinic and aromatic crude oils contain large amounts of saturated and aromatic hydrocarbons accordingly.

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Another relevant aspect effecting bitumen chemical structure is non-reversible ageing process [7, 6, 8]. Bitumen ageing is caused by the processes of oxidation, volatilization and steric hardening which are directly related to oxygen, ultraviolet light and heating. Volatilization and oxidation of bitumen are effected by chemical reactions or the changing of the bitumen structure, whereas steric hardening of bitumen occurs by intermolecular reconstruction [9, 7, 10]. Bitumen starts quickly ageing during the storage, asphalt mixing, transportation, laying process (short-term ageing) as well as under the influence of oxidation in the asphalt pavement structure during the service life (long term ageing) [11]. During these two ageing periods, two phases of bitumen ageing where determined: in the first phase (short term ageing) - mainly sulphur oxidation, in the second phase (long term ageing) – benzylic position oxidation. Petersen, C. and Glaser, R. (2011) and other authors analysed bitumen oxidation mechanisms, especially the formation of ketones, identified as a major factor leading to asphaltenes formation, which leads to viscosity increase on ageing [7, 12-14].

Bitumen consists of an infinite variety of organic compounds that vary widely in molecular structure, molecular size and polarity [15, 16]. Analysing bitumen chemical composition, especially fractional composition (SARA), the attention falls into the components (saturates, aromatics, resins and asphaltenes) interaction which influence bitumen behaviour and changes the sensitivity to ageing. SARA fractions have been commonly used to study the chemical changes in bitumen due to oxidative ageing [17]. Bitumen itself is non-polar comparing with the environment however it contains slightly more polar molecules (such as asphaltenes) and non-polar molecules (saturates). The polarity is very important aspect since it effects the oxidation process in bitumen [18]. Changes in chemical fractions (SARA) due to oxidation process have been interpreted as a movement of components from non-polar fractions up to the more polar fractions (i.e. from saturates to asphaltenes) [9]. The increase of polarity creates a way to oxygen-containing functional groups in bitumen's molecules which have different reactivity to oxidation. Finally, we get a loss of aromatics and resins, with a consequent increase in the number of asphaltenes. Saturate fraction is highly resistant to oxidation since they are non-polar and, as a consequence, has low reactivity [9, 12].

Lots of investigations have been done on bitumen ageing process and influence to bitumen fractional composition [19, 20]. However, there is limited research done on how the fractional composition of bitumen changes after extremely long term ageing and how it effects asphalt pavement performance under the real conditions. Chemical changes of bitumen before and after ageing include the formation of functional groups, transformation of fractions, changes in microstructure and in molecular weight. Seki, H. and Kumata, F. investigated structural changes of asphaltenes and resins by hydrodemetallization (HDM) reaction. From the Laser Desorption Mass Spectrometry (LD-MS), the molecular weight of both asphaltenes and resins decreased with HDM temperature, showing an opposite change in molecular weight distribution [21]. Cuciniello, G. et all investigated the changes in the microstructure of SBS modified bitumen. The results showed that neat bitumen binders after one cycle of long term ageing (PAV), bitumen components, such as aromatics, resins and asphaltenes, shifted towards heavier molecules [22]. Aguiar-Moya, J. P. et all (2017) concluded that colloidal stability of bitumen fraction is affected by a loss of low molecular weight components as well as air oxidising the bitumen. It was determined that increase in stiffness depends on polar components, while adhesiveness is associated mainly with nonpolar components. Other scientists Redelius and Soenen (2015) determined that increased stiffness of bitumen is due to increased interactions between the molecules. During the chemical reaction with oxygen, increases the polar interaction in bitumen, the size of molecules as well as increases the condensed aromatics, as a consequence, increasing other molecular interactions such as and dispersive interactions [23]. Filippelli, L. et al. 2012 determined that aged bitumen binders have higher reprocessing temperatures because some of their aromatic components and resins, which are responsible for a certain grade of mobility, are oxidized to asphaltenes.

Hence, asphaltene micelles became larger so that the fluidity of the system is reduced [24]. The main purpose of this article is to analyse ageing process at molecular level and to investigate how bitumen fractional composition can be effected by extended long-term ageing. In order to structurally characterize bitumen, the SARA (saturates, aromatics, resins, asphaltenes) method was used [17], which relies on Chromatography separation, based on polarity and molecular mass.

2 Experimental research

2.1 Materials

The original (unaged) neat 100/150 bitumen was chosen from two kind of crude oils (paraffinic and naphthenic) for the experimental research (Table 1). This type of bitumen was selected due to the research orientation to one-layer asphalt pavements, which usually are used for lower volume roads. Moreover, previous research showed that there is no big difference in bitumen structural composition depending on bitumen penetration grade.

Table 1 Summary of tested materials

Bitumen Penetration Grade	Ageing	Code (Paraffinic Crude Oil)	Code (Naphthenic Crude Oil)
100/150	Unaged	P-NS	N-NS
100/150	RTFOT	P-RT	N-RT
100/150	PAV I (20 h)	P-PV20	N-PV20
100/150	PAV II (40 h)	P-PV40	N-PV40
100/150	PAV III (60 h)	P-PV60	N-PV60
100/150	PAV VI (80 h)	P-PV80	N-PV80
100/150	PAV V (100 h)	P-PV100	N-PV100
100/150	PAV VI (120 h)	P-PV120	N-PV120
100/150	PAV VII (140 h)	P-PV140	N-PV140

2.2 Methods

2.2.1 Laboratory ageing procedure

The neat bitumen 100/150 from naphthenic and paraffinic crude oils were aged in eight steps: (1) short-term ageing to simulate the ageing effect of asphalt mixture production and layer compaction; (2) long-term ageing (20 h) to simulate 5-15 years of pavement in-service; (3) extended (40 h) long-term ageing; (4) extended (60 h) long-term ageing; (5) extended (80 h) long-term ageing; (6) extended (100 h) long-term ageing; (7) extended (120 h) long-term ageing; (8) extended (140 h) long-term ageing. The Rolling Thin Film Oven Test (RTFOT) was used for short-term ageing of bitumen samples according to EN 12607-1 [25]. The bottles with 35±0.5 g of bitumen were placed in the oven with carousel at 163ºC, where hot air was periodically injected inside at a rate of 4000 ± 200 ml/min for 75 min. The Pressure Ageing Vessel (PAV) test was used for long-term and extended long-term ageing of bitumen after RTFOT according to EN 14769 [26]. The pans with 50±0.5 g of bitumen were placed in the pressure camber. The long-term ageing for 20 h and 40 h were performed at 100°C and 2.1±0.1 MPa air. The extended long-term ageing for 60 h, 80 h, 100 h, 120 h, 140 h were performed at 85°C and 2.1±0.1 MPa air pressure following the standard EN 14769 requirements.

2.2.2 Bitumen fractional composition (SARA)

The bitumen fractional composition (saturates, aromatics, resins, and asphaltenes - SARA) was determined using the IATROSCAN MK6s Thin-Layer Chromatograph with Flame-Ionization Detection (TLC-FID) with referring to IP 469/01 [27]. The samples were prepared dissolving 1 % ±0.1 % (m/V) bitumen in toluene. After cleaning the activated quartz rods (Chromarods), the 1 µl of sample solution was spotted on each rod with semi-automatic spotter. The frame with ten Chromarods was placed in the drying chamber at 80°C for around 2 min to evaporate the residual toluene. The bitumen fractional composition was separated placing rod frame into three tanks with different solvents: Tank A - n-heptane (100 %) to extract saturates; Tank B - toluene (80 %) and n-heptane (20 %) to extract aromatics; and Tank C - dichloromethane (95 %) and methanol (5 %) to extract resins. Finally, the quartz rods were scanned in the TLC-FID analyser. For each quartz rod the four peak areas were integrated and calculated the percent concentrations for saturates, aromatics, resins and asphaltenes.

3 Results and discussion

3.1 Ageing processes at molecular level

During the short-term ageing, efforts are made to reproduce as closely as possible the conditions for storing, mixing, transporting and laying asphalt mixture, i.e. constant air supply and slow mixing of bitumen at high temperature. On the chemical side, during short-term ageing, the oxidation of a fragment of asphaltene or resin molecule occurs by reacting heteroatoms with atmospheric oxygen to form oxidised functional groups. [O] is a general representation of an oxidizer - it can be oxygen (O_2) or an oxygen atom from other functional oxidative properties, for example, from sulfoxide.
During the short term ageing of bitumen most often occurs oxidation of sulphur. Oxidation of thioether to the sulfoxide during a short-term ageing is shown in Figure 1.

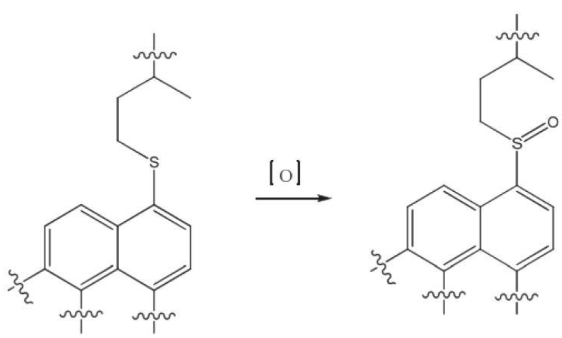

Figure 1 Oxidation of thioether to the sulfoxide during a short-term ageing

Long-term ageing seeks to influence the rheological properties of bitumen therefore the temperature is reduced up to 85-100 °C in order to reduce chemical reactions, to create atmospheric pressure, and maintain such conditions for longer. On the chemical side, during the long-term ageing, the oxidation of the asphaltene or resin fragment of molecule with atmospheric oxygen occurs when the oxygen molecule tears the hydrogen atom from the benzylic position or near the double bond to form carboxyl groups, ketones and etc. (Figure 2).

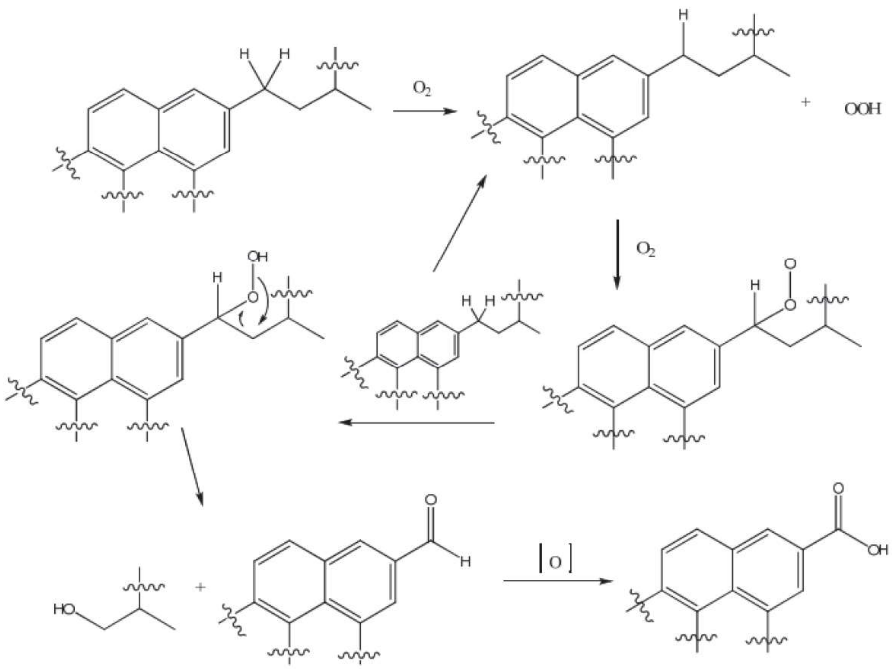

Figure 2 Oxidation of benzylic-type situation during a long-term ageing

3.2 SARA results

Four fractions, namely saturates, aromatics, resins and asphaltenes (SARA), were obtained from the same type of asphalt binder (100/150) but different crude oil sources (naphthenic and paraffinic). The results of SARA fractions were analysed by a Thin Layer Chromatography to evaluate their sensitivity to ageing (Table 1). The main idea was to check how bitumen fractions (saturates, aromatics, resins, asphaltenes) are changing depending on the ageing time as well crude oil type. The average values of five rod readings of bitumen fractional composition was used for analysis.

Investigation of the SARA fractions of bitumen after extended long-term ageing up to 140 h proved that ageing has a direct effect on transformation of fractions interpreted as a movement of components from non-polar fractions up to the more polar fractions (i.e. from saturates to aromatics – resins - asphaltenes). The results showed that unaged bitumen had the highest amount of aromatics and its amount decreased over ageing time. The dramatic decrease of aromatic fractions occurred in the period of short term ageing and 20 h of long term ageing and its content constantly decreased over ageing time. In terms of resins, the unaged bitumen had the lowest amount of this fraction which increased with the ageing time. The significant increase of resins occurred in the period of short term ageing and 20 h of long term ageing. It was expected that amount of asphaltenes will increase significantly over ageing time however asphaltene fraction increased slowly.

Table 2 Results of SARA fractions

Bitumen	Asphaltenes	Resins	Aromatics	Saturates
P-Neat	14,67	25,42	54,34	5,57
N-Neat	19,99	23,27	50,01	6,73
P-RT	16,94	25,13	52,33	5,60
N-RT	21,96	21,34	49,54	7,15
P-PV20	16,50	38,32	39,81	5,63
N-PV20	23,29	35,00	34,97	6,75
P-PV40	18,86	42,70	32,81	5,63
N-PV40	24,61	37,33	31,43	6,96
P-PV60	14,74	42,89	36,27	5,70
N-PV60	19,43	38,13	35,37	7,06
P-PV80	15,37	42,99	36,38	5,54
N-PV80	20,33	40,13	32,43	6,94
P-PV100	13,37	51,27	29,42	5,78
N-PV100	19,28	46,58	26,59	7,02
P-PV120	16,17	52,10	26,21	5,52
N-PV120	22,90	46,44	23,49	7,04
P-PV140	16,99	53,38	24,28	5,36
N-PV140	22,82	46,95	24,25	6,52

Since saturate fraction is known as stable paraffin's fraction, a mixture of pure aliphatics, aliphatics with side chains, cycloaliphatics, and cycloaliphatics with side chains, the content of saturates remains almost constant during the overall ageing process. To conclude, the ageing limit of bitumen was not reached. Longer ageing or different ageing procedure is needed in order better represent long term ageing and also so that the chromatography could show resins transformation into asphaltenes (Figure 3).
Analysis of bitumen SARA fractions from different crude oil showed that bitumen from naphthenic crude oil has obviously larger amount of asphaltenes comparing with the paraffinic crude oil, less resin and aromatic fractions. Since naphthenic crude oil contains a higher amount of sulphur, the short term ageing is faster in bitumen from naphthenic crude oil. However, in the long term perspective, the naphthenic crude oil is more resistance to ageing than paraffinic crude oil.

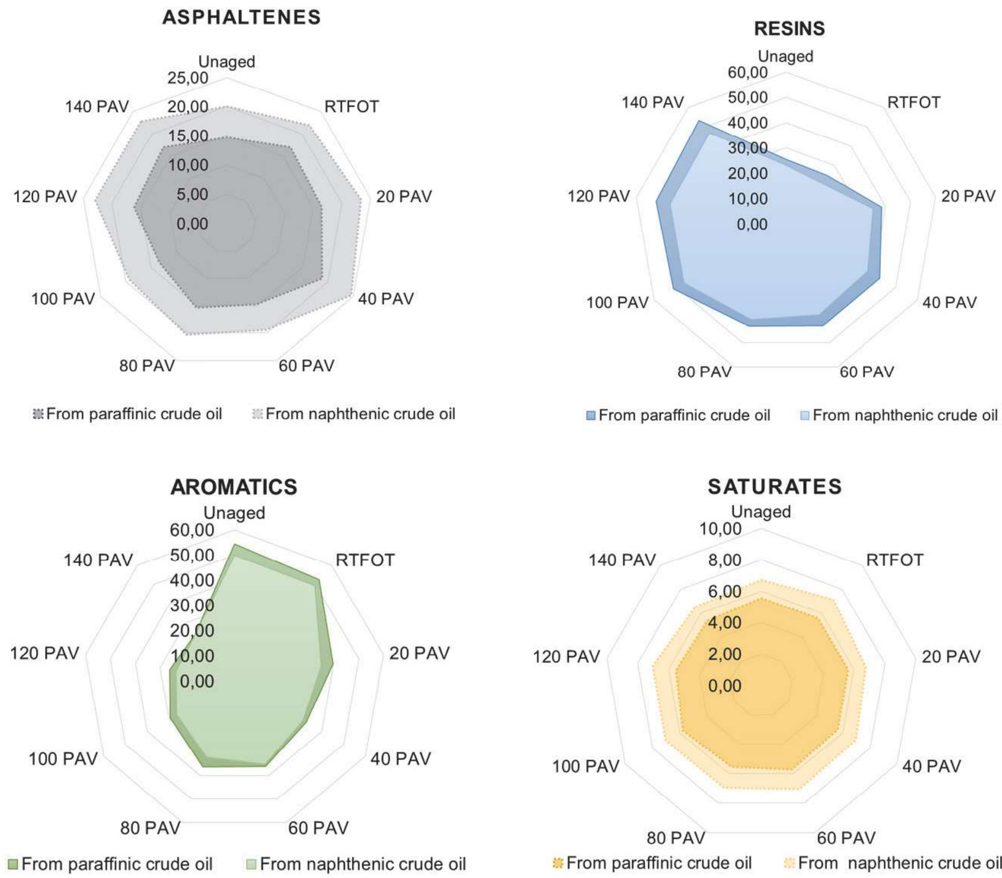

Figure 3 Comparison of SARA fractional composition depending on the ageing time and crude oil type

4 Conclusions

The study presented in this article analysed the ageing effect of neat (100/150) bitumen from naphthenic and paraffinic crude oils. The bitumen was aged up to 140 hours and after every 20 hours of ageing tested with a Thin-Layer Chromatograph. The following conclusions are summarised below:

- Short and long term ageing processes of bitumen were presented at molecular level which showed the main chemical processes and final chemical products obtained. During these two ageing processes, two phases of bitumen ageing where determined: in the first phase (short term ageing) - mainly oxidation of sulphur occurred, in the second phase (long term ageing) – oxidation of benzylic position.
- Investigation of SARA fractions of bitumen after extended long-term ageing (up to 140 h) proved that ageing has a direct effect on transformation of fractions interpreted as a movement of components from non-polar fractions up to the more polar fractions. Increasing the ageing time, the evident transformation was noticed on decrease of aromatics and increase of resins. Asphaltene fraction increased slightly, not as it was expected, since the size of asphaltene-type molecules has not increased in molecular mass yet enough so that Chromatography would attribute it as asphaltene fraction. The saturates fraction remained stable because of their low reactivity and non-polarity.
- SARA fractions showed their sensitivity to ageing especially aromatics and resins. The significant increase of resins and decrease of aromatics occurred during the period of short term ageing and 20 h of long term ageing as well as during the period of 80 h and 100 h of extended long term ageing.

- After maximum 140 h of ageing, the ageing limit or the expiry date of bitumen was not reached. That means that standard long-term ageing procedure do not represent natural long term ageing. Longer ageing or different ageing procedure is needed so that Chromatograph could show the transformation of resins into asphaltenes.

References

[1] Rossini, F.D.: Hydrocarbons in Petroleum, 1906; 554–61

[2] Sakib, N., Bhasin, A.: Measuring polarity-based distributions (SARA) of bitumen using simplified chromatographic techniques, International Journal of Pavement Engineering, 20 (2019) 12, pp. 1371-1384, DOI: 10.1080/10298436.2018.1428972

[3] Speight, J.: The Chemistry of Technology of Petroleum, Taylor Francis Group, 2006.

[4] Paliukaitė, M., Vaitkus, A., Zofka, A.: Influence of bitumen chemical composition and ageing on pavement performance, Baltic Journal of Road and Bridge Engineering, 10 (2015), pp. 97–104

[5] Nagy, B.U.C.: Fundamental Aspects of Petroleum Geochemistry, 1967.

[6] Al-Dahhan, W.H., Mahmood, S.M.A.: Classification of Crude Oils and its Fractions on the Basis of Paraffinic, Naphthenic and Aromatics, 2019.

[7] Petersen, J.C.: TRB Transportation Research Circular E-C140: A Review of the Fundamentals of Asphalt Oxidation: Chemical, Physicochemical, Physical Property, and Durability Relationships, 2009, doi: DOI: 10.17226/23002

[8] Taylor, P., Airey, G.D.: State of the Art Report on Ageing Test Methods for Bituminous Pavement Materials, International Journal of Pavement Engineering, 4 (2003) 3, pp. 165–176, doi: 10.10850/1029843042000198568

[9] Petersen, J.C., Harnsberger P.M. R.: Factors affecting the kinetics and mechanisms of asphalt oxidation and the relative effects of oxidation products on age hardening, Chemical Society, Division of Fuel Chemistry, 41 (1996) 4

[10] Yao, H., Dai, Q., You, Z.: Fourier Transform Infrared Spectroscopy characterization of aging-related properties of original and nano-modified asphalt binders, Construction and Building Materials, 101 (2015), pp. 1078–87, doi: org/10.1016/j.conbuildmat.2015.10.085

[11] Jing, R., Varveri, A., Liu X., Scarpas, A.: Ageing effect on chemo-mechanics of bitumen, Road Materials and Pavement Design, 22 (2019) 5, pp. 1044–1059, doi: org/14680629.2019.1661275

[12] Petersen, J.C.: The Chemistry of Technology of Petroleum J.C.: Chemical Composition of Asphalt As Related To Asphalt Durability: State of the Art, Transportation Research Record, pp. 13–30, 1984.

[13] Petersen, J.C., Glaser, R.: Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited, Journal Road Materials and Pavement Design, 12 (2011) 4, pp. 795-819, 2011.

[14] Petersen, J C.: Quantitative functional group analysis of asphalts using differential infrared spectroscopy and selective chemical reactions – application and theory, Transportation Research Record, pp.106–119, 1986.

[15] Wang, T., Wang, J., Hou, X., Xiao, F.: Effects of SARA fractions on low temperature properties of asphalt binders, Road Materials and Pavement Design, 2019, pp. 1–18, doi.org/14680629.2019.1628803.

[16] Lesueur, D.: The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. Advances in Colloid and Interface Science, 145 (2009), pp. 42–82

[17] Corbett, L.: Composition of asphalt based on genericfractionation, using solvent deasphaltening, elution-adsorption chromatography, and densimetric characterization. Analytical Chemistry, 41 (1969) 4, pp. 576–579

[18] Eberhardsteiner, L., Füssl, J., Hofko, B., Handle, F., Hospodka, M., Blab, R.: Towards a microstructural model of bitumen ageing behaviour, International Journal of Pavement Engineering, 16 (2015), pp. 939–49

[19] Stangl, K., Jäger, A., Lackner, R.: Microstructure-based identification of bitumen performance, Road Materials and Pavement Design, 7 (2006), pp. 111–42, doi: abs/10.1080/14680629.2006.9690061.

[20] Qin, Q., Schabron, J.F., Boysen, R.B., Farrar, M.J.: Field aging effect on chemistry and rheology of asphalt binders and rheological predictions for field aging, Energy Fuels, 121 (2014), pp. 86–94, doi: org/10.1016/j.fuel.2013.12.040.

[21] Seki, H., Kumata, F.: Structural Change of Petroleum Asphaltenes and Resins by Hydrodemetallization, Energy Fuels, 14 (2000) 5, pp. 980–985, doi: https://doi.org/10.1021/ef000009m

[22] Cuciniello, G., Leandri, P., Filippi, S., Presti, D., Polacco, G., Losa, M., Airey, G.: Microstructure and rheological response of laboratory-aged SBS-modified bitumens, Road Materials and Pavement Design, 22 (2019) 2, pp. 372-396, doi: org/14680629.2019.1621771.

[23] Redelius, P., Soenen, H.: Relation between bitumen chemistry and performance, Energy Fuels, 140 (2015), pp. 34–43, doi: 10.1016/j.fuel.2014.09.044

[24] Filippelli, L., Gentile, L., Rossi, C.O., Ranieri, G.A., Antunes, F.E.: Structural Change of Bitumen in the Recycling Process by Using Rheology and NMR, Industrial & Engineering Chemistry Research, 51 (2012) 50, doi: 10.1021/ie301899v.

[25] LST EN 12607-1: Bitumen and bituminous binders - Determination of the resistance to hardening under influence of heat and air - Part 1: RTFOT method, Lithuanian standards board, Vilnius, 2015.

[26] EN 14769: Bitumen and bituminous binders - Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV), 2012.

[27] IP 469/01: Determination of saturated, aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionization detection, 2006.