# INFLUENCE OF WAXES ON POLYMER MODIFIED MASTIC ASPHALT PERFORMANCE

#### Y. EDWARDS

Royal Institute of Technology, Highway Engineering, Brinellvägen 34, 10044 Stockholm, SWEDEN

#### ABSTRACT

The paper contains a short introduction and background concerning wax additives in bitumen and asphalt mixtures. Focusing on polymer modified coarse aggregate mastic asphalt, the use of wax additives in Europe is reviewed. Commercial wax such as FT-paraffin and montan wax are typical so-called bitumen flow improvers, which are used in practice for asphalt pavements and mastic asphalt to reduce the mixing temperature and thereby energy consumption and emissions. Workability may be improved as well. These waxes differ a great deal from natural bitumen wax concerning molecular weight and molecular weight distribution. They have high congealing points around 100°C and higher melting areas compared to natural wax in bitumen.

Results are presented from an ongoing joint Swedish project about wax as flow improver in polymer modified bitumen for mastic asphalt production. Different aspects are dealt with. The aim of the project is to make mastic asphalt used in Sweden today (for bridges, parking decks etc.) more environment friendly and easier to handle. However, wax modification must not have any noticeable negative impact on the performance of mastic asphalt products at medium and lower temperatures.

The project involves laboratory testing of wax and polymer modified binders and mastic asphalt mixtures. Field studies are included as well. Effects of adding two commercial waxes to one polymer modified bitumen are presented in this paper.

The results show that both waxes have a flow improving/viscosity depressant impact on the polymer bitumen at higher temperatures, indicating a possible lower laying temperature for the mastic asphalt if modified with such waxes. Moreover, there is a stiffening effect at medium and high temperatures (below laying temperature), indicating a certain positive effect on stability.

Concerning low temperature performance, there are results indicating negative impact on crack susceptibility at low temperatures, larger effect by the addition of FT-paraffin than by the addition of montan wax.

Keywords: wax, modified binders, mastic asphalt

#### **1. INTRODUCTION**

As a consequence of lower limit values for bitumen emissions in connection with asphalt works, and harder requirements for lower carbon dioxide emissions, new temperature reducing asphalt technologies have been developed. One way of reducing the asphalt mixing temperature is by adding special flow improving products such as waxes. The chief purpose of adding the wax is to reduce the mixing temperature of the asphalt in order to reduce energy consumption and emissions of bitumen fumes and aerosol. As a rule, the workability of the asphalt is improved as well. Below the laying temperature, there may also be an increase in viscosity due to wax crystallization, and by that some stiffening effect. Consequently, the asphalt pavement may gain better resistance to plastic deformation. In the case of asphalt concrete, lower void content due to better compaction properties may make the pavement more durable. However, other pavement properties, such as crack susceptibility at low temperatures, fatigue resistance and adhesion could be affected by the addition of flow improvers as well [1]. Different bitumen compositions are more or less sensitive to wax additives. Bitumen of different origin ought to be specially studied, in order to at least adjust the flow improver to the bitumen and avoiding deterioration of bitumen properties as a result of adding the flow improver. Coarse aggregate mastic asphalt products require high working temperatures, and the use of wax additives therefore has become more frequently used, especially in Germany.

For bridges and parking decks in Sweden, mainly mastic asphalt is used. As a rule, the mastic asphalt is polymer modified and the laying temperature is between 200 and 230°C, depending on laying conditions. This paper focuses on the addition of wax to polymer modified bitumen intended for use in mastic asphalt pavements. A short introduction and background concerning wax additives in bitumen and asphalt mixtures is given in the following chapter.

Results from a recently initiated joint Swedish project about wax additive in polymer modified bitumen for mastic asphalt is presented.

#### 2. THE USE OF WAX ADDITIVES IN BITUMEN AND ASPHALT MIXTURES

Typical viscosity lowering products used for asphalt pavements are FT-paraffin, montan wax, oxidized polyethylene wax, thermoplastic resins and fatty acid amide. Molecular weight distributions of such products vary, as well as their impact on asphalt concrete or mastic asphalt properties. Zeolites are another type of additive belonging to a group of hydrated aluminium silicates [2]. However, zeolites are not used in mastic asphalt. Most used in practice are FT-paraffins and montan waxes. Addition of 2-3 % wax by mass of the bitumen in mastic asphalt normally has been used.

Structurally, FT-paraffin is similar to natural paraffin wax in bitumen. The difference between bitumen paraffin wax and FT-paraffin lies in the considerably longer molecules of FT-paraffin, of which n-alkanes lie in the range of 40 to 115 carbon atoms. The longer molecules result in a considerably larger melting area for the pure FT-paraffins, 65-120°C, and a congealing point of about 100°C. FT-paraffin is produced in a so-called Fischer Tropsch synthesis, where carbon monoxide is converted into higher hydrocarbons and oxygenates in catalytic hydrogenation followed by a distillation process. The viscosity lowering effect on a binder due to the addition of such wax may allow working temperatures to be decreased by up to 50°C [3].

Montan wax is a partly bituminized fossil ester wax which can be extracted from brown coal. It has a more complicated structure compared to FT-paraffin and is available in a number of product variants depending on range of use (type of bituminous product). Since the beginning of the 1980's, montan waxes have been used as additive for mastic asphalt, initially as a result of harder requirements for lower carbon dioxide emissions in Germany, but later also for obtaining better workability of asphalt mixtures. Montan waxes have been modified specifically for this purpose, but also with the intension of improving for instance asphalt pavement adhesion properties. Typical montan wax products have congealing points in the area of 75 to 125°C.

So, the main purpose of adding wax to bitumen normally is to lower the viscosity within a certain temperature range. In turn, this may lead to better workability, perhaps a longer paving season and less needed roller compaction (for asphalt concrete mixtures). Energy consumption reductions are considered to be a very important benefit of wax addition (and other similar techniques). Production costs at the asphalt plant may be lower due to lower production temperature and shorter production time. Less wear of equipment in the plant is another possible favourable consequence. On the other hand, production costs may increase by the extra cost of wax, and if equipment modification is needed for the new production process. Lower production temperature also means reduced emissions, which otherwise may be a problem, or even injurious to health, during asphalt production and paving. Bitumen fume in connection with indoor asphalt works is known to be most problematic.

Wax as flow improver shows a softening effect on the binder and asphalt mix at higher temperature (above 80°C). In addition to that, a stiffening effect occurs below the paving temperature as a result of wax crystallization. By that, the asphalt pavement resistance to permanent deformation may increase as well. Rheological effects of adding wax to bitumen can be studied using dynamic mechanical analysis (DMA). In DMA, the ratio of peak stress to peak strain is defined as the complex modulus  $|G^*|$ , which is a measure of the overall resistance to deformation of the sample tested. The phase difference between stress and strain is defined as the phase angle  $\delta$ , and is a measure of the viscoelastic character of the sample. For a completely viscous liquid, the phase angle is 90° and for an ideal elastic solid material, the phase angle is 0°. Complex modulus and phase angle of bitumens are functions of temperature and frequency, which may be changed by the addition of different additives such as waxes and polymers.

Laboratory and field studies are being performed in Germany for a large set of wax/binder systems. The project is a joint project between BASt (Bundesastalt für Strassenwesen), BMVBW (Bundesministerium für Verkehr, Bau- und Wohnungswesen) bitumen producers, wax producers and others. Test sections were constructed in June 2004 on the motorway A7 near Flensburg, and will be studied for at least a period of eight years. The aim of the project is to develop some ZTV Asphalt requirements specifications for so called TA Asphalt (temperaturabsenkende) in Germany [4]. Other test sections were constructed near Schwerin the same year. In both cases, polymer modified bitumen (Pmb 45 A) was used as reference. None of the test sections is mastic asphalt. However, polymer modified mastic asphalt pavements containing wax additive most certainly have been used in practice.

Also in France, technical temperature reduction procedures are known to be used for mastic asphalt [5].

In Sweden, several laboratory studies regarding the influence of wax additives on bitumen and asphalt concrete properties have been performed recently. One of these studies deals with polymer modified mastic asphalt and the influence on binder and mix properties of adding two different types of commercial wax products. Results from the binder study are presented and discussed in the following chapter.

#### 3. EXPERIMENTAL

## 3.1 Materials

The polymer modified bitumen used was a 50/100-75 class product (Pmb 32) produced by Nynas. The commercial wax additives were FT-paraffin (Wax S) and montan wax (Wax A). Their characteristics are presented in Table 1. Levels of 3 and 6% wax by mass of the bitumen were used. Mixing was carried out by the bitumen producer. Samples were aged using the RTFO (Rolling Thin Film Oven) test.

Additive	Characteristics	Value
Wax S,	Congealing point (ASTM D 938)	100 (°C)
(FT paraffin wax)	Penetration at 25°C (ASTM D 1321)	<1 (dmm)
	Penetration at 65°C (ASTM 1321)	7 (dmm)
Wax A, Solidification point		120-130 (°C)
(Montan wax)	Dropping point	125-135 (°C)
	Viscosity at 150°C	5-20 (mPas)

# 3.2 Methods of analysis

The following test methods were used:

- Softening point (EN 1427)
- Penetration at 25°C (EN 1426)
- Breaking point Fraass (EN 12593)
- Dynamic viscosity, Brookfield at 135 and 180°C (ASTM D442)
- Elastic recovery at 10°C (EN 13398)
- Force ductility at 10°C (EN 13589, EN 13703)
- Storage stability at 180°C (EN 13399)
- DSR temperature sweep from -30 to +80°C at a frequency of 10 rad/s (AASHTO TP5)
- BBR analysis at -18 and -24°C (EN 14771)
- DSC (Differential Scanning Calorimetry)

## 4. RESULTS AND DISCUSSIONS

Results are presented in Table 2 and show a viscosity reduction of approximately 60 units at 180°C by the addition of 6% Wax S or Wax A, corresponding to a possible temperature reduction in laying temperature of about 10°C.

Adding Wax S shows a somewhat larger stiffening effect, compared to Wax A, at temperatures around 30 to 60°C. This is indicated by higher complex modulus and lower phase angle as shown for original samples in Figure 1, and laboratory aged samples in Figure 2. The influence on softening point and penetration also is larger for Wax S compared to Wax A, especially for original samples.

Storage stability seems to be improved by the addition of wax. Or rather, the softening point is increased to an extent corresponding to what also happens during laboratory ageing in RTFO. Pmb 32 containing no wax is not storage stable, and the softening point is marginally changed after laboratory ageing. Consequently, the softening point initially is increased by the addition of wax, but also further increased if stored or aged. After storage for 72 hours at 180°C, all samples containing wax show a softening point of about 100°C. After ageing, the softening point is about 90-100°C for all samples containing wax. It should be noted about Pmb 32 that the softening point could vary depending on sample preparation temperature and time.

The elastic recovery at 10°C is somewhat decreased by the addition of 3 % wax. At the higher wax level, test specimens break before reaching the elongation length of 200 mm (as specified in the test method). After ageing, all samples containing wax break during the test. Elastic recovery was determined at 10°C (not 25°C) as this is required in the Swedish specification for pmb products.

Also in force ductility at 10°C, all aged samples containing wax break (before elongation to the specified 40 cm according to that test method). As force ductility is considered to be a measure of cohesion and homogeneity of the test sample, the test results indicate a stiffening effect at 10°C related to probably a decrease in cohesion.

Concerning low temperature performance, the breaking point is slightly affected by the addition of wax. Low temperature testing by BBR shows an overall increase in stiffness at -18°C, indicating a negative impact on crack susceptibility at low temperatures, larger by the addition of Wax S than by the addition of Wax A.

For controlling the low temperature cracking propensity according to SHRP, the BBR test is performed at a temperature 10°C above the expected lowest pavement temperature for the actual PG (Performance Grade). In order to fulfil the requirements, the creep stiffness must not exceed 300 MPa and the m-value must be at least 0,300. A lower limit temperature (LST at which S=300 MPa or LmT at which m=0.300) can be determined from BBR results at two or more different temperatures. This was done based on test results at -18 and  $-24^{\circ}$ C. Additional BBR analyses were performed at  $-6^{\circ}$ C for aged samples containing wax. For original samples, the results show that the limit temperatures were somewhat affected by the addition of wax. The highest stiffness limit temperature ( $-17^{\circ}$ C) as well as highest m-value limit temperature ( $-12^{\circ}$ C) of original samples was registered for the binder containing 6% Wax S. For aged samples, the lower limit temperatures were even more affected by wax additives. For instance, adding 6% Wax S made the m-value limit temperature increase from -18 to approximately  $-5^{\circ}$ C.

Characteristics	Pmb 32	Pmb 32 +3% Wax S	Pmb 32 +3% Wax A	Pmb 32 +6% Wax S	Pmb 32 +6% Wax A
Softening point, °C	74	96	70	94	77
Penetration, dmm	56	39	51	35	45
Breaking point Fraass, °C	-15	-11	-12	-10	-13
Elastic recovery 10°C, %	79	75	73	Break at	Break at 15-
,,,				7-8 cm	18 cm
Force ductility 10°C, Nm	5,5	6,7	5,1	5,5	5,6
Brookfield visc. 135°C, mPas	1 636	1 419	1 150	1 192	945
Brookfield visc. 180°C, mPas	299	273	260	239	236
BBR -18°C, S MPa /m-value	225/0,319	234/0,282	214/0,318	314/0,260	212/0,296
BBR -24°C, S MPa /m-value	451/0,259	463/0,230	440/0,225	456/0,222	460/0,238
LST,°C	-20	-20	-20	-17	-20
LmT, °C	-20	-16	-19	-12	-18
Storage stability at 180 °C:					
Softening point top, °C	100	103	95	106	100
Softening point bottom,°C	72	93	94	101	99
DSC wax melted out temp, °C	-	114	112	114	120
After RTFOT					
Softening point, °C	70	94	88	99	90
Penetration, dmm	38	25	28	22	30
Breaking point Fraass, °C	-11	-11	-14	-7	-14
Elastic recovery 10°C, %	65	Break at	Break at	Break at	-
		6 cm	9 cm	2 cm	
Force ductility 10°C, J/cm <sup>2</sup>	6,1	7,2*	7,3*	5,4*	4,6*
BBR -18°C, S MPa / m-value	239/0,304	303/0,248	294/0,275	363/0,225	299/0,278
BBR -24°C, S MPa / m-value	461/0,234	540/0,216	434/0,221	574/0,197	527/0,212
BBR -6°C		84/0,346	59/0,433	115/0,297	77/0,388
LST,°C	-20	-18	-18	-16	-18
LmT, °C	-18	-8 (-12)**	-15	-2 (-5)**	-16

\* Break at  $\geq$  30 cm

\*\* Estimated from measurements performed at -24, -18 and -6°C.

Table 2:Test results for Pmb 32 with and without wax additive

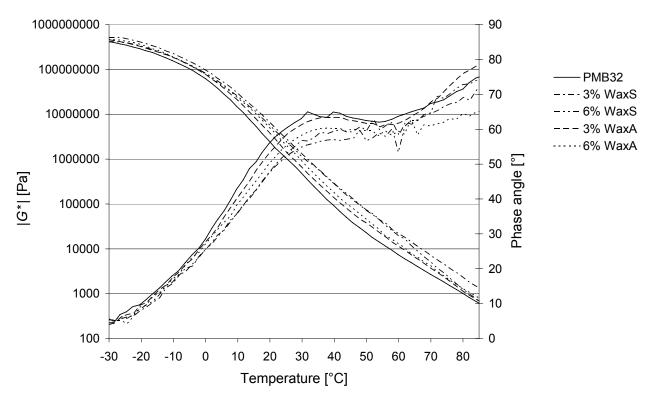


Figure 1: DSR temperature sweep from -30 to 80°C at a frequency of 10 rad/s for Pmb 32 containing wax

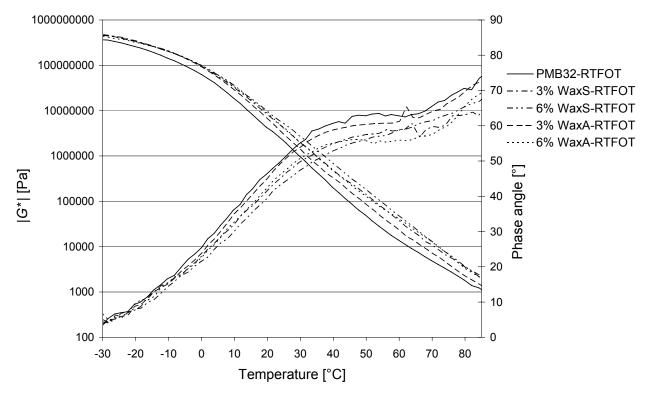


Figure 2: DSR temperature sweep from -30 to 80°C at a frequency of 10 rad/s for Pmb 32 containing wax, after laboratory ageing

### 5. CONCLUSIONS AND FURTHER WORK

Based on results for binder mixtures so far in this study, the following preliminary conclusions may be drawn:

 Both waxes (Wax S and Wax A) have a flow improving/viscosity depressant impact on Pmb 32 at higher temperatures, indicating a possible lower mixing and laying temperature for mastic asphalt products if modified with such waxes.

- Concerning binder performance at temperatures lower than approximately 100°C, there is a stiffening effect due to
  wax modification, indicating a certain positive effect on stability. This was shown in DSR temperature sweeps,
  increase in softening point and decrease in penetration value.
- However, this stiffening effect appears also at very low temperatures, indicating a negative impact on crack susceptibility, larger by the addition of Wax S than by the addition of Wax A. Most affected is the lower limit mvalue temperature by BBR. For aged samples containing 6% Wax S, this lower limit m-value increased by about 15°C, while the corresponding increase for samples containing 6% Wax A was only 2°C.

Further laboratory testing will be performed on mastic asphalt test specimens containing selected binder mixtures. Indentation value at 40°C will be determined and dimensional stability at 80°C (according to EN 12970, Annex B). The tensile strain restrained specimen test (TSRST) will be carried out as well for further knowledge about low temperature performance of mastic asphalt containing polymer- and wax modified binders.

#### 6. REFERENCES

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