Synthetic Wax Additives for Modifying the Viscosity of Road Bitumen

MIHAELA BOMBOS[1] GABRIEL VASILIEVICI[1], DORIN BOMBOS[2]*

[1]National Institute for Research Development for Chemistry and Petrochemistry- ICECHIM-Bucuresti, 202 Splaiul Independetei, 060021, Bucharest, Romania

[2] Petroleum - Gas University of Ploiesti, 39 Calea Bucuresti,100520, Ploiesti, Romania

Using environmentally friendly products in the roads construction like friendlier warm mix asphalts, involves reducing the temperature of asphalt mixtures manufacturing. For this purpose it is recommended to identify synthetic additives that reduce the temperature of asphalt mixture preparation and therefore energy costs of asphalting process. The waxes presence in conventional bitumen road was considered along time inopportune. Three types of amide waxes were synthesized by treating ethylene diamine with a fatty acid and a dicarboxylic acid. Prepared additives characterization was performed by determining the melting points and thermogravimetric behaviour.

Keywords: bitumen, wax additive, catalyst

Asphalt surfaces subject to heavy traffic, in hot climates may suffer permanent deformation processes (rutting/grooving), their appearance is the result of heavy car whose tires exercise high pressures. Reducing these phenomena can be achieved by improving the synthesis process bitumen [1], by additivation or modification of road bitumen [2,3] or by reducing the temperature of asphalt mixtures manufacturing in order to avoid the bitumen aging. Reducing the temperature of asphalt mixture manufacturing require the use of a bituminous binder with a suitable fluidity at the fabrication temperature. This is achieved by using a suitable additive.

The waxes presence in conventional bitumen road was considered along time inopportune. In a recent paper was presented an analysis for the study of the effect of bitumen wax on performance and rheological behaviour of bitumen. Such bitumen mixtures with a high wax content tend to be very soft at higher temperatures leading to rutting problem on pavement. Also, the rheological behaviour of bitumen is strongly influenced by the bitumen wax content. To prevent potential negative effects of the bitumen waxes, many European countries limited to 2.2% the wax content. Dynamic shear rheometer test results (Dynamic Shear Rheometer) at seven asphalt bitumen indicated that the performance at both high and intermediate temperatures were affected by the bitumen wax content. DMA tests can adequately describe the effect of wax content on the bitumen rheological properties. The wax melting point has a value of 20-55°C when this is in bitumen, temperature which is about 20°C lower than of the isolated wax [4].

Five different waxes such as Fischer-Tropsch synthetic hydrocarbons, wax Montana and amide waxes were used in addition of road bitumen. The effects of these waxes on the rheology of the binder has been shown to be primarily controlled by the characteristics of these waxes [5].

Using environmentally friendly products in the roads construction like friendlier warm mix asphalts, involves reducing the temperature of asphalt mixtures manufacturing. For this purpose it is recommended to identify synthetic additives that reduce the temperature of asphalt mixture preparation and therefore energy costs of asphalting process.

In a recent paper were evaluated main advantages and disadvantages of using multiple bitumen mixtures and synthetic wax (eg, reduced production temperature, resistance to fatigue and permanent deformation), in order to select the best option application of these hot asphalt mixtures. It was revealed that adding these synthetic waxes have little effect on reducing the bitumen viscosity, on the production and application temperatures. The best solution for production of hot mix asphalt bitumen is to use softer bitumen for the incorporation of these additives based on synthetic wax, in order to maximize the mixing temperature reduction [6] .

In another paper it was studied the effect of the three types of commercial waxes and phosphoric acid on three types of bitumen 160/220 penetration by using various types of laboratory equipment, such as dynamic shear rheometer, bending beam rheometer, differential scanning calorimeter, ductilometer force and equipment to determine conventional parameters such as penetration, softening and Frass breaking point. This paper studies the influence of low temperatures on thermal cracking resistance of asphalt. The results show that the size and type of effects on bitumen rheology depend on the bitumen type, as well as the type and amount of additive used. Bitumen composition proved to be the most important factor affecting the asphalt performance. The polyethylene wax and polyphosphoric acid addition, in particular for a nonwaxy bitumen 160/220, shows a positive impact on the rheological behavior at low temperature. There could not be found correlations between wax content and bitumen characteristics. Thus the DSC enthalpy change is not a good indicator for sensitivity to low temperature cracking. For example, a bitumen containing 3.8 % crystallized product fraction (natural bitumen wax), determined by DSC showed a 53 % physical strengthening at -25°C while bitumen containing 10.5 % of DSC crystallized fraction (wax commercial) showed only 7 % [7].

Another paper proposes a technology using hot asphalt with bitumen additives based wax or surfactants additives. Using both surfactants compounds and waxes as additives can reduce manufacturing asphalt mixture temperature

* email: dorin_bombos@yahoo.com

No.crt.	Characteristics	Values
1.	Appearace	yellow liquid
2.	Water content, ppm	200
3.	Flash Point, °C	184
4.	Density, g/cm^3	0,839
5.	Saponification index , mg KOH/g	152

Table 1
CHARACTERISTICS OF FATTY ACID METHYL ESTERS FROM SOYBEAN OIL

No.crt.	Technical characteristic	D50/70
1.	Penetration, 1/10 mm	61
2.	Softening point , ^{0}C	45,3
3.	Ductility at 25^{0}C, cm	>145
4.	Breaking point, ^{0}C	-15
5.	Adhesion, %	79,2
6.	RTFOT	
6.1	Mass variation, %	-0,167
6.2	Residual penetration, %	55
6.3	Ductility, cm	10,3
6.4	Softening point, ^{0}C	56,5
6.5	Softening point increase , ^{0}C	11,2

Table 2
CHARACTERISTICS OF ROAD BITUMEN D50-70

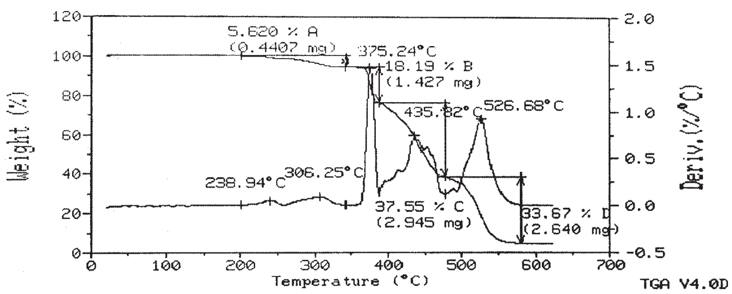

Fig 1. Thermal behavior of road bitumen D50-70

to 140°C, with similar mechanical characteristics like hot mix asphalt. The bitumen with surfactant used in the hot asphalt has reduced fuel consumption. Thus, fuel consumption in the hot mix asphalt preparation can be reduced by 35%. The results showed that the use of wax or surface additives in hot mix asphalt paving technology do not have a negative effect on the pavement mechanical properties [8].

Results and expertise about the negative effects of wax on bitumen road is mainly based on laboratory research. Only a few studies on the effect of wax on bitumen were conducted on industrial asphalt mixtures. This paper aims to assess the influence of some synthetic waxes on the bitumen rheological characteristics.

Experimental part

In the experimental program were prepared three types of amide waxes which differ in dicarboxylic acid nature (oxalic acid 99% Sigma Aldrich and terephthalate acid 98% Sigma Aldrich) and the fatty acid type (stearic acid Sigma Aldrich and fatty acid methyl esters from soybean oil whose physical characteristics are presented in table 1), aliphatic amine used in the synthesis is ethylenediamine Sigma Aldrich 99%.

Waxes obtained were used for addition in the road bitumen D50-70. The physical characteristics of road bitumen D50-70 are presented in table 2, and its thermal behaviour its was determined on a DuPont Instruments device “Thermal Analyst 2000/2100” coupled with a “Thermogravimetric Analizer 951” module is shown in figure 1.

Variation of mass loss with temperature for road bitumen used in experiment highlights a volatile content with distillation range 240 -375^{0}C over 5%, a light mineral oil content of approx. 18% and a heavy mineral oil content of about 38%.

The raw materials used for additive preparation were ethylenediamine p.a. Aldrich, stearic acid p.a. Aldrich, oxalic acid p.a. Aldrich, terephthalic acid p.a. Aldrich and fatty acid methyl esters from soybean oil whose characteristics are presented in table 2.

The molar ratio of reactants was: ethylene diamine / dicarboxylic acid / fatty acid = 2/1/2. The condensation process was performed in a three-necked flask equipped with stirring and a horizontal condenser at 180 ^{0}C temperature during 8 hours.

Characterization of reaction products was performed by thermogravimetric analyzes and by determining the melting points. Road bitumen was mixed with 2% wt. waxes in an autoclave at 180^{0}C during 6 h. Viscosity variation with temperature for bitumen with amide waxes was performed using a Viscotester Haake. Influence of waxes content on penetration of bitumen road was studied for wax whose melting temperature is the nearest for the temperature at which is desired to produce mix asphalt, respectively approx. 140^{0}C.

Fig. 2.Melting points of the waxes obtained in the experimental reactions

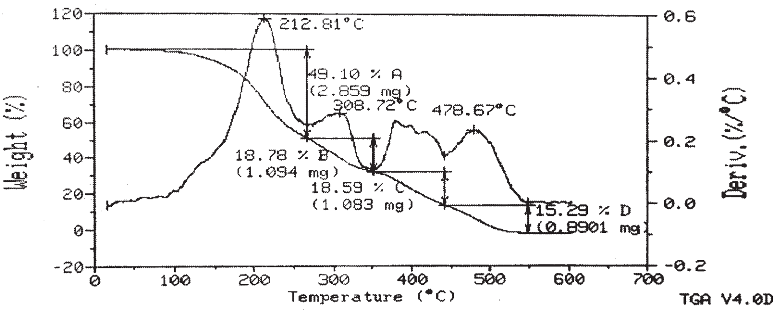

Fig. 3. Thermal behavior of Csoy wax

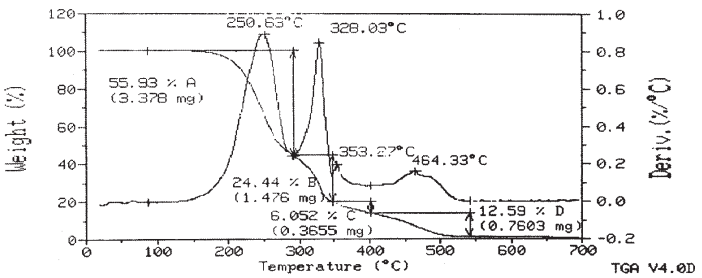

Fig. 4. Thermal behaviour of Cste wax

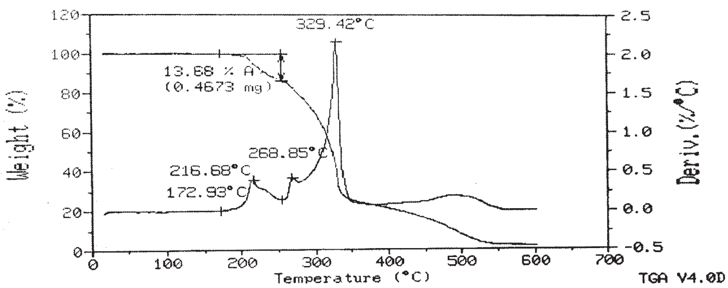

Fig. 5. Thermal behaviour of Cox wax

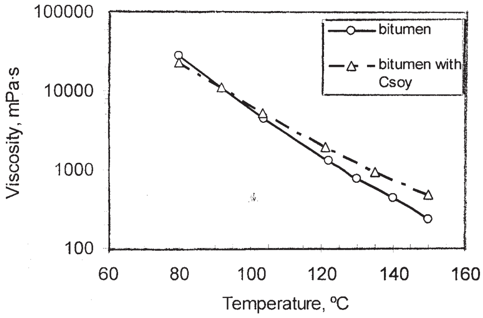

Fig. 6. Influence of the addition of Csoy wax on road bitumen viscosity

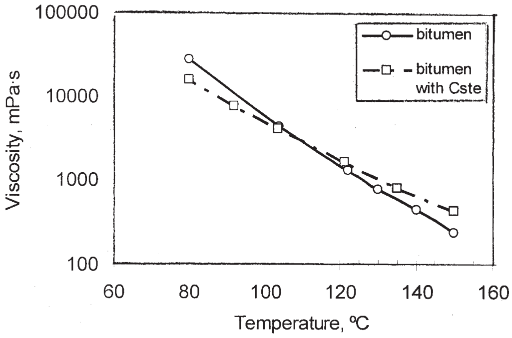

Fig. 7. Influence of the addition of Cste wax on road bitumen viscosity

Results and discussions

In the experimental program were prepared three bisamidic waxes that differ by carboxylic acids nature. Thus, for the first wax synthesis (Csoy) was used methyl esters of soybean oil fatty acids as the monocarboxylic acid and terephthalic acid as dicarboxylic acid, for the second wax synthesis (Cste) was used stearic acid as monocarboxylic acid and terephthalic acid as dicarboxylic acid and for the synthesis of the third wax (Cox) was used stearic acid as a monocarboxylic acid and oxalic acid as dicarboxylic acid. Melting points of synthesized waxes determined with Boethius device, are summarized in figure 2.

Note that the melting point of bisamidic waxes increases with the melting point of fatty acids used in the preparation of waxes and decreases when changing oxalic acid with terephthalic acid.

Thermal analysis for the three waxes is shown in Figure 3-5. In the case of waxes based on fatty acids of soybean oil (Csoy) the weight loss takes place in the temperature range of 100^{0}C -550^{0}C and about half the loss of weight being made up to 310 ^{0}C. There are four maximum for mass loss, the most obvious being the first at a temperature of 213^{0}C (fig. 3).

The wax based on stearic acid (Cste) have a mass loss at temperature range of 150^{0}C -525^{0}C, over half of the mass loss being made up to 280^{0}C. There are three maximum for mass loss, the first at temperatures of 250^{0}C, second at 328^{0}C and third at 464 ^{0}C (fig. 4).

The wax based on oxalic acid based have the mass loss at temperature range of 180^{0}C -550^{0}C, more than half of the mass loss being achieved at temperatures of 300^{0}C - 350^{0}C. There are four maximum mass loss, the most obvious being at the temperature of 330^{0}C (fig. 5).

Influence of the waxes addition on road bitumen viscosity was studied at a 2% wax concentration and is shown in figure 6-8.

From figure 6 it is observed that at values of temperature below 90^{0}C, the viscosity of bitumen modified with wax on fatty acids from soybean oil becomes greater than that of the bitumen without additives, growth of temperature at higher value increasing its fluidity.

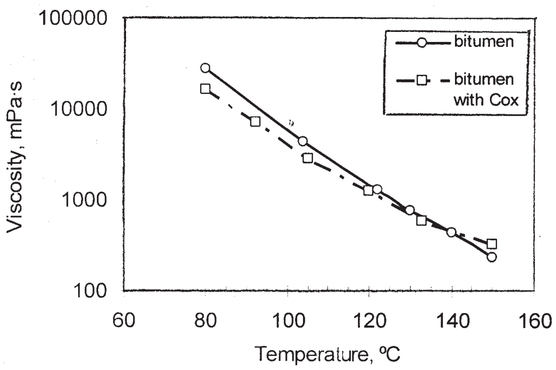

Fig. 8. Influence of the addition of Cox wax on road bitumen viscosity

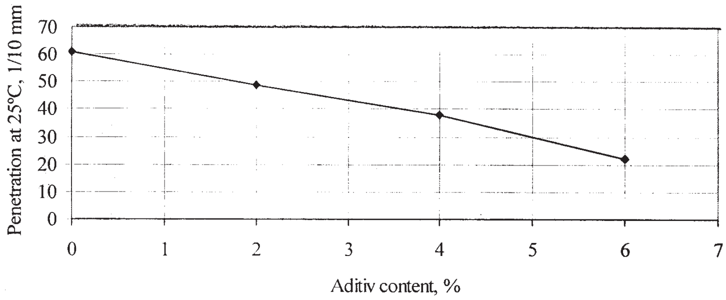

Fig. 9. Influence of Cox wax content on bitumen penetration

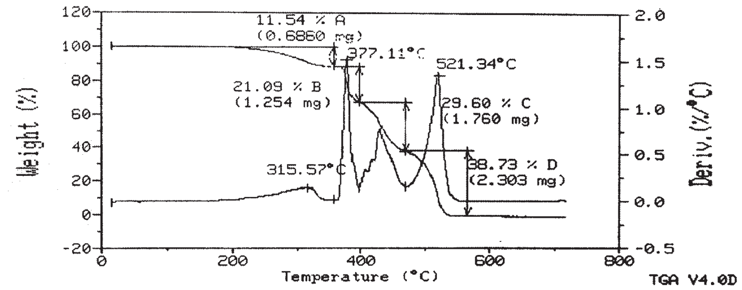

Fig. 10. Thermal behaviour of bitumen modified with 2% wax Cox

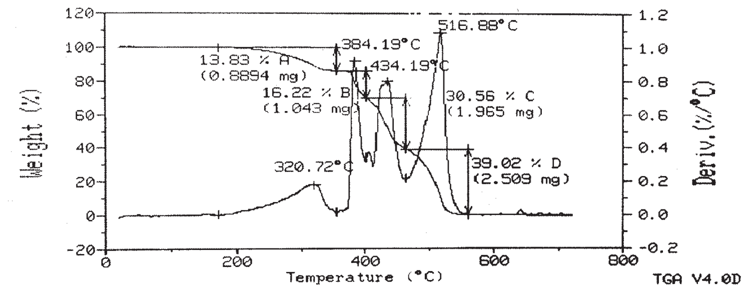

Fig. 11. Thermal behaviour of bitumen modified with 4% wax Cox

From figure 7 it is observed that the slope of the variation of viscosity of bitumen additived with wax based on stearic acid is less than for unmodified bitumen, the temperature of the two curve intersecting being approx. 110^{0}C. Increasing the temperature at higher that 120^{0}C, fluidity of bitumen additivated increase better that of unmodified bitumen.

From figure 8 it is observed that in the case of bitumen additived with wax based on oxalic acid slope of the variation of viscosity is lower than for unmodified bitumen, the two curve of the test intersecting at over 130^{0}C.

The influence of Cox wax content on road bitumen penetration is shown in Figure 8 and the thermogravimetric curves of bitumen admixed with 2 and 4% Cox wax are shown in figures 9 and 10.

It is seen from figure 10 that the penetration of bitumen decreases with increasing wax content at a constant value of slope.

The increase of the content of wax based oxalic acid favours increasing the volatile content which distilled until 375^{0}C; variation curves are similar for both asphalt additives. There are four maximum of mass loss, the most obvious being at the temperature of 330^{0}C.

Conclusions

Three types of amide waxes were synthesized by treating ethylene diamine with a fatty acid and a dicarboxylic acid. The reactants molar ratio was: ethylene diamine / dicarboxylic acid / fatty acid: 2/1/2. Dicarboxylic acid was oxalic acid or terephthalic acid and fatty acid was stearic acid or fatty acid methyl esters from soybean oil.

Prepared additives characterization was performed by determining the melting points and thermogravimetric behaviour. Melting point of bisamidic waxes increases with melting point of fatty acids used in the preparation of waxes and decreases when changing oxalic acid with terephthalic acid.

Mass loss curves are similar for the 3 types of wax, showing a higher content of volatile compounds in wax-based fatty acids for soybean oil.

Influence of the waxes addition on road bitumen viscosity was studied at a 2% wax concentration. Curves of variation of viscosity with temperature for bitumen modified with the three types of waxes differ by the temperature at which they intersect the curve of variation of viscosity with temperature for unmodified bitumen.

Influence of waxes content on penetration of bitumen road was studied for wax whose melting temperature is the nearest for the temperature at which is desired to produce mix asphalt, respectively for oxalic based wax; the penetration of bitumen decreases with increasing wax content at a constant value of slope.

Use in road bitumen of bis amidic waxes improved rheological characteristics, representing a viable alternative to replace classical additives.

References

1. VASILIEVICI, G., BEICA, V., BOMBOS, D., BOMBOS, M., ZAHARIA, E., Rev. Chim. (Bucharest), **62**, no.6, 2011, p. 672

2. BOMBOŞ, D., BOLOCAN, I., BOMBOŞ, M., JUGANARU, T., NAUM, N., Rev. Chim. (Bucharest), **57** , no.11, 2006, p.1162-1166

3. DIMONIE, M., DIMONIE, D., VASILIEVICI, G., BEICA, V., BOMBOS, D., Mat. Plast., **44**, no. 1, 2007, p.72-76

4. WING-GUN WONG, GANG LI, Constr. Build. Mater., **23**, 2009, p.2504–2510

5. POLACCO, G., FILIPPI, S., PACI, M., GIULIANI, F., MERUSI, F., Fuel, **95**, 2012, p.407–416

6. SILVA, M.R.D. H., OLIVEIRA, R.M. J., PERALTA, J., ZOOROB, S. E., Constr. Build. Mater., **24**, 2010, p.1621–1631

7. EDWARDS Y., TASDEMIR Y., ISACSSON U., Fuel, **85**, 2006, p. 989–997

8. PEREZ-MARTINEZ, M.., MORENO-NAVARRO, F., MARTIN-MARIN J., RIOS-LOSADA C., C., RUBIO-GAMEZ, M. C., J. Clean. Prod., 2013, in press

Manuscript received: 17.09.2013