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Innovative Road Rehabilitation and Recycling Technologies
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By

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SUMMARY

From a performance point of view, bitumen is one of the most important constituents of an asphalt mixture. The quality and properties of bitumen depend largely on the chemical composition of the bitumen, which is mainly controlled by the crude oil and production process. This paper covers the life cycle of bitumen. It starts with a brief discussion about the influence of crude oil and production process on the quality and properties of the bitumen. Also, some attention is paid to models, which describe the bitumen structure.

Usually the contractor or asphalt producer selects the bitumen. Ideally, the selection is based on the performance requirements for the asphalt mixture/asphalt layer. To be able to do so, they should know about the asphalt pavement performance requirements, the significance of bitumen with respect to the performance requirements for asphalt mixtures/asphalt layers and the performance/properties of the available bitumen. These aspects are thoroughly discussed in this paper. Special attention is paid to the asphalt and bitumen performance requirements for hot and arid regions like the Middle East and North Africa, and ageing of bitumen, i.e. the ageing mechanisms, determination of ageing resistance and changes in bitumen composition and performance/properties due to ageing. Finally, some ways to improve the performance/properties of bitumen are also discussed.

In this paper relevant test data from international studies as well as studies performed by Ooms Avenhorn Holding are presented. Included are many examples of well performing bitumen and some examples of unsuitable bitumen.

INTRODUCTION

For areas with hot temperatures the most important performance requirements for asphalt mixtures and asphalt layers are resistance to permanent deformation (rutting) and resistance to surface cracking induced by ageing. The bitumen has a great influence on these performance requirements.

In this paper all major aspects related to quality and properties of bitumen are discussed. Included are bitumen composition and structure, bitumen production, physical characterization, specifications, ageing, upgrading and modification of bitumen. Special attention is given to the performance requirements for bitumen used in areas with hot temperatures like the Middle East and North Africa.

CHEMICAL CHARACTERISATION OF BITUMEN

Elemental composition

Bitumen is a complex mixture of molecules of a predominantly hydrocarbon nature, which vary widely in their composition. They contain amongst others minor amounts of heteroatoms containing sulphur, nitrogen and oxygen and trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides. The chemical composition of bitumen depends on the origin of the crude oil and the processes used during bitumen manufacture. Since the chemical composition of bitumen is extremely complex with the number of molecules with different chemical structures being astronomically large, it is not feasible to attempt a complete analysis of bitumen. Besides, the elemental composition of bitumen provides little information of what types of molecular structure are present in the bitumen. This knowledge is necessary for a fundamental understanding of how the composition of the bitumen affects the physical properties and chemical reactivity.

Fractional composition

There are three principal types of molecules found in bitumen: aliphatics (or paraffinics), naphthenics (or cyclics) and aromatics. The physical and chemical behaviour of bitumen is affected by the various ways in which these compounds interact with one another. The molecules are held together through chemical bonds that are relatively weak and can be broken by heat and/or shear forces.

In general bitumen can be divided into two broad chemical groups: asphaltenes and maltenes. The maltenes can be further subdivided into saturates, aromatics and resins. Although these groups are not completely defined and have some overlap, they enable to compare bitumen properties with broad chemical composition.

Various techniques have been developed to separate bitumen into fractions. These techniques are based on differences in molecular size, chemical reactivity and/or polarity. Chromatographic techniques are the most common methods. They are based on differences in chemical reactivity and polarity. The basis of the chromatographic techniques is to initially precipitate the asphaltenes with a n-alkane (usually n-pentane), followed by chromatographic separation of the remaining maltene material. Using this technique, bitumens can be separated into the four groups: asphaltenes, resins, aromatics and saturates. These groups are called SARA fractions (Saturates, Aromatics, Resins and Asphaltenes). Their main characteristics are as follows:

Asphaltenes

Asphaltenes are considered as highly polar, complex aromatic materials with a tendency to interact and associate. They have fairly high molecular weights ranging from about 1,000 to 100,000. The asphaltene content has a large effect on the rheological characteristics. Increasing the asphaltene content produces harder bitumen with a lower Penetration, higher Softening Point and consequently higher viscosity. Generally, bitumen contains 10 to 20% asphaltenes.

Resins

Resins (polar aromatics) are very polar in nature, which make them strongly adhesive. They are dispersing agents for the asphaltenes. Resins have molecular weights ranging from 500 to 50,000. Generally, bitumen contains 10 to 25% resins.

Aromatics

Aromatics (naphthene aromatics) are weakly polar. They serve as the dispersion medium for the peptised asphaltenes and constitute 55 to 70% of the total bitumen. The average molecular weight ranges from 300 to 2,000.

Saturates

Saturates (aliphatics) are non-polar viscous oils with a similar molecular weight range to aromatics. The components include both waxy and non-waxy saturates. Saturates form 5 to 15% of the bitumen.

Bitumen structure

Colloidal Model

Bitumen is traditionally regarded as a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltenes together with an absorbed sheath of high molecular weight aromatic resins, which act as a stabilising solvating layer and peptise the asphaltenes within the solvent maltenes phase. Away from the centre of the micelle there is a gradual transition to less polar aromatic resins and, finally, to less aromatic oily dispersion medium.

In bitumens with sufficient quantities of resins and aromatics of adequate solvating power, the asphaltenes are fully peptised and the micelles have good mobility within the bitumen. These bitumens are known as solution or 'SOL' type bitumens. If the quantity of the aromatic/resin fraction is insufficient to peptise the micelles or has insufficient solvating power, the asphaltenes can associate to form large agglomerations or even a continuous network throughout the bitumen. These bitumens are known as gelatinous or 'GEL' type bitumens. In practice most bitumens are of intermediate character.

The Index of Colloidal Instability (CI), which is defined as the ratio of the amount of asphaltenes and saturates to the amount of resins and aromatics, is sometimes used to describe the stability of the colloidal structure. The higher CI, the more the bitumen is regarded as 'GEL' type bitumen. The lower CI, the more stable the colloidal structure.

The degree to which asphaltenes are peptised will considerably influence the viscosity of the bitumen. The viscosity of the saturates, aromatics and resins depend on their molecular weight distributions. The higher the molecular weight the higher the viscosity. The viscosity of the maltenes imparts an inherent viscosity to the bitumen, which is increased by the presence of the dispersed asphaltenes. Saturates decrease the ability of the maltenes to solvate the asphaltenes.

SHRP Model

Under the Strategic Highways Research Program (SHRP) a microstructural model was developed. The model states that the bitumen structure consists of microstructures (comprised of polar, aromatic, asphaltene-like molecules that tend to form associations) dispersed in a bulk solvent moiety consisting of relatively non-polar, aliphatic molecules. Many of the molecules comprising the dispersed phase are assumed to be polyfunctional and capable of associating through hydrogen bonds, dipole interactions and B-B interactions to form primary microstructures. Under proper conditions, the primary microstructures can associate into three-dimensional networks,

which may be broken, together with the microstructures, by heat and shear stress. According to the model, bitumen physical properties are described by the effectiveness with which the polar, associated materials are dispersed by the solvent moiety rather than being described by global chemical parameters such as elemental composition.

BITUMEN PRODUCTION

Most of the bitumen used in asphalt pavements is produced during the distillation processes of crude oil. Only a small amount comes from natural resources, like Trinidad Lake Asphalt.

Crude oils

Crude oils differ in both their physical and chemical properties. Physically they range from almost solid to free flowing at room temperature. The physical state can be described with the API gravity, which is directly related to the density of the crude oil. The API gravity varies from 0.0 (e.g. Sesmaria crude oil from Brazil) to more than 70 (e.g. San Roque crude oil from Bolivia). Crude oils with a low API gravity are viscous and generally contain a high percentage of bitumen. Bitumen has an API number of 2 to 4. Some examples of crude oils with their API gravity, density and percentage bitumen are given in table 1.

Parameter	Boscan (Venezuela)	Arabian Heavy (*1)	Nigeria Light
API gravity	10.1	28.2	38.1
Density	0.999	0.886	0.834
Bitumen	58%	27%	1%

*1: blend of several crude oils
Table 1 Details of some crude oils

Chemically, crude oils may be predominantly paraffinic, naphthenic or aromatic. The K factor indicates whether the crude oil is paraffinic (K factor: 12.5–13.0) or naphthenic-aromatic (K factor: 10.5–12.5). Paraffinic crude oils are not suited for bitumen production. The K factor is calculated from the average boiling point and the density of the crude oil. Other important parameters are the paraffin or wax content and the Bromine number. The paraffin or wax content is important with respect to the Rheological and adhesive properties of the bitumen. It should be lower than 0.5%. The Bromine number is an indication for the presence of reactive compounds (olefines) which have a large influence on the ageing behaviour of bitumen. The amount of Vanadium and Nickel is unique for each crude oil and can therefore serve as a fingerprint of the crude oil.

Production processes

Distillation

Bitumen is produced by fractional distillation of crude oil. Usually, distillation is done in two steps.

First the crude oil is heated up to 300-350°C and introduced into an atmospheric distillation column. Lighter fractions like naphtha, kerosene and gas oil are separated from the crude oil at different heights in the column. The heaviest fractions left at the bottom of the column are called long residue.

The long residue is heated up to 350-400°C and introduced into a distillation column with reduced pressure (vacuum column). By using reduced pressure it is possible to further distillate lighter products from the residue because the equivalent temperature (temperature under atmospheric conditions) is much higher. If second distillation were carried out under atmospheric conditions and by increasing the temperature above 400°C, thermal decomposition of the long residue would occur. The residue at the bottom of the column is called short residue and is the feedstock for the manufacture of bitumen.

The viscosity of the short residue depends on the origin of the crude oil, the temperature of the long residue, the temperature and pressure in the vacuum column and the residence time. Usually, the conditions are such that short residue is produced with a Penetration between 100 and 300 dmm. The amount of short residue decreases and the relative amount of asphaltenes increases with increasing viscosity of the short residue.

Bitumen manufactured from the short residue is called straight run bitumen. The differences in properties between high and low penetration grade bitumen are mainly caused by different amounts of molecule structures with strong interactions. Low penetration grade bitumen contains more of these molecule structures. This is the main reason why their viscosity, Fraaß Breaking Point, Softening Point, etc., is so much higher than for high penetration grade bitumen. The fact that they contain less low viscosity products is of less significance.

Blowing

One way to make bitumen harder is to blow air through it. This process is called blowing. Air is heated up to 150–250°C and introduced at the bottom of a blowing column. It then migrates through the bitumen to the top of the column. The chemical reactions result in bitumen with a different mixture of molecular structures. Catalysts can influence this process.

Blown bitumen has more and stronger molecular interactions than the original bitumen and is therefore more cohesive. Blowing causes the Softening Point to increase and the Penetration to decrease. However, the increase in softening Point is usually more than the decrease in Penetration. This means that blowing reduces the temperature susceptibility of bitumen. The effectiveness of blowing depends largely on the original bitumen (i.e. the original mixture of molecular structures).

With respect to the composition, generally the amount of saturates do not change, the amount of aromates decreases because some oxidized aromates behave like resins, the amount of asphaltenes increases due to transformation of some resins and the total amount of resins stays the same. This can also be observed in figure 1, which gives the composition of a Pen 200 bitumen after different blowing times in a laboratory oxidation column.

When bitumen is strongly blown it becomes so cohesive that the adhesive properties become so poor that it is not suited for asphalt applications anymore. Therefore, only semi-blown bitumen is suited for asphalt applications. Semi-blown bitumen can have both improved cohesion and improved adhesion.

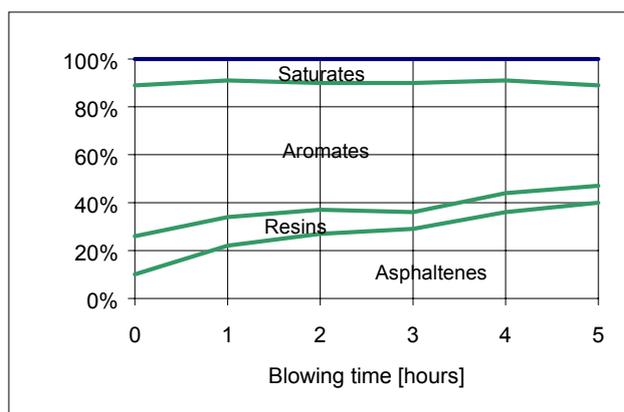


Figure 1 Change in chemical composition of Pen 200 bitumen during blowing at 260°C

Visbreaking

Light products have a higher selling value than heavy products like bitumen. Visbreaking is a way to break heavy products (e.g. the residue from crude oil distillation or even very heavy crude oils) into lighter products. Hereto, the crude oil or residue is heated up to 450 °C and kept at that temperature for 1 to 20 minutes. During this period a large amount of molecular structures are broken into smaller structures. The product from the visbreaking process (VB product) is further normally distilled.

Bitumen produced from VB products age very fast. This is because these products contain very reactive constituents (oleofins). Even blends of straight run bitumen with bitumen from VB products have the same ageing

problems. This makes them unsuitable for most asphalt applications. The properties may be somewhat improved by blowing. A comparison between two straight run bitumen and blends of straight run bitumen with bitumen from VB products is given in table 2.

Property	Straight run bitumen		Bitumen from VB residue		
			(*1)		
Penetration @ 25°C [dmm]	119	139	122	169	181
Softening Point R&B [°C]	42.7	42.0	43.2	41.5	42.0
Penetration Index	-1.0	-0.7	-0.8	0.4	0.5
After laboratory ageing					
Retained Penetration @ 25°C [%]	78	73	56	53	41
Increase in Softening Point R&B [°C]	3.6	1.8	5.0	7.8	7.9
Penetration Index	-0.6	-1.2	-0.9	-0.2	-0.3
*1: semi-blown					

Table 2 Properties of straight run bitumen and bitumen from VB residue

PHYSICAL CHARACTERISATION OF BITUMEN

The response of bitumen to stress depends on temperature and loading time. At low temperatures and/or short loading times bitumen behaves predominantly elastic. At high temperature and/or long loading times bitumen behaves like a liquid (viscous behaviour). For typical pavement temperatures and load conditions bitumen generally exhibits both viscous and elastic behaviour. Measurements of the physical properties of bitumen are usually associated with the characterization of the rheological (flow) behaviour of bitumen.

A large number of test methods have been developed to characterize bitumen. Most of these tests are empirical, i.e. the determined properties are not directly related to the performance of the bitumen. To discuss the different test methods, the bitumen properties are divided into four groups:

- Performance properties;
- Index properties;
- Properties related to mixing and construction and
- Control properties.

Performance properties

Performance properties are real material properties and as such directly related to the performance of the material. Bitumen stiffness and strength are two examples of performance properties.

The viscoelastic behaviour of bitumen can be measured with a Dynamic Shear Rheometer (DSR). During the test, a small sample of bitumen that is placed between two parallel plates is subjected to oscillatory shear stresses or

strains (figure 2). From the response stresses or strains the complex shear modulus (G^*) and phase angle δ are calculated. The complex shear modulus is the ratio of total shear stress to total shear strain. It consists of two components: the storage modulus G' (elastic component) and the loss modulus G'' (viscous component). The phase angle is an indicator of the relative amounts of elastic and viscous behaviour. For example, for purely elastic materials, the phase angle is 0° , while for purely viscous materials (for example water), the phase angle is 90° . By performing these tests for a wide range of temperatures and loading times (frequencies) a complete picture (fingerprint) of the rheological behaviour of the bitumen can be obtained.



Figure 2 Detail of DSR

The results can be presented in several forms. The most common forms are: isochronal plots (viscoelastic data versus temperature at constant frequency), isothermal plots (viscoelastic data versus frequency at constant temperature), mastercurves (several isothermal plots shifted along the frequency axis to produce a smooth curve) and black diagrams (complex shear modulus against phase angle). To produce mastercurves use is made of the time-temperature superposition principle. This principle implies that there is an equivalency between time and temperature, which is true for most straight run bitumen.

The Superpave Asphalt Binder Specification is the first and only bitumen specification in which performance properties are incorporated. To address resistance to permanent deformation minimum values are given for $G^*/\sin\delta$ (rutting factor). These requirements apply to fresh and short-term aged bitumen. To address resistance to fatigue cracking maximum values are given for $G^*\cdot\sin\delta$ (fatigue cracking factor). These requirements apply to long-term aged bitumen.

Index properties

Index properties are related to performance properties but are not real material properties. Examples are elastic recovery (only relevant for Polymer Modified Bitumens) and kinematic viscosity at 60°C. Both are related to the resistance to permanent deformation. A high viscosity at 60°C may entail a high resistance to permanent deformation. Some bitumen specifications are viscosity-graded specifications.

Mixing properties

The most important property related to mixing, transport and construction is the shear viscosity at high temperature. To allow selection of optimum mixing temperature and the temperature interval for compaction, the temperature-viscosity relation of the bitumen should be known. Ideally, the mixing temperature is the minimum temperature at which the viscosity allows quick and good coating of the aggregate. Higher temperatures only cause additional ageing.

Control properties

Control properties include Penetration, Softening Point, Fraaß Breaking Point, Ductility, etc. The test conditions under which these properties are determined differ significantly from the load/temperature conditions in the pavement. Consequently, they are all empirical properties and thus not (directly) related to the performance of the bitumen. These properties are used for quality control and to grade bitumen.

Many bitumen specifications are Penetration-graded specifications. In some of these specifications additional properties are included (for example Softening Point, Fraaß Breaking Point, changes in Penetration and Softening Point due to ageing, etc.). However, all these bitumen specifications are only grading systems and not related to pavement performance.

BITUMEN AGEING

Ageing mechanisms

The rheological properties of bitumen change with time (i.e. bitumen becomes harder and more elastic). This phenomenon is called ageing. The amount and rate of ageing depend on many factors like for example temperature, exposure to oxygen, chemical composition and structure of the bitumen, etc. Basically, there are four mechanisms of bitumen hardening: oxidation, loss of volatiles, physical hardening and exudative hardening.

Oxidation

Oxidation is considered to be the main cause of bitumen ageing. Like many organic substances, bitumen slowly oxidises when in contact with air. Polar groups are formed which tend to associate into micelles of higher molecular weight. The increased and stronger interactions make the bitumen more viscous. However, results from studies show that not all bitumens harden (age) to the same extent. This may be explained by differences in bitumen structure. For 'SOL' type bitumen the polar groups are well peptized, which makes them almost inaccessible for oxygen. Therefore, oxidation of the highly reactive asphaltenes and resins is difficult. For 'GEL' type bitumen this is not the case. The polar groups of these bitumens have rather formed a continuous network with a large surface area, which make them easy accessible for oxygen. Besides, newly formed polar groups are probably quickly dispersed in 'SOL' type bitumen, while in 'GEL' type bitumen these groups can further react.

Some aggregates act as catalyst for the oxidation reactions, while others have inhibitive effects. Ultraviolet rays from the sun act also as catalyst. This is especially relevant for areas high above sea level, for areas with a lot of hot sunshine (like the Middle East) and for asphalt wearing courses with high void contents (like Drain Asphalt). Even elements present in the bitumen can act as catalyst. An example is Vanadylporphyrin. Probably the most used inhibitor is Calcium Hydroxide ($\text{Ca}(\text{OH})_2$). It was found that the ageing resistance of an asphalt mixture is sometimes improved when Calcium Hydroxide is used. The reason for this is not known. Besides, Calcium Hydroxide is often used to improve the adhesion properties of bitumen. Sodium Hydroxide (NaOH) can have the same positive effect on the ageing resistance but often has a negative effect on the adhesion properties.

Oxidation causes the fractional chemical composition of bitumen to change. The asphaltene content increases continuously due to oxidation of polar resins. Part of the aromatics changes in such a way that in the composition analysis it is included with the resins. Since these 'new resins' do not have the natural properties of resins, an evaluation of the properties of aged bitumen on basis of the SARA fractions can be misleading.

Irrespective of the ageing resistance of the bitumen, the degree and rate of oxidation depend on temperature, time, exposure to oxygen and bitumen film thickness.

With respect to temperature the most severe conditions are found during bitumen storage, mixing and transport. When bitumen is stored at high temperature normally very little oxidation occurs. This is because the surface of the bitumen exposed to oxygen is very small in relation to the volume. However, care should be taken during heating up. When the temperature difference between the bitumen and the heating oil is large

(more than 30°C), reactive constituents (oleofins) are formed, which have a detrimental influence on bitumen. During mixing at high temperature the molecular mixture of the bitumen and the viscosity change significantly. Apart from temperature, oxidation during mixing depends on mixing time, bitumen content, temperature difference between aggregate and bitumen and type of mixing plant. During storage and transport oxidation continuous, but at a slower rate. Important are duration of storage and transportation, initial temperature and the exposure to air (oxygen). Special care should be taken with transport and storage of pre-coated chippings. Because of their loose packing air has easy access to the coated surfaces, which involves a real danger for severe oxidation of the bitumen.

During service life oxidation depends, apart from climatic conditions and the ageing resistance of the bitumen, mainly on the amount of airvoids in the asphalt (determines the exposure to oxygen and UV radiation) and the bitumen film thickness. To minimize oxidative hardening low void contents and thick bitumen films are required.

Loss of volatiles

Evaporation of volatile components depends mainly on temperature and the conditions of exposure. Penetration grade bitumens are relatively involatile and therefore the amount of hardening resulting from loss of volatiles is usually fairly small.

Physical hardening

Physical hardening occurs during cooling and continues at service temperature. It is attributed to reorientation of bitumen molecules and crystallization of waxes. Slow cooling speeds up the process, while instant cooling to low temperature slows the process down (especially relevant for laboratory testing of bitumen). Physical hardening is strongly influenced by aggregate-bitumen interactions. Directly after cooling asphalt sometimes appears to be soft as if it was still warm, while a few days later the asphalt seems to have matured. This phenomenon is called setting and is caused by slow physical hardening. Reheating can reverse physical hardening.

Exudative hardening

If the constitution of a bitumen is unbalanced it may, when in contact with a porous aggregate, exude an oily component into the surface pores of the aggregate, resulting in a hardening of the bitumen film remaining on the aggregate surface. Exudation is primarily a function of the ratio between the amount of low molecular weight paraffinic components and the amount and type of asphaltenes. Hardening as a result of exudation can be substantial when both the exudation tendency of the bitumen and the porosity of the aggregate are high. Otherwise, exudative hardening will be negligible.

Determination of ageing resistance

Several methods are developed to simulate short-term and long-term oxidative ageing of bitumen.

The two most used methods to simulate ageing during mixing, transport and construction (short-term ageing) are the Thin Film Oven Test (TFOT) and Rotating Thin Film Oven Test (RTFOT). In the TFOT a certain amount of bitumen is placed on a steel sample pan with certain dimensions and stored in an oven at 163°C for 5 hours. In the RTFOT the bitumen is put into a glass cylinder of certain dimensions. The glass cylinder is fixed in a rotating shelf. During the test the bitumen flows around the inner surface of the container and is exposed to heat and air for 85 minutes. The test temperature is also 163°C. This ageing procedure is included in the Superpave Asphalt Binder specification.

Under SHRP a new procedure was developed to simulate in-service ageing (long-term ageing). The procedure involves the use of a Pressure Ageing Vessel (PAV). In the PAV the bitumen is exposed to high pressure (2.1 MPa) and high temperature for 20 hours. The test temperature depends on the high-temperature Performance Grade of the bitumen and is either 90, 100 or 110°C. The PAV ageing procedure is included in the Superpave Asphalt Binder specification and uses bitumen aged in the RTFO. The test does not account for mixture variables.

The ageing resistance can be evaluated by means of the ageing index, which is defined by the ratio between the value of a certain property measured on aged bitumen and the value for the same property measured on fresh bitumen.

Changes in bitumen composition and properties

Generally, (oxidative) ageing makes straight run bitumen harder and more elastic. The asphaltene content increases. These changes are discussed in more detail on the basis of results from three studies.

In 1990 three test sections of Stone Mastic Asphalt (SMA) with different Polymer Modified Bitumens (PMBs) were constructed on a highway in The Netherlands. Also a reference section with 80/100 bitumen was constructed. In 1990, 1992, 1993 and 1999 cores were taken from these sections and tested for some functional properties. The bitumen is recovered and tested for Penetration and Softening Point. For the 80/100 bitumen the changes in Penetration and Softening Point during mixing, transport, construction and nine years service life are shown in figure 3. In the first year the Penetration has dropped significantly (24%). This illustrates the significance of the oxidative ageing that takes place during mixing, transport and construction. During the nine years of service the Penetration continuously decreases, however at a very slow rate (approximately 2 dmm per year). The Softening

Point does not change at all during these years. The bitumen ages slowly because the exposure to oxygen is limited, i.e. the void content of the asphalt is low (average 5.5%) and the bitumen films are thick, i.e. the bitumen content of the mixture is high (average 6.4%).

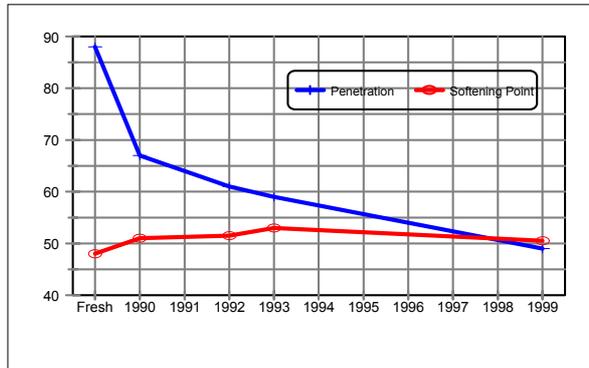


Figure 3 Properties of 80/100 bitumen recovered from SMA

Also in 1990 three test sections of Drain Asphalt with PMBs and a reference section with 80/100 bitumen were constructed on a motorway around Amsterdam (The Netherlands). In 1990, 1991, 1993 and 1999 cores were taken from these sections and tested for some functional properties. The bitumen is recovered and tested for Penetration and Softening Point. For the 80/100 bitumen the changes in Penetration and Softening Point during mixing, transport, construction and four years service life (results from 1999 are not available yet) are shown in figure 4. The drop in Penetration due to oxidation during mixing, transport and construction is about 29%. Compared to the 80/100 bitumen of the SMA, the bitumen has aged slightly more. This can probably be contributed to the lower bitumen content of drain asphalt (4.6%). During the first four years of service the Penetration decreased with about 10 dmm per year and the Softening Point increased with 5.0°C. Due to the high void content of Drain Asphalt (average 18.9%) the bitumen films of the whole asphalt layer are well exposed to air (oxygen) and UV radiation. The effect on the rate of ageing is apparent. There are many cases known that after 8 to 10 years (average lifetime for Drain Asphalt with standard bitumen) the Penetration is as low as 10 dmm.

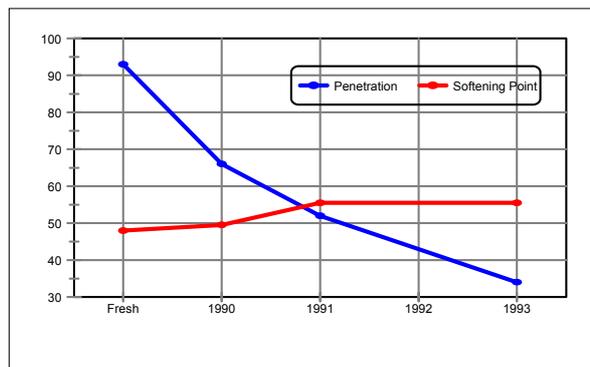


Figure 4 Properties of 80/100 bitumen recovered from Drain Asphalt

The data for the last example comes from a research project that was carried out between 1994 and 1998 by a number of European Institutes. Although the project was related to quality analysis of PMB, also three standard bitumens were included as reference. The standard bitumens originated from Russia, Venezuela and the Middle East. The bitumens were subjected to laboratory short-term and long-term ageing in the RTFO and PAV. The fractional composition (SARA fractions) and performance, index and control properties of both fresh and aged bitumen were determined.

The fractional composition and the index of colloidal instability (CI) of the three bitumens and the changes due to short-term (RTFOT) and long-term (RTFOT + PAV) ageing are shown in table 3. All three bitumens show an increase in asphaltenes and resins, a decrease in aromatics and an unchanging amount of saturates. This agrees with the expected changes due to oxidative ageing. The fractional composition of the bitumen with the highest CI (Venezuelan 70/100) is relatively less changed.

Bitumen	Condition	Sa [%]	Ar [%]	Re [%]	As [%]	CI
Middle East 45/60	Fresh	5	69	15	11	0.19
	RTFOT	6	61	20	13	0.23
	RTFOT+PAV	6	52	24	18	0.32
Russian 80/100	Fresh	4	68	19	9	0.15
	RTFOT	4	64	21	11	0.18
	RTFOT+PAV	5	52	28	15	0.25
Venezuelan 70/100	Fresh	11	58	17	14	0.33
	RTFOT	13	54	17	16	0.41
	RTFOT+PAV	12	47	21	20	0.47

Table 3 Changes in fractional composition due to ageing

The ageing resistance of bitumen can also be assessed by measuring the increase of oxidative products (carbonyl and sulphoxide) which are formed during ageing. The increases in carbonyl and sulphoxide for the three bitumens are shown in table 4. The Venezuelan bitumen forms least oxidative products and the Russian bitumen most. However, the differences are small.

Bitumen	Condition	Carbonyl	Sulphoxide	Carbonyl + Sulphoxide
Middle East 45/60	RTFOT - fresh	0.071	0.068	0.139
	RTFOT+PAV - fresh	0.279	0.295	0.574
Russian 80/100	RTFOT - fresh	0.065	0.071	0.136
	RTFOT+PAV - fresh	0.302	0.327	0.629
Venezuelan 70/100	RTFOT - fresh	0.078	0.031	0.109
	RTFOT+PAV - fresh	0.327	0.244	0.571

Table 4 Increase in oxidative products

The shear viscosity and some control properties of the three bitumens and the changes due to short-term and long-term ageing are shown in table 5. The test data show for all bitumens a decrease in Penetration and Ductility and an increase in Shear Viscosity, Softening Point and Fraaß Breaking Point. This indicates a hardening of the bitumen, which corresponds to the observed changes in fractional composition. It appears that the properties of the Venezuelan bitumen change relatively most (especially after long-term ageing).

	Property	Condition			Ageing Index	
		Fresh	RTFOT	RTFOT +PAV	RTFOT/fresh	PAV/fresh
Middle East 45/60	Penetration [dmm]	60	45	24	0.8	0.4
	Softening Point [°C]	48.8	52.6	59.3	1.1	1.2
	PI	-1.1	-0.8	-0.7	0.7	0.6
	Fraaß [°C]	-18	-14	-12	0.8	0.7
	Ductility @10°C [cm]	21	6	-	0.3	-
	Viscosity [Pa.s]					
	@60°C	260	510	2,050	2.0	7.9
@135°C	0.51	0.66	1.03	1.3	2.0	
Russian 80/100	Penetration [dmm]	73	51	24	0.7	0.3
	Softening Point [°C]	47.0	50.8	57.3	1.1	1.2
	PI	-1.1	-1.0	-1.1	0.9	1.0
	Fraaß [°C]	-12	-11	-11	0.9	0.9
	Ductility @10°C [cm]	63	8	-	0.1	-
	Viscosity [Pa.s]					
	@60°C	170	340	1,050	2.0	6.2
@135°C	0.37	0.47	0.76	1.3	2.1	
Venezuelan 70/100	Penetration [dmm]	81	53	28	0.7	0.3
	Softening Point [°C]	46.8	51.2	59.2	1.1	1.3
	PI	-0.9	-0.8	-0.4	0.9	0.4
	Fraaß [°C]	-28	-21	-15	0.8	0.5
	Ductility @10°C [cm]	>130	23	-	0.2	-
	Viscosity [Pa.s]					
	@60°C	210	460	1,950	2.2	9.3
@135°C	0.38	0.52	0.87	1.4	2.3	

Table 5 Bitumen properties and changes due to ageing

To determine the rheological properties of the bitumens oscillatory tests were carried out with a Dynamic Shear Rheometer (DSR). The tests were carried out at 7 temperatures (10 to 65°C) and 14 frequencies (0.01 to 15 Hz). Both the complex modulus G^* and the phase angle δ^* were determined. It is of course unfeasible to present all results here. Besides, the three bitumes behaved all in the same way, i.e. both stiffness and elastic behaviour increased after ageing. The isochronal plots for the Middle East bitumen given in figure 5 can illustrate this behaviour. In table 6 the values for the complex modulus and phase angle are given for the two most

extreme test conditions (0.01 Hz / 65°C and 15 Hz / 10°C). The increase in complex modulus is relatively highest at high temperature and low frequency (representing long loading times). However, the phase angle does not change at all under these conditions (the behaviour of the bitumen remains completely viscous). At low temperature and high frequency (representing short loading times) the aged bitumen is both stiffer and more elastic (lower phase angle). It appears that the rheological properties of the Venezuelan bitumen change relatively most, which was also the case for the index and control properties.

	Property	Condition			Ageing Index	
		Fresh	RTFOT	RTFOT +PAV	RTFOT/ fresh	PAV/ fresh
ME 45/60	$G^*_{10^\circ\text{C}, 15\text{ Hz}}$ [MPa]	34.6	39.5	60.4	1.1	1.7
	$G^*_{65^\circ\text{C}, 0.01\text{ Hz}}$ [Pa]	10	18	59	1.8	5.9
	* $10^\circ\text{C}, 15\text{ Hz}$ [°]	38	35	28	0.9	0.7
	* $65^\circ\text{C}, 0.01\text{ Hz}$ [°]	90	90	88	1.0	1.0
Russian 80/100	$G^*_{10^\circ\text{C}, 15\text{ Hz}}$ [MPa]	32.6	34.8	60.3	1.1	1.8
	$G^*_{65^\circ\text{C}, 0.01\text{ Hz}}$ [Pa]	6	11	37	1.8	6.2
	* $10^\circ\text{C}, 15\text{ Hz}$ [°]	39	34	27	0.9	0.7
	* $65^\circ\text{C}, 0.01\text{ Hz}$ [°]	89	89	89	1.0	1.0
Venezuelan 70/100	$G^*_{10^\circ\text{C}, 15\text{ Hz}}$ [MPa]	20.0	27.7	42.7	1.4	2.1
	$G^*_{65^\circ\text{C}, 0.01\text{ Hz}}$ [Pa]	7	14	54	2.0	7.7
	* $10^\circ\text{C}, 15\text{ Hz}$ [°]	45	40	33	0.9	0.7
	* $65^\circ\text{C}, 0.01\text{ Hz}$ [°]	90	89	89	1.0	1.0

Table 6 Rheological properties and changes due to ageing

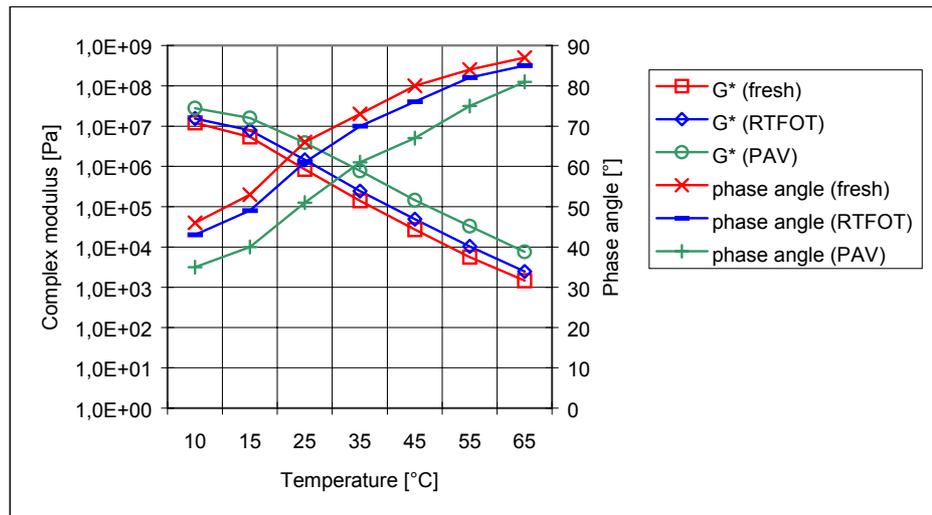


Figure 5 Isochronal plot at 1.5 Hz for Middle East 45/60

PERFORMANCE REQUIREMENTS FOR ASPHALT MIXTURES AND ASPHALT LAYERS

At the Eurobitume Workshop in 1999 it was concluded that for areas with hot temperatures the following performance requirements for asphalt mixtures and asphalt layers are most important:

- Friction (only for surface layers);
- Resistance to permanent deformation (especially for surface layers);
- Resistance to surface cracking induced by ageing (especially for surface layers);
- Resistance to reflective cracking (both for surface layers and binder/base layers)
- Contribution to structural strength (only for binder/base layers)

Resistance to stripping/ravelling and noise emission was considered of minor importance.

INFLUENCE OF BITUMEN ON THE PERFORMANCE OF ASPHALT MIXTURES AND ASPHALT LAYERS

The significance of bitumen with respect to the performance requirements for asphalt mixtures and asphalt layers was also discussed at the Eurobitume Workshop. The conclusions are summarized in table 7.

Performance requirements for asphalt mixtures and layers	Bitumen significance	
	Surface layer	Binder/base layers
Friction	Low	-
Permanent deformation	High	High
Surface cracking induced by ageing	High	Medium
Stripping/ravelling	Low	Low
Contribution to structural strength	Low to medium	High
Noise emission	Low	-
Other cracking	Medium	High

Table 7 Influence of bitumen on performance of asphalt mixtures and layers

The next step was to determine what bitumen properties are related to the performance requirements for asphalt mixtures and asphalt layers. For most performance requirements this is not so evident. However, a list of suggested bitumen properties was prepared, which is shown in table 8. Most of these properties and methods to measure them are discussed elsewhere in this paper.

It is very important that selection of bitumen is based on the performance requirements for asphalt mixtures and asphalt layers and the related bitumen properties.

Performance requirements for asphalt mixtures and layers	Related bitumen properties (suggested)
Permanent deformation	Rheological (viscosity, G^* , δ)
Surface cracking induced by ageing	Ageing (RTFOT and PAV)
Stripping/ravelling	Binder/aggregate interaction
Contribution to structural strength	Rheological (G^*)
Fatigue cracking (thin layers)	Failure (fatigue, healing)
Manufacturing and Laying	Viscosity and storage stability

Table 8 Performance requirements for asphalt mixtures/layers and related bitumen properties

SPECIFIC ASPHALT AND BITUMEN REQUIREMENTS FOR HOT AND ARID CLIMATES

Bitumen used in areas with hot and arid climates should perform well under extremely high temperatures, large day-night temperature variations and a lot of hot sunshine (UV radiation).

The type of asphalt pavement failure associated with high temperatures is permanent deformation. Pavement design, asphalt mixture type(s), asphalt mixture design(s), aggregate quality and bitumen all play an important role with respect to the resistance to permanent deformation. The main requirement for the bitumen is that it does not easily deform at the prevailing maximum pavement temperatures. Therefore, the bitumen should exhibit a certain stiffness at these temperatures. However, since it is only the viscous deformation that adds to permanent deformation, there should be compensation for the amount of elastic behaviour. This is exactly formulated by the rutting parameter ($G^*/\sin\delta$) of the Superpave Asphalt Binder Specification. Ideally, the rutting parameter should be known for a range of loading times. Since bitumen becomes harder and more elastic during service, it should be tested in a state that is representative for its state just after construction. In the Superpave Binder Specification the minimum values for the rutting parameter are for one loading time only. To allow for long loading times a higher Performance Grade needs to be specified.

Large day-night temperature variations results in the development of stresses in the bitumen (films) between the aggregates. When the bitumen can not withstand these stresses it will break, which eventually will lead to surface cracking. Low stiffness at long loading times and good relaxation behaviour minimize the developed stresses. These properties are good performance indicators for standard bitumen. However, for PMBs (especially for elastomer modified bitumens) these properties may underestimate the performance.

The Superpave Asphalt Binder Specification addresses (low) temperature cracking by limiting the stiffness of the bitumen and specifying a minimum level of relaxation. Stiffness and relaxation are measured with a Bending

Beam Rheometer (BBR). Since bitumen becomes harder and more elastic (i.e. more brittle) during service, it is tested in a state that is representative for its state after the pavement has been in service for some time. The Superpave requirements based on BBR tests are not suited to assess the low temperature performance of PMBs. For these binders (repeated) direct tension tests are probably more appropriate.

Bitumen becomes harder and more elastic under the influence of hot sunshine and UV radiation. With respect to the resistance to permanent deformation this may cause no problem. However, with respect to surface cracking this may be catastrophic. Therefore, bitumen in hot and arid climates needs to be very resistant to ageing. To limit hardening of bitumen asphalt with low void content and high bitumen content is desirable.

Recently the King Fahd University of Petroleum and Minerals in Saudi Arabia has carried out a research study about bitumen requirements for Gulf countries and the quality of available bitumens. Six Gulf countries were included in the study: Saudi Arabia, Kuwait, Bahrain, Qatar, United Arab Emirates and Oman.

Data from weather stations located across these countries was used to divide the total area in regions with the same minimum air temperature and average seven-day maximum temperature. The minimum air temperature is nowhere lower than -10°C . The average seven-day maximum temperature is for most places about 50°C . Based on the prevailing minimum and maximum temperatures and considering slow transient loads four bitumen Performance Grades were recommended: PG 76-10, PG 70-10, PG 64-10 and PG 58-10.

The bitumen specifications in these Gulf countries are primarily based on Penetration and Viscosity. The available bitumens were graded: Pen 45/60, Pen 60/70, AC-20, AC-40, AR-4000 and AR-8000. All these bitumens had a Penetration between 40 and 60. According to the Superpave Binder Specification most of these bitumens were graded PG 64-22, three were graded PG 64-28 and one was graded PG 70-22 (semi-blown bitumen).

On basis of these results it was concluded that locally produced bitumen (with a PG grade of at least 64-10) can perform satisfactorily in less than 30% of the area of the six Gulf countries. Semi blown bitumen (with a PG grade of at least 70-10) can satisfy the performance requirements for another 25% of the area. For the remaining area (more than 45%) Polymer Modified Bitumens with a Performance Grade of at least 76-10 are required.

BITUMEN IMPROVEMENT

The properties/performance of bitumen can be improved by improving the structure/composition of the bitumen (upgrading) and/or by adding additives to the bitumen (modification).

Bitumen upgrading

Some big oil companies have developed technologies (refinery processes) to produce upgraded bitumens. These so-called semi-hard multigrade bitumens are stiffer at high temperature and less brittle at low temperature than conventional bitumen with the same Penetration at 25°C (i.e. they are less temperature susceptible). They are mainly applied to improve the resistance to permanent deformation. Only a few oil companies have the facilities and knowledge to produce these bitumens. Therefore, this technology can not be applied to upgrade local bitumen.

Ooms Avenhorn Holding (OAH) has developed a technology to upgrade bitumen without the need for expensive facilities. This technology is called gelation technology. The principle is to restore and/or improve the balance between the chemical fractions of the bitumen (particularly between the asphaltenes and resins). This is achieved by adding special additives to the bitumen. To assure that these additives are fully incorporated in the bitumen they need to be compatible with the bitumen. Bitumen upgraded this way is stiffer, less temperature susceptible and more resistant to ageing than the original bitumen. The level of improvement depends on the original bitumen.

Bitumen modification

Most of the modified bitumens for pavement applications are polymer modified. Therefore, only Polymer Modified Bitumens (PMBs) will be discussed here. There are basically two types of polymers used for bitumen modification: plastomers and elastomers.

Plastomers increase the stiffness and viscosity of the bitumen. The effect of plastomers diminishes above their crystallisation temperature (50 to 80°C). Plastomer modified bitumens are mainly applied to improve the resistance to permanent deformation. Since they are often prone to phase separation, continuous mixing during storage is required. Examples of plastomers are EVA (Ethylene-Vinyl Acetate) and PE (Polyethylene).

Elastomers increase the elasticity of the bitumen and reduce the stiffness at low temperatures. Styrene-Butadiene-Styrene copolymer (SBS) is the most used elastomer. In bitumen it forms a highly elastic network. The network disappears above 100°C but reforms on cooling. It is found that SBS also improves the resistance against oxidative ageing. The amounts of oxidative products formed during long-term ageing (RTFOT + PAV) for three standard bitumens and a SBS modified bitumen are shown in figure 6. It is important to note that the quality of SBS modified bitumen depends to a large extent on the production process. SBS modified bitumen is not only applied to improve the resistance to permanent deformation but also to improve the resistance to cracking (fatigue, temperature and reflective cracking).

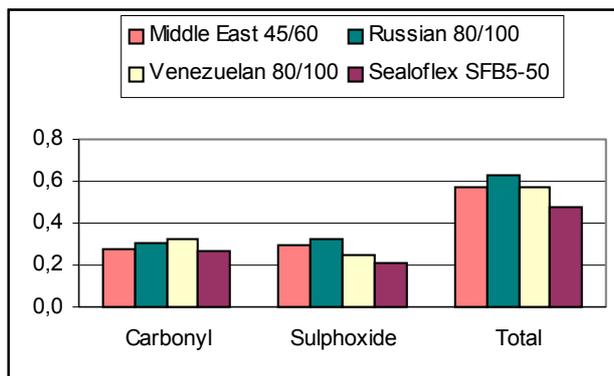


Figure 6 Amounts of oxidative products formed during long-term ageing (RTFOT + PAV)

Results from a creep-recovery test carried out on Sealoflex SFB5-50 (SBS modified bitumen from OAH) are shown in figure 7. The results clearly demonstrate the elastic behaviour of this PMB.

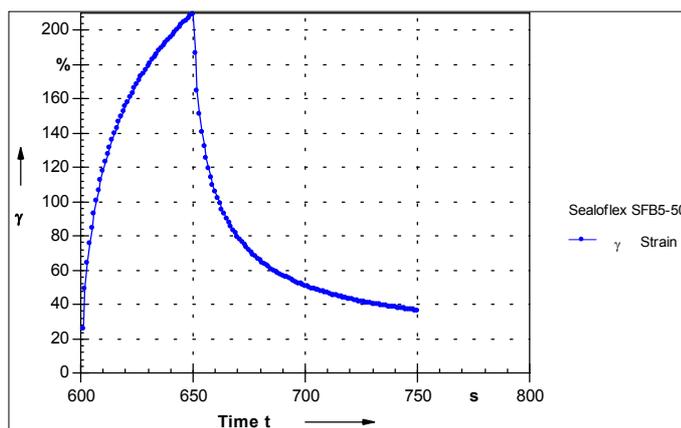


Figure 7 Creep-Recovery test at 60°C, 600 kPa, sample is unloaded at 650 s

The effect of polymer modification not only depends on the type of polymer but also on the amount of polymer. In bitumen polymers swell to maximum nine times their original volume.

Up to about 4% of polymer (by mass) the bitumen remains the continuous phase. The properties of these PMBs are dominated by the properties of the base bitumen. However, the polymer can already have a significant effect. This can be illustrated by results from a study that was carried out by OAH to improve the properties of bitumen from a number of refineries in China. The fractional composition of these bitumens is so extreme (asphaltene content less than 5% and a resins content of up to 40%) that upgrading had little effect. However, the addition of about two percent SBS polymer improved the resistance to permanent deformation by a factor of more than ten. Asphalt prices increase with about 10 to 20% when these kind of low polymer content PMBs are used.

Above 5% the polymer usually forms the continuous phase. For these PMBs the polymer dominates the properties. Both PMBs with a continuous bitumen phase and PMBs with a continuous polymer phase are used (see figure 8).

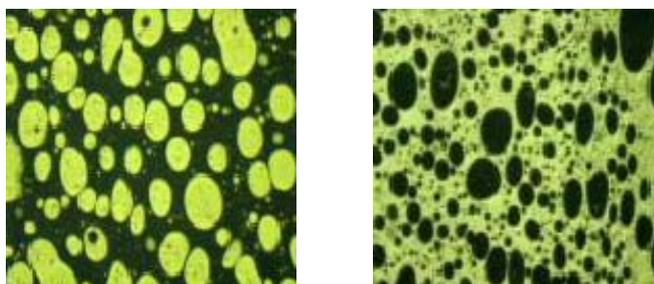


Figure 8 Microscopic images of PMBs under fluorescent light (left: continuous bitumen phase, right: continuous polymer phase)

Two recent examples of projects in the Middle East where PMBs are used, are the rehabilitation and upgrading of the runway and taxiways at Cairo International Airport in Egypt and the rehabilitation of the runway at Aden International Airport in Yemen.

Cairo International Airport is the busiest airport in the Middle East. The bitumen of the existing dense wearing course was severely aged (Penetration of 10 to 20 dmm and a Softening Point of 70 to 80°C). A combination of poor quality (too high wax content and low asphaltenes) bitumen, high pavement temperatures and a lot of hot sunshine (ultraviolet radiation) had caused this severe ageing. For the new wearing course jet fuel resistant PMB was required. This bitumen had to comply with the requirements for Superpave Performance Grade 76-10. The bitumen that was selected for modification was a local standard Pen 60/70 bitumen with Superpave Performance Grade 64-16. The Performance Grade of the modified bitumen (Sealoflex SFB5-JR) was 76-22. This means that the high temperature performance (i.e. resistance to permanent deformation) was improved by two grades and the low temperature performance (i.e. resistance to cracking) was improved by one grade. Construction work started at the end of 1997 and was finished eight months later. During this period approximately 260,000 tons of jet fuel resistant asphalt was applied. The production of the PMB took place in a mobile plant at the construction site.

The pictures of figure 9 show clearly the difference between asphalt that is resistant to jet fuel and asphalt that is not. Both specimens were immersed in jet fuel for 24 hours. The Marshall specimen with jet fuel resistant bitumen had a weight loss of less than 0.5%. The Marshall specimen with standard bitumen (Pen 45/60) had a weightloss of approximately 7%.



Figure 9 Marshall specimens after 24 hours immersion in jet fuel

For Aden International Airport the PMB had to meet the requirements for the same Superpave Performance Grade (PG 76-10). It appeared that the local bitumens available for modification had a relatively high asphaltene content and low resins content (especially the Pen 60/70 bitumen). The chemical composition of the Pen 60/70 and Pen 80/100 bitumen are given in table 9. Generally, these bitumens are not very suitable for modification with polymers. For example, modification of the Pen 60/70 bitumen resulted in a PMB with a very high shear viscosity which increased during storage (up to 29 Pa·s at 135°C). Modification of the Pen 80/100 did not show this tendency (the shear viscosity at 135°C was only 2.0 Pa·s). The Performance Grade of the modified bitumen (Sealoflex SFB5-JR) was 82-16, which is three grades better than specified. Construction work was carried out in 1999/2000. During this period approximately 40,000 tons of modified asphalt was applied.

	Pen 60/70 bitumen	Pen 80/100 bitumen
Saturates	2 %	10 %
Aromatics	73 %	64 %
Resins	7 %	10 %
Asphaltenes	18 %	16 %

Table 9 Fractional composition of local bitumens in Aden (Yemen)

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