

An Investigation into the Effect of Composition on Performance of Penetration Grade Road Bitumens

Part 1: SARA Analysis

Zoorob S.E. and Airey G.D.
Nottingham Centre for Pavement Engineering, The University of Nottingham, NG7 2RD, U.K.

Synopsis

This paper forms the first half of an investigation into the effects of the chemical composition of penetration grade road bitumens on performance, in particular their ageing properties. The paper briefly reviews evidence from the literature suggesting that bitumens having the same grade, but originating from different crudes, can perform quite differently when subjected to thin film oven ageing tests. Simple explanations of the ageing mechanisms are presented based on analysis of changes that occur amongst the various bitumen fractions produced by chromatographic separation or fractional precipitation techniques. Bitumen samples having several grades, from Middle Eastern and Venezuelan sources were tested in this investigation in their virgin, short term oven aged and following interaction with crumb rubber. All the samples were fractionated into their saturates, aromatics, resins and asphaltenes using TLC-FID analysis. The results show consistent differences in the percentage of saturates and aromatic hydrocarbon fractions between Middle Eastern and Venezuelan bitumens. As expected, an increase in the asphaltene contents as a result of ageing was shown for all bitumens. On the other hand, ageing seems to have a different effect on the saturate fractions of the two bitumen types. The colloidal instability coefficient was also shown to be a useful tool in highlighting differences between the two bitumen types. The paper describes the principles of operation of an Iatroscan, sample preparation steps and analysis of results. Possible sources of error and scatter of results is also described together with recommendations for improvements.

An Investigation into the Effect of Composition on Performance of Penetration Grade Road Bitumens

Part 1: SARA Analysis

Bitumen is manufactured from crude oil which is a complex mixture of hydrocarbons varying in molecular weight and consequently in boiling range. Crude oils differ in both physical and chemical properties. Physically they vary from viscous black liquids to free-flowing straw coloured liquids. Chemically they may be predominantly paraffinic, naphthenic or aromatic, with combinations of the first two being common. There are nearly 1500 different crude oils produced world wide. Based on the yield and the quality of the product produced, only a few of these are considered suitable for the manufacture of bitumen. In the UK, bitumens are principally manufactured using either Middle Eastern or South American crudes (Morgan & Mulder, 1995).

From a petroleum geochemistry perspective, bitumens were defined by Languri *et al.* (2002) as emulsions of cross-linked flat sheets of polycyclic aromatic and heterocyclic hydrocarbons (asphaltenes) 'dissolved' in a mixture of lower molecular weight aliphatic and alicyclic hydrocarbons (maltenes). Depending on the geological origin, there may be a substantial amount of sulphur compounds present, presumably contributing to S-linkages to the network polymer system. Aliphatic hydrocarbon chains with variable chain length ($C_2 - C_{40}$) link most of the aromatic centres.

An extensive investigation by Traxler (1961) of the rheological and colloidal properties of penetration grade bitumens have indicated that the amount of dispersed material (asphaltenes, which are the n-pentane insoluble component of the bitumen) and the chemical composition of the petrolenes (n-pentane soluble component, also known as maltenes) control the properties of a bitumen. If the petrolenes possess a high content of unsaturated or cyclic compounds the heavy asphaltic bodies are well dispersed. On the other hand, large amounts of saturated compounds will cause flocculation of the heavier bodies and the appearance of internal structure in the bitumen.

CHEMICAL FRACTIONATION OF BITUMENS

The Corbett Method

Although there are a variety of procedures and techniques for separating bitumens, these generally do not separate bitumens into distinct hydrocarbon types. This has made analysis very difficult because of the broad range of both molecular size and molecular type. Corbett *et al.* (1960) found that a fairly good separation of hydrocarbon types can be made by judicious use of chromatography. Even though this separation was argued to be arbitrary, it is nonetheless reasonably repeatable.

Corbett's method involves separation of the original bitumen into five hydrocarbon types. The first step is the precipitation of asphaltenes with normal hexane followed by their removal by filtration. The soluble portion from this separation, called petrolenes (maltenes), are then fractionated by use of chromatography using an active alumina as adsorbent and various solvents for elution. The flow diagram (Figure 1) illustrates the scheme of this separation and the order of elution using the various solvents.

A Nuclear Magnetic Resonance (NMR) spectrometer was used to measure the distribution of hydrogen among various kinds of carbon atoms, e.g., those on aromatic rings, those alpha to aromatic rings, and aliphatic types.

The following identifying characteristics were calculated (Corbett *et al.*, 1960):

- Branchiness Index (BI) which is the ratio of the methyl to methylene hydrogens exclusive of the hydrogens on the alpha carbon. Basically, this is a measure of the relative amount of hydrocarbon branching.
- Carbons per side chain (C/SC) which is sometimes referred to as the chain length is the average number of alkyl carbon atoms per side chain. Any carbon atom substituted on an aromatic ring is considered

a side chain. This is a significant measure of the structure of a hydrocarbon as it portrays the length or size of the aliphatic derivative.

- Aromatic rings per molecule (AR) is the average number of individual unsaturated rings. This identifies the size of the basic aromatic nucleus around which the hydrocarbon structure is built.

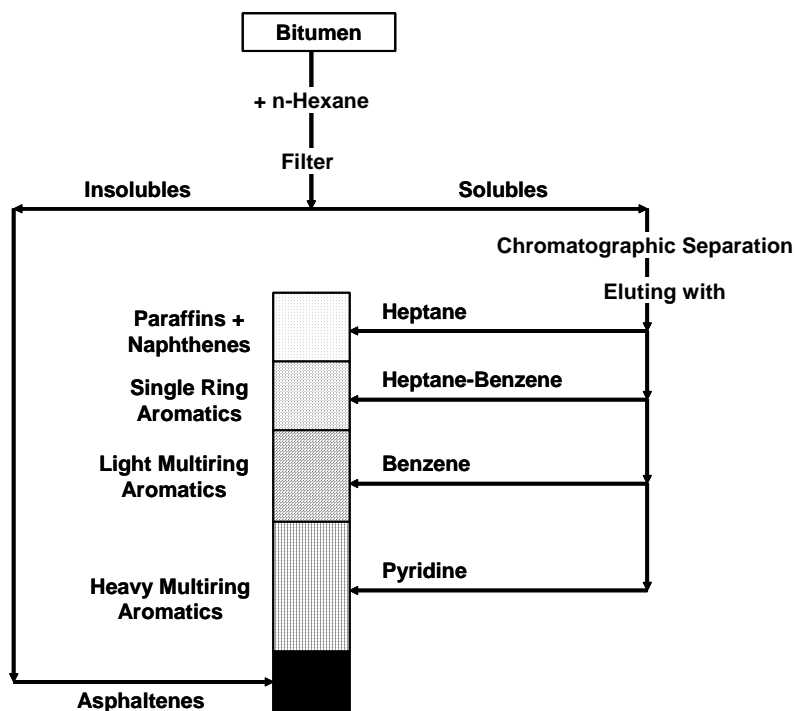


Figure 1: Major hydrocarbon types that can be separated from bitumen (Corbett *et al.*, 1960).

By use of the characterization described above, Corbett *et al.* (1960) was able to identify the average chemical structure of each fraction as reproduced below in Table 1.

Table 1: Identification of the chemical structure of bitumen fractions.

Fraction	MW	C/H	BI	C/SC	AR
Paraffins + Naphthenes	600	6.2	0.36	-	-
Single Ring Aromatics	674	6.9	0.50	13.3	1.2
Lighter Multiring Aromatics	708	7.9	0.55	6.7	5.1
Heavy Multiring Aromatics	956	8.4	0.60	5.5	6.7
Asphaltenes	3000	10.6	0.75	3.1	-

Notes: Paraffins = n + iso-alkanes; Naphthenes = cyclo-alkanes; MW = molecular weight; C/H = carbon to hydrogen ratio (aromaticity).

A trend in character was observed, such that each fraction may be characterized (Corbett *et al.*, 1960);

- Paraffins + Naphthenes – a mixture of pure paraffins plus naphthene hydrocarbons with alkyl side chains.
- Single Ring Aromatics – primarily a single ring aromatic type with several long aliphatic type side chains.
- Lighter Multiring Aromatics (LMA) – a mixture of multiple aromatic rings with much shorter side chains than those in the previous fraction.
- Heavy Multiring Aromatics – basically a multiple ring type similar to LMA but higher in average molecular weight.
- Asphaltenes are structurally multiple ring aromatics with very short aliphatic side chains. This fraction is distinctively higher in molecular weight than any of the above.

The Traxler Method

The first step of this method consists of dividing bitumens into 3 parts by fractional precipitation using 1-butanol followed by cold acetone. The 1-butanol precipitate (Fraction I) was composed of asphaltenes and

other higher viscosity materials. The 1-butanol soluble material was fractionated by treatment with acetone, the portion soluble in cold acetone (Fraction II) was called cyclics because it contained a preponderance of aromatic and unsaturated materials, the portion insoluble in acetone (Fraction III) was called paraffinics or saturates because of the large amounts of saturated compounds present (Traxler, 1961).

In the second step, the asphaltene (n-pentane insoluble) content of each bitumen was also determined. The asphaltene content was subtracted from Fraction I and the difference, Fraction IV, was called asphaltic resins.

Traxler (1961) proposed a coefficient of dispersion "X" which was indicative of the colloidal characteristics of a bitumen, where;

$$X = (R+C)/(A+S) = (\text{Resins} + \text{Cyclics})/(\text{Asphaltenes} + \text{Saturates})$$

When the amounts of Asphaltenes and Saturates are excessive, the value of the coefficient "X" is low and the bitumen is a poorly dispersed (due to flocculation of the heavier bodies and appearance of internal structure in the bitumen) or gel-type system resulting in marked non-Newtonian flow properties. On the other hand, when the Resins and Cyclics predominate, the value "X" is high and the heavy asphaltic bodies are well dispersed, the bitumen is thus a well dispersed sol-type bitumen possessing little internal structure and essentially Newtonian flow characteristics (Traxler, 1961).

Influence of Composition on Hardening Based on The Traxler Fractionation Method

Traxler (1961) presented data, reproduced in Table 2, to indicate that a correlation does exist between the Relative Viscosity "D" of a heated bitumen and the composition of the bitumen as expressed by the Coefficient of Dispersion "X". For the six bitumens tested there was a range in the values for "D", representing differences in hardening resulting from heating in the absence and presence of air, and in the values for "X" indicating considerable variation in degree of dispersion.

The six bitumens in Table 2 were listed in two groups which may be classed as poor or good in reference to degree of dispersion and rate of hardening. Three bitumens, with a high average value of "D", possess a low average value for "X". The other three bitumens with a low average value for relative viscosity "D" after heating for 4 hours at 107°C show a high average value for "X". Traxler (1961) drew the general conclusion that the susceptibility of a bitumen to hardening by heat and oxidation is related to its colloidal nature (degree of dispersion), which in turn is governed by the chemical composition.

Table 2: Relationship between composition and Resistance to Hardening for 85-100 penetration bitumens (Traxler, 1961).

Bitumen	Relative Viscosity, D		Coefficient of Dispersion $X = \frac{\text{Resins} + \text{Cyclics}}{\text{Asphaltenes} + \text{Saturates}}$
	15 micron film heated for 4 hours at 107°C in:		
	Nitrogen	Air	
1	3.8	10.9	0.5
2	3.7	9.1	0.49
3	2.2	6.9	0.55
Average	2.2	9.0	0.51
4	2.0	4.8	1.03
5	2.0	4.0	0.96
6	1.3	3.0	1.22
Average	1.8	3.9	1.07

BITUMEN AS A COLLOIDAL SYSTEM

A more recent definition of the colloidal state of bitumens was referred to as the "colloidal instability coefficient" (CI), which is represented by the ratio:

$$CI = [\text{Asphaltenes} + \text{Saturates}] / [\text{Resins} + \text{Aromatics}]$$

This ratio accounts for the sol-gel behaviour of bitumens. As the ratio increases, the gel behaviour of the material will become more pronounced and thus its colloidal stability will be worse. The colloidal instability coefficient has been correlated with several rheological parameters including the Frass breaking point temperature (T_F). T_F is the temperature below which the material becomes brittle (Jimenez-Mateos *et al.*, 1996).

BITUMENS AND THEIR AGEING PROPERTIES

Bitumen Ageing During Manufacture and Laying of Asphalts

Long-term studies have shown that if a bituminous surfacing is to achieve its design life, it is important that the bitumen is not excessively hardened during hot storage, the bituminous mixture manufacturing process, or in service on the road.

When molten bitumen flows into the mixer of a hot mix plant, and is spread as thin films over the surface of hot aggregate in the presence of an oxidizing atmosphere (air), oxidation and volatilization occurs. Volatilization and oxidation increase the viscosity of all bitumens and for some the hardening may be excessive. Experience in the field indicates that a bitumen which is highly susceptible to hardening by heat and oxidation usually possesses limited serviceability as a road binder.

Further, during transport of the hot mixture to the paving site, additional hardening can and often does take place. In the process of transferring the hot mixture to the paving machine and during the spreading and compaction operation there is still further opportunity for oxidation and volatilization.

After completion of construction and opening the pavement to traffic, the binder is subjected to a variety of stresses imposed under different conditions of speed, loading and temperature. Further, the bitumen film is subjected to the elements, and weathering may induce changes in the original engineering properties such that the binder is no longer effective (Traxler, 1961; Traxler 1963; Hveem *et al.*, 1963).

Traxler (1963) presented data, which have been reproduced in Table 3, on the hardening behaviour of an 86 penetration grade bitumen as it passes from the storage tank through the mixing, handling and compaction operations and during the first 2 weeks on the road. In this short time the viscosity of the binder had increased almost four-fold. The author mentioned other cases that were encountered where the bitumen relative viscosity increased 5.5 fold by the time it had reached the paving machine.

Table 3: Progressive increase in relative viscosity of a typical bitumen (Traxler, 1963)

Sample	Pen. @ 25°C	Viscosity (Stokes) @ 135°C	Viscosity (Poises) @ 25°C	Relative Viscosity
Original bitumen* temp. 149°C	86	2.3	1.0×10^6	-
Recovered from mix leaving hot-mix plant. Temp. 141°C.	72	2.4	1.4×10^6	1.4
Recovered at paver, 3.5 hours after leaving plant. Temp. 129°C.	68	2.6	1.9×10^6	1.9
Recovered from sample taken from road 15 days after pavement was laid. Very hot weather.	48	3.0	3.8×10^6	3.8
Recovered from sample taken from road 4 months after pavement was laid.	42	3.2	7.8×10^6	7.8
Original bitumen. 15 micron-film subjected to oxidation for 2 hours at 107°C.	-	-	4.0×10^6	4.0

* taken immediately prior to entering hot-mix plant.

Numerous investigations have determined that when the recovered bitumen penetration at 25°C is around 20 and the ductility has fallen to a low value, the binder is in a critical state and failure may quickly result in areas of relatively high pavement deflection. Hveem (1963) argued that bitumens that do not exceed 20 megapoises viscosity at 25°C, shear rate 0.05 sec^{-1} will provide a satisfactory binder during service life, if the ductility requirements are also met. Similarly, it was proposed to control contraction cracking by limiting the viscosity at 0.001 sec^{-1} shear rate to 60 megapoises (equivalent to 6 MPa.s). This value was based on available field evidence.

Influence of Asphaltene Content and Size on Bitumen Rheological Properties

Large variations in asphaltene content were found in bitumens of equal penetration, ring and ball softening point, and penetration index but from different sources. For bitumens from each source the asphaltene content increased with decreasing penetration (increasing viscosity) but for equal penetrations the asphaltene content varies with the source. This feature was attributed to a variation in the molecular weight

of the asphaltenes or in the viscosity of the maltenes in bitumens from different sources. For bitumens from the same source, the maltene viscosity and asphaltene content increased as the bitumen viscosity increased (Moavenzadeh & Brady, 1964).

VARIATIONS IN EXTENT OF AGEING OF EQUIVALENT GRADE BITUMENS OBTAINED FROM DIFFERENT SOURCES

Background

The rate at which six samples of 85-100 penetration grade bitumens hardened was investigated by Traxler (1961). At the time of the investigation, the bitumens selected were all being used for road building by the Texas Highway Department. The bitumens were specifically chosen from a range of manufacturers to have the same penetration grading but at the same time to represent a wide range of resistance to hardening and a considerable difference in composition. Bitumen samples were heated in ovens for a range of durations. The viscosities of the original and hardened bitumens were determined at 25°C in a microfilm viscometer using films 25 to 30 microns thick. The quotient "D" (= aged/original viscosity), was called the relative viscosity, and was used as a measure of the hardening of the bitumen. A high "D" value meant that the bitumen hardened excessively.

Oven Ageing Thick Films of Bitumen

Table 4, reproduced from work by Traxler (1961) shows the viscosity data of the six 85-100 pen grade bitumens and the relative viscosity "D" for each of the samples after heating to 163°C. The bitumen samples were placed in metallic trays to a depth of 3175 microns and were conditioned in ovens at the test temperature. Sample 1 shows poor resistance to hardening whereas sample 6 shows low susceptibility to heat and oxygen.

Oven Ageing Thin Films of Bitumen

In the same paper, Traxler (1961) showed results of tests on 13-15 micron films of bitumen that were oxidized on glass plates in an oven for 2 and 4 hours at 107°C. The 15 micron film thickness was selected as representative of the average thickness of bitumen films present in most types of pavements. The results are reproduced below in Table 5.

Table 4: Hardening of thick films of 85-100 penetration bitumens heated in air (Traxler, 1961)

Bitumen no.	Viscosity, Megapoises, 25°C at 5×10^{-2} sec. ⁻¹				Relative Viscosity "D"		
	Original bitumen	1/8 inch (3175 Micron) Film heated at 163°C for:					
		5 hours	10 hours	15 hours	5 hours	10 hours	15 hours
1	1.10	9.1	15.1	21.0	8.2	13.5	19.1
2	0.90	4.8	7.1	11.7	5.3	8.0	12.2
3	1.30	4.9	8.6	12.0	3.8	6.6	9.3
4	0.80	2.9	4.5	6.5	3.6	5.6	8.1
5	0.85	1.9	3.7	5.8	2.2	4.3	6.8
6	0.70	1.5	3.1	4.0	2.1	4.4	5.7

Table 5: Hardening of thin films of 85-100 penetration bitumens heated in air (Traxler, 1961)

Bitumen	Viscosity, Megapoises, 25°C at 5×10^{-2} sec. ⁻¹				
	Original bitumen	15 Micron Film heated at 107°C for:		Relative Viscosity "D"	
		2 hours	4 hours	2 hours	4 hours
1	1.10	6.6	12.0	6.0	10.9
2	0.90	4.1	8.2	4.5	9.1
3	1.30	5.2	9.0	4.0	6.9
4	0.80	2.0	3.8	2.5	4.8
5	0.85	2.4	3.4	2.8	4.0
6	0.70	1.5	2.1	2.1	3.0

Tables 4 and 5 show that the ranking of results from either binder thickness was the same. Sample 1 had high susceptibility to hardening and sample 6 showed a low rate of hardening. Sample 3 was intermediate in its reaction to heat and oxygen. It was found that the data obtained with the 15 micron films were most consistent.

Figure 2 shows the effect on relative viscosities of heating 15 micron films of bitumen samples 1 and 6 at 107°C for extended periods of time and highlights the differences between the two samples (Traxler, 1961).

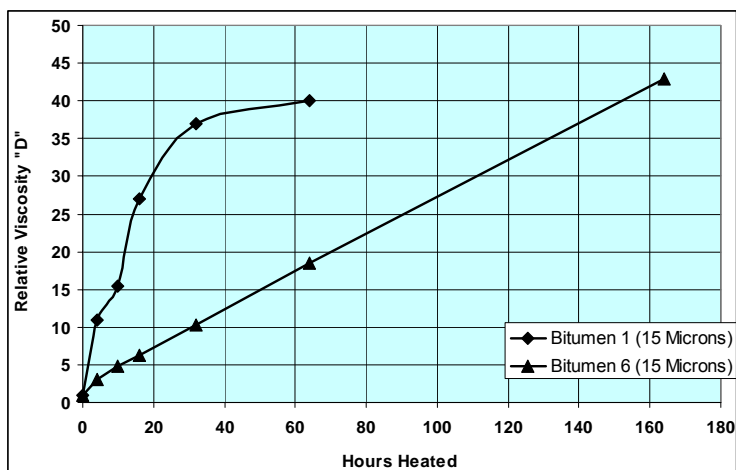


Figure 2: 85-100 penetration bitumens, 15 microns films heated in air at 107°C (Traxler, 1961).

Heating Thin Films of Bitumens in a Nitrogen Atmosphere

The increase in viscosity discussed earlier were caused by (a) volatilization of oils and (b) oxidation. In order to assess the relative importance of these two factors, additional experiments were conducted by Traxler (1961) which consisted of heating thin bitumen films (15 microns) from the same six 85-100 penetration grade samples as reported in the previous section at 107°C under one atmosphere of nitrogen. With no oxygen present, any increase in viscosity was assumed to be caused chiefly by evaporation of oils from the bitumen films. At the test temperature of 107°C, some polymerization was assumed to occur but most of the increase in consistency was ascribed to volatilization.

It appears from the data obtained on the thin films investigated, that the proportion of hardening caused by these two factors varies somewhat between the six 85-100 penetration grade bitumens obtained from different manufacturers. Table 6 below gives the % of viscosity increase due to volatilization and oxidation as calculated from the relative viscosities "D", after 4 hours treatment. A greater proportion of the hardening in bitumens 1, 2 and 3 was caused by oxidation than in the case of samples 4, 5 and 6. It was suggested that the somewhat greater susceptibility of bitumens 1, 2 and 3 to oxidation is possibly related to their higher asphaltene contents indicated in Table 6.

Table 6: Data on 85-100 penetration bitumens heated in Air and Nitrogen at 107°C (Traxler, 1961).

Bitumen	% of Hardening Attributed to		% Asphaltene content
	Oxidation	Volatilization	
1	65	35	17.8
2	60	40	19.0
3	66	34	24.6
average	<u>64</u>	<u>36</u>	<u>20.5</u>
4	58	42	9.3
5	50	50	8.1
6	58	42	1.0
average	<u>55</u>	<u>45</u>	<u>6.1</u>

RELATIONSHIPS BETWEEN BITUMEN COMPOSITION AND HARDENING

Influence of Air Blowing on Hardening of Bitumens Based on The Corbett Fractionation Method

When a bitumen is air blown the percentage of some of the fractions change perceptibly, and in some cases the character also changes. This was investigated by Corbett *et al.* (1960) using the example of a flux converted to a roof coating bitumen as reproduced in Figure 3. First it will be noted that there was almost no quantity change in the paraffins + naphthenes fraction and only a slight change in the single ring aromatics fraction. The light multiring aromatics decreases slightly while a large quantity of heavy multiring aromatics

disappears. All of this is balanced by a large increase in asphaltenes, which essentially accounts for the increase in the bitumen's consistency or hardness. Thus, it was apparent that the predominating change is conversion of heavy multiring aromatics to asphaltenes.

Looking at the comparative character of each fraction it was noted that the molecular weight in each case increases to a small degree, which is evidence of some polymerization. There was also a loss in chain length, especially in the case of the single ring aromatics fraction. This was explained by dehydrogenation of naphthenes or by cyclo-aromatization, i.e. the formation of new naphthenes followed by dehydrogenation. The formation of asphaltenes was described as a polymerization reaction, although the mechanism of this reaction was not understood. However, it was apparent that this hardening change was largely due to the conversion of the heavy multiring aromatics to asphaltenes (Corbett *et al.*, 1960).

To better understand the changes involved, each of the aromatic fractions was air blown separately but under the same conditions, i.e. 238°C, four hours, and constant air rate as reproduced in Figure 4. This confirmed the earlier observation of Corbett *et al.* (1960) that the heavy multiring aromatic fraction contributes primarily to the making of asphaltenes.

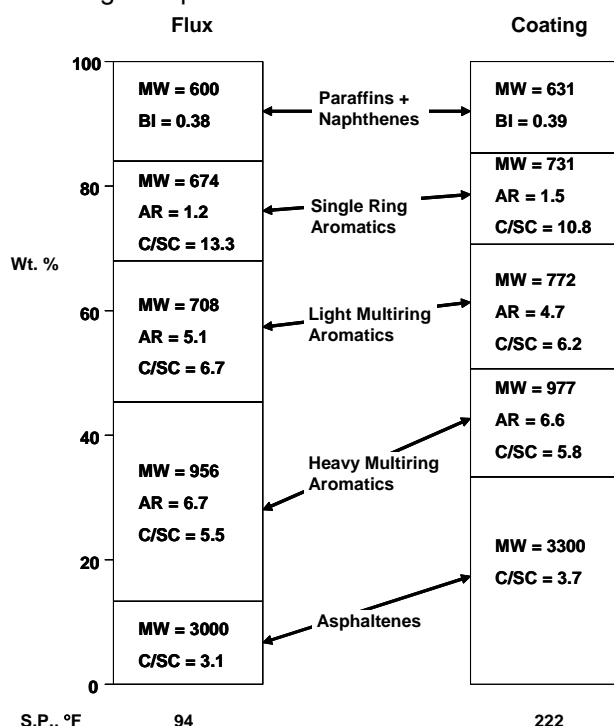


Figure 3: Primary reaction in air blowing is polymerization of Heavy Multiring Aromatics to Asphaltenes (Corbett *et al.*, 1960).

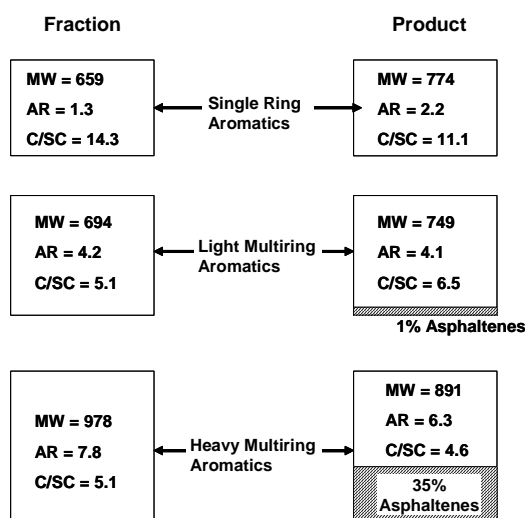


Figure 4: Blowing of each fraction separately emphasises reactivity of Heavy Multiring Aromatics (Corbett *et al.*, 1960).

The extent or the amount of asphaltenes made is largely a function of the time and temperature of the process, and thus the data was considered strictly as a comparison. In the single ring aromatic fraction Corbett *et al.* (1960) found a notable loss in carbons per side chain and an increase in aromatic rings. This again was explained on the basis of dehydrogenation and cyclo-aromatization. However, the most pronounced change was the conversion or polymerization of 35% of heavy multiring aromatics to asphaltenes compared with negligible quantities in the other fractions. The oil product from this conversion, after removal of asphaltenes, is of lower molecular weight and fewer aromatic rings. This indicated that the highest molecular weight and most aromatic constituents are being reacted out of the system. All of this supported the earlier indications that the reactivity of the heavy multiring aromatics is really the most important factor in hardening by air blowing (Corbett *et al.*, 1960).

Influence of Field Ageing on Hardening of Bitumens Based on The Corbett Fractionation Method

In addition to the air blowing study, a comparison was also made by Corbett *et al.* (1960) between a bitumen recovered from a 3-year old asphalt pavement and the original bitumen retained as a sample. The penetration at 25°C, dropped from 82 to 56 over this period and the asphaltene content increased from 14.5 to 17.0 weight per cent, as shown in Figure 5. It must be emphasised that this included the loss in penetration during mixing.

The fractions were observed to undergo minor structural changes during this process. The heavy multiring aromatics were found to decrease in molecular weight and carbons per side chain while there was an increase in the number of aromatic rings. In air blowing an appreciable change in the quantity of this fraction was found, resulting in a fraction of lower molecular weight and aromatic content when treated separately. The difference here was interpreted to mean that another reaction probably occurs simultaneously with the conversion to asphaltenes, and this reaction increases the number of aromatic rings at the expense of side chains. It was also found that the molecular weight of the asphaltenes increased appreciably during this period. Corbett *et al.* (1960) had no explanation for this.

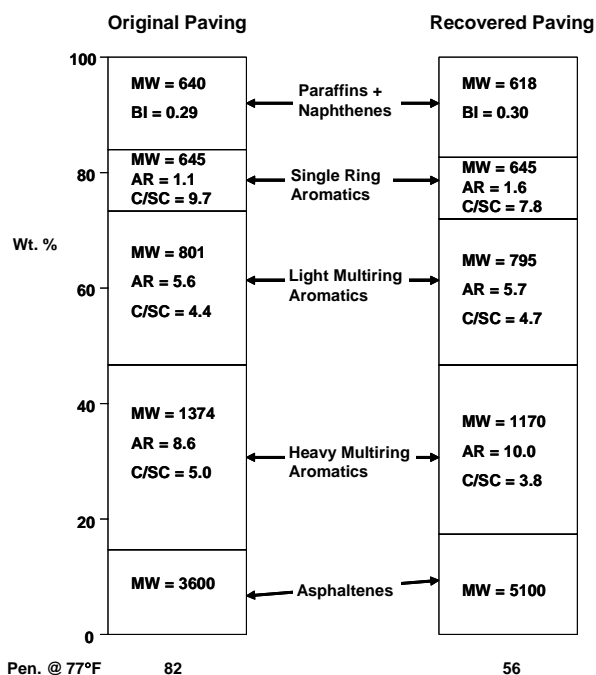


Figure 5: Hardening of paving involves an increase in asphaltenes (Corbett *et al.*, 1960).

MORE RECENT WORK ON BITUMEN AGEING

According to Begak *et al.* (2002), the colloidal stability of bitumens and their physicochemical properties are controlled not only by the proportion of oils, resins, and asphaltenes in them, but also by their chemical nature. The presence of a fairly large amount of oil fraction characterised by high carbon content in cyclic structures and aromaticity imparts the colloidal stability and desirable physicochemical characteristics to bitumens. However in this case they demonstrate relatively higher temperature sensitivity and low elasticity.

In the case of an insufficient content of the oil fraction, or when this fraction is of essentially naphtho paraffinic nature, the colloidal stability of the bitumen decreases as well as its ductility.

Begak *et al.* (2002) also suggest that the condition of the bituminous colloidal system depends not only on the asphaltene to maltene ratio, but also on the aromaticity of asphaltenes (C/H ratio) and solvency of maltenes (K_s);

$$K_s = C_{ar} + 1/3 C_n$$

where; C_{ar} and C_n are the carbon contents (%) in the aromatic and naphthenic structures, respectively.

In ageing initiated by thermal effects, the colloidal state of bitumen changes through aggregation of dispersed particles (free energy of the system decreases). The evolution occurs from a sol with a random distribution of particles via a structured sol to a gel. In this case, the orientation ordering of colloidal particles increases, and the free energy at the interface decreases. As ageing proceeds, micellar aggregates become more compact, the interparticle interaction increases, the volume of the system decreases and the bitumen hardness increases (Begak *et al.*, 2002).

MATERIALS USED IN THE INVESTIGATION

Bitumens

Four bitumen grades (vacuum residues of petroleum) were initially selected for this investigation, which were classed as; 35, 40/60, 70/100 and 160/220 penetration grade bitumens. For each grade, bitumen samples from two origins were obtained, a Middle Eastern source and a Venezuelan source. All Middle Eastern and Venezuelan virgin bitumen samples were obtained from the same bitumen manufacturer in the U.K.

At a later stage of the investigation, and in order to further assist in the binder characterisation phase of this investigation, a virgin Middle Eastern bitumen sample was also obtained directly from its source of production in the State of Kuwait. It must be noted that only one kind of bitumen, a 60/70 penetration grade bitumen, is produced by the Kuwait Oil Company and is available for use in road surfacings in Kuwait.

All the bitumen samples used in this investigation are listed below in Table 7 together with selected physical properties. In addition to characterising the bitumens in their virgin states, two sets of identical samples (with the exception of the Kuwaiti sample) were also subjected to additional conditioning. The first set was subjected to short term oven aging using the rolling thin film oven test (RTFOT) as explained below. As part of another project, the second set of samples were mixed with crumb rubber particles and maintained at equiviscous (0.2 Pa.s) temperatures for 48 hours before being recovered for testing, details of procedure are given below.

Table 7: Selected Physical Properties of the bitumen samples used in the investigation

Sample Designation*	Penetration Grade	Measured Penetration (dmm)	Equiviscous Temperature ** (°C) at 0.2 Pa.s	Asphaltene Content *** (%)
M4	35 pen	32	180	18
M3	40/60 pen	53	170	14
M2	70/100 pen	88	150	11
M1	160/220 pen	192	140	8
V4	35 pen	36	165	19
V3	40/60 pen	55	165	13
V2	70/100 pen	90	150	11
V1	160/220 pen	203	135	10
Q8	60/70 pen	74	not measured	

* M = bitumen samples of Middle Eastern source, V = bitumen samples of Venezuelan source, Q8 = a Kuwaiti bitumen sample.

** measured using a rotational shear viscometer.

*** Asphaltene content measured in accordance with BS 2000: Part 143: 1996.

BITUMEN CONDITIONING TESTS

Short Term Bitumen Oven Ageing

The RTFOT was used to short term age selected bitumen samples in accordance with ASTM D2872. The RTFOT simulates the bitumen ageing process during the manufacture and construction of hot mix asphalt pavements. In this test, 35g of bitumen is poured into a bottle, which is placed horizontally into a rack, which in turn is placed in an oven maintained at 163°C. The rack rotates at a prescribed rate around a horizontal

axis. The rotating bottle therefore continuously exposes fresh bitumen. The orifice of the sample bottle passes in front of an air jet during each rotation. The vapours accumulated in the sample bottle are purged by the heated air from the jet. The test duration is typically 75 minutes (Morgan *et al.*, 1995).

Soaking Rubber in Bitumen

The amount and rate of swelling of crumb rubber in bitumen is a function of time, temperature of immersion and bitumen grade. A swelling test, developed at the Nottingham Centre for Pavement Engineering (Airey *et al.*, 2003), subjects a 5g sample of crumb rubber (truck tyres), which is placed in a wire mesh basket with 0.3mm square apertures, to soaking in 40g of pre-heated bitumen in a fan assisted oven at 0.2 Pa.s for a set time. In this investigation the baskets containing the rubber samples were removed from the bitumen after 48 hours soaking and allowed to drain for 5 minutes, whilst suspended in the oven at the same temperature. The residual bitumen was then allowed to cool down to room temperature before being subjected to any additional tests.

TLC-FID ANALYSIS OF BITUMENS

General Description of Equipment

The Iatroscan ^{new}MK-5 is an automatic detector that performs quantitative analysis on organic mixtures separated on thin layer chromatography (TLC) and detected by Hydrogen Flame Ionization System (FID). The separation of components is performed on an exclusive thin layer chromatography media (Chromarod SIII) in the same manner as normal phase TLC. Its FID system has high sensitivity for almost all organic components. Ten Chromarods are held in a single rack allowing up to 10 samples to be applied at a time.

Chromarods

The Chromarod consists of a 0.9mm diameter and 15.2cm long quartz glass rod on which thin layer adsorbents (pore diameter 60Å, particle size 5µm) are sintered with non-organic binder. A sample(s) is developed and separated on this thin layer surface utilizing traditional normal phase chromatography methods. The Chromarod is then scanned through the Hydrogen Flame of the Iatroscan where the sample is ionized and removed from the surface of the Chromarod. Reactivation and cleaning of the Chromarod is accomplished by performing a Blank Scanning program on the Iatroscan. The Chromarod is reusable for many developments and detection cycles.

Principle of Operation

When a sample(s) is developed and separated on the Chromarod (thin layer quartz rod) and scanned directly into the Hydrogen Flame at the rated speed, organic components separated on this thin layer surface are ionized by the energy of the Hydrogen Flame. The ions generated are charged both negative and positive. The negative ions (-) flow to the Burner and the positive ions (+) flow to the Collector Electrode due to the electric field loaded between the FID electric poles (Burner +ve and Collector -ve). These ion currents flow between the Burner and the Collector proportionally to the mass of components being ionized in the Hydrogen Flame. The ion current is amplified by the FID circuit, and the components are quantitatively measured and recorded by the data processing unit.

Sample Spotting

The bitumen samples were diluted in dichloromethane (DCM) to a concentration of 10 mg/mL and kept in sealed vials overnight away from sunlight to reduce photo-oxidation. After Blank Scanning has been completed, the rod holder was removed from the scanning frame. The bitumen in DCM samples were spotted by use of a blunt tip syringe. 3 µL of sample was applied to each Chromarod at zero point on the rod holder. The sample spot was kept as small as possible (maximum 3mm band is recommended) and concentrated as possible. The larger the sample spot is spread at the origin, the poorer the separation performance.

In total, three racks were available for this investigation (10 Chromarods in each rack). Each bitumen sample was spotted on two rods to check for reproducibility of results. Additionally, the same bitumen samples were spotted on different racks.

A North Sea Oil standard of known composition was prepared at a target concentration of 10mg/mL (actual conc. = 10.74 mg/mL) and was also run on at least one rod of each rack.

Development of the Chromarods

Multiple developments in different solvents was required to adequately separate the sample components. Three tanks were used, the contents of which were changed at the beginning of each working day;

Tank 1 was filled to a depth of about 1.5cm with n-hexane (for elution of saturated hydrocarbons), Tank 2 was filled to a depth of about 1.5cm with Toluene (for elution of aromatic hydrocarbons), and Tank 3 was filled to a depth of about 1.5cm with 93% DCM + 7% Methanol (for elution of polar fractions).

Prior to rod development, at least one inner side of each TLC development tank was lined with a piece of filter paper. The developing solvent was poured into each tank, making sure that the filter paper was wet and the opening of each tank was covered with a glass lid to saturate the tank with sufficient solvent vapour.

After sample spotting was completed, the first rod holder was placed into the first tank in the upright position, so that the lower 0.5cm ends of the Chromarods were immersed in the solvent. The opening of the tank was covered with the lid immediately and development began. A strong light source was placed at the rear of each tank to enable easier viewing of the solvent front rising up the rods.

When the solvent front reached an appropriate height, the rod holder was removed from the tank. The appropriate heights for the solvent fronts for the various tanks were as follows:

- Tank 1 - not exceeding the 100 graduation mark on the rod holder (equivalent to 95% of rod length),
- Tank 2 - not exceeding the 60 graduation mark on the rod holder,
- Tank 3 - not exceeding the 30 graduation mark on the rod holder.

After each development was completed, the solvent remaining on the Chromarods was removed. Care must be taken to remove all of the solvents on the rods. Otherwise, the analytical results will not be reproducible. The FID system of the Iatroscan cannot determine the difference in the sample material and the development solvent. The solvent evaporation times of the rod holders were as follows:

- After removal from Tank 1, dry rods at room temperature for a minimum of 3 minutes,
- After removal from Tank 2, dry rods at room temperature for a minimum of 6 minutes,
- After removal from Tank 3, dry rods in an oven set at 60°C for exactly 90 seconds, to ensure a similar C₁₅₊ residue for all samples.

After the solvents were completely removed (i.e. after immersion in Tank 3), the Holder was placed in the Scanning Frame. The Chromarods pass automatically through the Hydrogen Flame to ionize the sample. The ionization (burning) causes changes in electric current flowing through the FID. These currents were recorded on the Iatroscorder, and the chromatogram was plotted.

Data Manipulation

The results from each scan were automatically recorded in the form of a chromatogram which, in an ideal situation, consisted of 4 distinct peaks (see Figure 6), each peak being representative of a particular oil fraction (i.e. Saturates, Aromatics, Resins and Asphaltenes). The Iatroscan software allowed the 4 areas under the graph, representative of the four fractions, to be easily calculated.

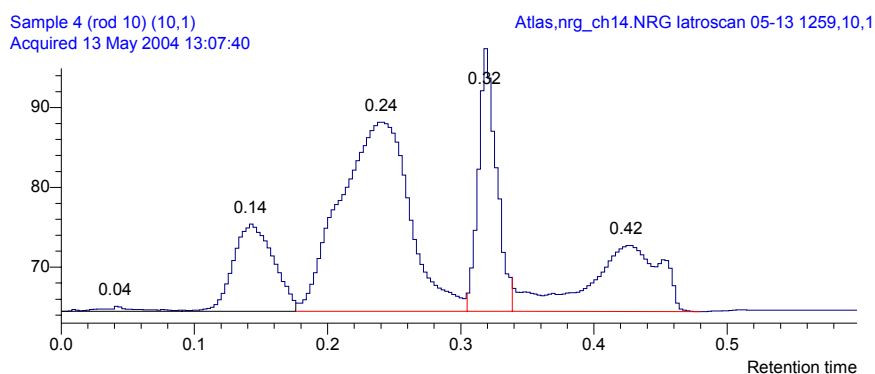


Figure 6: TLC-FID Chromatogram of a 50 penetration grade Venezuelan Virgin bitumen with well defined peaks.

Figure 7 below shows another example of a Chromatogram of the same bitumen sample which was not so easy to analyse. In this case the 4 peaks were not so distinct and co-elution of peaks 1 and 2 was quite severe. This was not an uncommon occurrence and a lot of judgement had to be exercised in order to select the beginning and end of each peak.

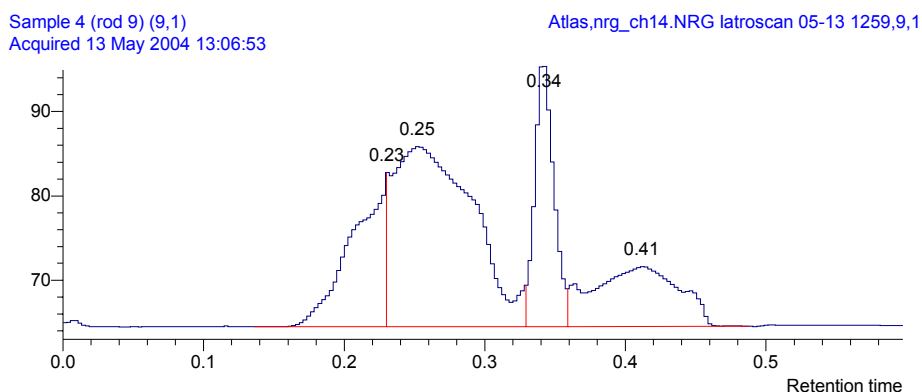


Figure 7: TLC-FID Chromatogram of 50 penetration grade Venezuelan Virgin bitumen with poorly defined peaks.

As mentioned earlier, the amount of North Sea Oil spotted per rod was 3 μ L which equates to 32.2 μ g of oil. The North Sea Oil sample used in this experiment had the following known composition: Saturates = 57%, Aromatics = 35%, Resins = 6% and Asphaltenes = 2%.

Therefore, for a Chromarod that has been spotted with North Sea Oil, the amount of any particular fraction can be easily calculated, e.g. amount of saturates, spotted on a single rod would be; 57% \times 32.2 μ g = 18.36 μ g.

To determine the Response Factor per μ g, which is equivalent to the Area under each peak of the chromatogram per μ g of sample, the calculations detailed in the following paragraphs were performed.

As mentioned earlier, prior to spotting the Chromarods with the samples, all Chromarods were activated and cleaned by performing a Blank Scan. The first step was thus to deduct the areas under the 4 chromatogram peaks from the areas of the 4 peaks obtained from a blank scan of the same Chromarod (i.e. the clean rod).

For example, assume a North Sea Oil chromatogram produces the following Areas (Sample Areas – Blank Areas); Saturates = 72.7, Aromatics = 76.2, Resins = 20.7 and Asphaltenes = 3.9. The Response Factor for the Saturates fraction of the North Sea Oil would be; 72.7 \div 18.36 = 3.959 units of Area / μ g. Similarly, the Response Factors for the other fractions can be easily calculated.

The Areas under the peaks of a particular Bitumen sample chromatogram may be as follows; Saturates = 26.4, Aromatics = 93.8, Resins = 29.3 and Asphaltenes = 24.8. To calculate the amount of Saturates on the Chromarod, the Area is simply divided by the Response Factor; 26.4 \div 3.959 = 6.66 μ g. The amounts of the other 3 bitumen fractions on the Chromarod can be similarly calculated and the values reported as percentages.

Reliability of Results

A large amount of scatter in the results was observed and some degree of judgement had to be exercised regarding elimination of erroneous results. The average results for all the bitumen samples tested are shown in Table 8. For ease of identification, the cells containing the Middle Eastern Virgin results have been shaded using a light grey tone, whilst the cells containing the Venezuelan Virgin results have been shaded with a darker grey tone.

A thorough statistical analysis was not carried out in this part of the investigation, nonetheless, the North Sea Oil standard sample and the 50 penetration Venezuelan virgin bitumen were selected for more detailed multiple analysis. The North Sea Oil sample was run 21 times and the 50 pen Venezuelan Virgin bitumen was run 10 times. Tables 9 and 10 show a summary statistical analysis of these two samples and illustrates that for the bitumen samples, the Coefficient of Variation = (standard deviation / mean) \times 100, ranges between 8 and 22% for the various bitumen fractions. The results for the North Sea Oil sample were even less reliable.

Table 8: Average results of Iatroscan analysis of all bitumen samples

Sample type	Saturates	Aromatics	Resins	Asphaltenes
Standard - North Sea Oil	57.09	35.15	5.95	1.81
35pen. Mid. East Virgin	12.37	62.13	8.03	17.47
35pen. Mid East Aged	18.19	52.64	10.56	18.61
35pen. Mid East Recovered	14.87	48.83	11.76	24.55
35pen. Ven. Virgin	19.17	57.38	6.51	16.95
35pen. Ven Aged	14.72	54.29	6.98	24.01
35pen. Ven Recovered	13.12	54.21	9.25	23.43
50pen. Mid. East Virgin	13.93	60.98	7.85	17.24
50pen. Mid East Aged	19.03	54.13	7.32	19.52
50pen. Mid East Recovered	19.29	55.13	7.31	18.26
50pen. Ven. Virgin	21.78	52.44	7.10	18.68
50pen. Ven Aged	17.67	53.89	6.81	21.62
50pen. Ven Recovered	21.17	48.64	8.07	22.12
100pen. Mid. East Virgin	19.74	58.59	6.15	15.51
100pen. Mid East Aged	18.32	60.57	6.76	14.35
100pen. Mid East Recovered	18.49	53.55	8.85	19.11
100pen. Ven. Virgin	23.71	53.96	6.91	15.42
100pen. Ven Aged	18.85	56.74	6.92	17.49
100pen. Ven Recovered	15.96	57.36	8.14	18.55
200pen. Mid. East Virgin	18.06	61.87	6.80	13.27
200pen. Mid East Aged	19.13	58.78	6.54	15.56
200pen. Mid East Recovered	19.32	56.46	8.81	15.41
200pen. Ven. Virgin	26.58	51.74	8.17	13.51
200pen. Ven Aged	25.83	47.66	8.85	17.65
200pen. Ven Recovered	17.33	55.86	7.35	19.46
60/70pen. Q8 Virgin	16.01	59.88	7.40	16.71

Notes: Aged bitumen samples have been subjected to short term oven ageing using the RTFO test. Recovered bitumen samples indicate that the bitumens have been mixed with crumb rubber & recovered.

Table 9: TLC-FID summary statistics on North Sea Oil calibration standard (21 samples)

	Saturates	Aromatics	Resins	Asphaltenes
Mean	57.091	35.147	5.950	1.810
Standard Error	0.642	0.569	0.217	0.219
Median	57.575	35.061	5.670	1.323
Standard Deviation	2.943	2.609	0.995	1.003
Sample Variance	8.664	6.811	0.990	1.007
C.V. (%)	5.155	7.425	16.726	55.431
Range	13.434	12.972	3.728	3.205
Minimum	48.071	29.805	4.253	0.808
Maximum	61.505	42.778	7.982	4.014

Note: Coefficient of variation (C.V.) = (standard deviation / mean) × 100

Table 10: TLC-FID summary statistics on 50 penetration Venezuelan virgin bitumen (10 samples)

	Saturates	Aromatics	Resins	Asphaltenes
Mean	21.782	52.441	7.096	18.678
Standard Error	0.800	1.338	0.506	0.604
Median	21.271	51.696	6.811	19.254
Standard Deviation	2.532	4.234	1.601	1.912
Sample Variance	6.412	17.928	2.563	3.658
C.V. (%)	11.625	8.074	22.559	10.240
Range	9.198	12.207	5.270	7.354
Minimum	16.823	47.560	5.287	14.100
Maximum	26.022	59.768	10.557	21.455

Precision and Accuracy From Earlier Investigations

Based on work by Karlsen *et al.* (1991), the analytical precision (10 rods, run 3 times) was found to be $\pm 3\%$ for tricosane and 1,4-dicyclohexylbenzene and $\pm 5\%$ for the polar compounds DSTDP (disteryl ester of thiodipropionic acid, M.W.=684), DNPD (di- β -naphthyl-p-phenylene diamine, M.W.=360), and 1-decanol. It was also suggested that the standard deviations of saturated and aromatic hydrocarbon fractions of oils are usually 2-5% higher than those of the pure hydrocarbon standards.

ANALYSIS OF RESULTS

Interpretation of Results Based on Changes in Individual Bitumen Components

Table 8 shows the TLC-FID analysis of all the virgin bitumen samples investigated. The first general observation that could be made was that as expected, the asphaltene content, with the exception of the 50 pen Venezuelan sample, did decrease as the penetration value increased. It is also noticeable that the asphaltene content values obtained from TLC-FID analysis as shown in Table 8 are not identical to those measured using ASTM D2007-93 as shown earlier in Table 7. This was expected, as apportioning the high molecular weight polar materials between resins and asphaltenes, which is always based, rather arbitrarily on solvency, inevitably will vary from the ASTM method since the solvents used are not identical (Fan & Buckley, 2002)

A more interesting observation from Table 8 was that the saturates content of both the Middle Eastern and Venezuelan bitumens, with the exception of the 200 pen Middle Eastern sample, all increased as the penetration value increased. If the virgin bitumen samples are considered on their own, it appears that the saturates contents of any particular grade of Middle Eastern bitumen is always lower than an identical grade Venezuelan virgin bitumen. On the other hand, the aromatics content of any particular Middle Eastern bitumen was always higher than an identical grade Venezuelan virgin bitumen.

Table 8 clearly shows that as expected the process of short term oven ageing of the bitumens has caused an increase in the asphaltene content for all bitumen grades and types. It was not possible to reliably calculate this percentage rise due to the relatively large variation in results.

Another interesting observation that emerged from Table 8 was that, except for the 100 pen Middle Eastern bitumen sample, all other Middle Eastern Virgin bitumens experienced an increase in the amount of saturates following short term oven ageing. On the other hand, in the case of the Venezuelan Virgin bitumens, the opposite trend was observed. All Venezuelan Virgin samples experienced a decrease in the amount of saturates following short term ageing.

In the majority of cases it was observed that the recovered bitumens (after being in contact with crumb rubber particles) had an even greater percentage of asphaltenes than the oven aged bitumens.

Figure 8 is a ternary diagram representing the saturated hydrocarbons, aromatic hydrocarbons and resins + asphaltenes for all virgin bitumen samples. It is interesting to note that there appears to be two distinct clusters of data points based on bitumen origin. The picture becomes less clear when the short term oven aged samples are added to the data points as shown in Figure 9. In Figure 9 it is clear that the data points are shifting towards the (resins + asphaltenes) apex of the triangle as a result of oven ageing, thus indicating an increase in the proportion of these two fractions as a consequence of ageing.

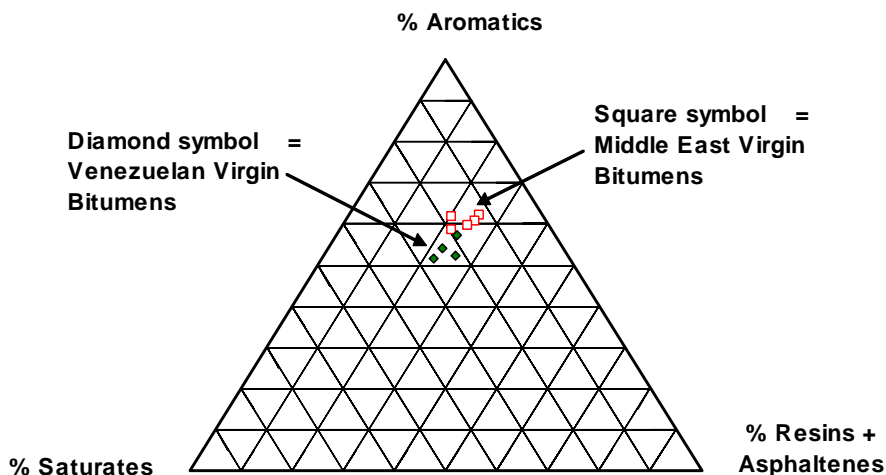


Figure 8: A ternary diagram depicting saturated HC, aromatic HC, and resins + asphaltene distributions in virgin Middle Eastern and Venezuelan bitumen samples.

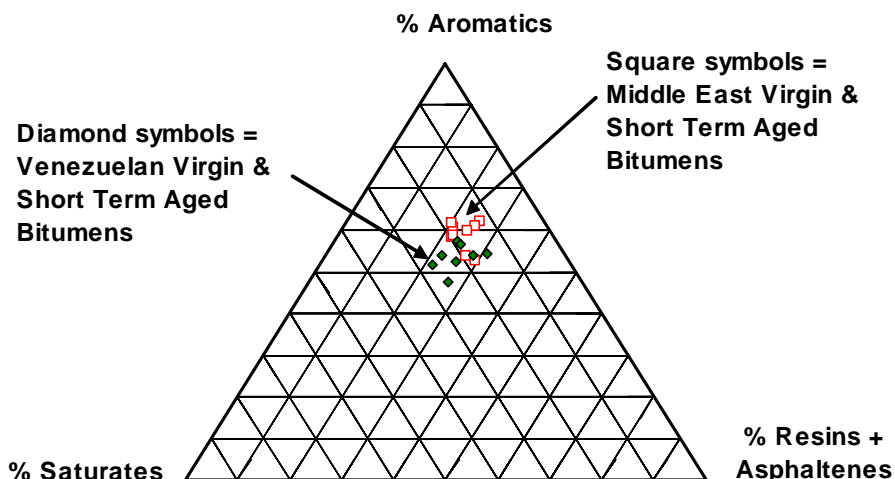


Figure 9: A ternary diagram depicting saturated HC, aromatic HC, and resins + asphaltene distributions in both Virgin and short term oven aged Middle Eastern & Venezuelan bitumen samples.

Interpretation of results based on colloidal instability coefficients

Further analysis of the SARA results was carried out by calculating the following ratios:

- The colloidal instability coefficient "CI" = (asphaltenes + saturates) / (resins + aromatics),
- The coefficient of dispersion "X" = (resins + aromatics) / (asphaltenes + saturates) = (1/CI),
- The ratio 'P' = (resins + asphaltenes) / (saturates + aromatics + resins + asphaltenes),

Specific gravity can sometimes be used to differentiate oils quickly from different sources. Biodegradation increases oil specific gravity and increases sulphur and other heteroatoms by selectively removing saturates and aromatics compared to resins and asphaltenes. Thus related oils can show different specific gravities if some are biodegraded. Both specific gravity and viscosity typically show a systematic relationship with the ratio of (resins + asphaltenes) ÷ (saturates + aromatics + resins + asphaltenes) for related oils (Peters & Moldowan, 1993). The results for the various ratios are shown in Table 11.

Table 11: Analysis of Iatroscan results based on variations of the colloidal instability coefficients.

Sample type	CI	X	P
Standard - North Sea Oil	1.433	0.698	0.078
35pen. Mid. East Virgin	0.425	2.351	0.255
35pen. Mid East Aged	0.582	1.717	0.292
35pen. Mid East Recovered	0.651	1.537	0.363
35pen. Ven. Virgin	0.565	1.769	0.235
35pen. Ven Aged	0.632	1.582	0.310
35pen. Ven Recovered	0.576	1.736	0.327
50pen. Mid. East Virgin	0.453	2.208	0.251
50pen. Mid East Aged	0.627	1.594	0.268
50pen. Mid East Recovered	0.601	1.663	0.256
50pen. Ven. Virgin	0.680	1.472	0.258
50pen. Ven Aged	0.647	1.545	0.284
50pen. Ven Recovered	0.763	1.310	0.302
100pen. Mid. East Virgin	0.544	1.837	0.217
100pen. Mid East Aged	0.485	2.061	0.211
100pen. Mid East Recovered	0.603	1.660	0.280
100pen. Ven. Virgin	0.643	1.556	0.223
100pen. Ven Aged	0.571	1.752	0.244
100pen. Ven Recovered	0.527	1.898	0.267
200pen. Mid. East Virgin	0.456	2.192	0.201
200pen. Mid East Aged	0.531	1.883	0.221
200pen. Mid East Recovered	0.532	1.879	0.242
200pen. Ven. Virgin	0.669	1.494	0.217
200pen. Ven Aged	0.769	1.300	0.265
200pen. Ven Recovered	0.582	1.718	0.268
60/70pen. Q8 Virgin	0.486	2.056	0.241

A quick glance at the figures presented in Table 11 shows that the values of the ratio "CI" all vary within a narrow range. Hence observing trends across samples would not be very easy. On the other hand, the values of the ratio $X = 1/CI$ were found to cover a wider range, making it slightly easier to analyse.

Traxler (1961) presented data (shown earlier in Table 2) to indicate that a correlation does exist between the relative viscosity of a heated bitumen and the composition of the bitumen expressed by the coefficient of dispersion "X". Table 11 shows that there was some trend indicating that ageing of bitumens reduces the values of "X", though the data do show considerable scatter. Interestingly, the "X" values of the Middle Eastern virgin bitumens were always higher than the "X" values of the Venezuelan virgin bitumens of equivalent grade. Similarly, when comparing bitumens of the same grade, the "X" values of the Middle Eastern aged bitumens were always higher than the "X" values of the Venezuelan aged bitumens.

With respect to change in composition as a result of ageing, a much improved trend was observed when considering the ratio "P". With a single exception, the "P" values increased as the Venezuelan and Middle Eastern bitumens were aged from the virgin state. Similarly with a couple of exceptions, the ratio "P" increased as the bitumen condition changed from aged to recovered. According to Peters and Moldowan (1993), both API gravity and viscosity are directly related to the ratio "P". To ascertain the validity of such a statement with respect to road bitumens demands a more detailed investigation.

OTHER FACTORS AFFECTING QUALITY OF RESULTS

Use of Alternative Solvents

As explained in earlier sections on chemical fractionation of bitumens, chromatographic techniques do not separate bitumens into distinct hydrocarbon types, and hence there are several procedures, techniques and solvents that can be used to separate bitumens into various fractions. In this investigation, n-hexane, toluene and DCM/methanol were used to fractionate the bitumen samples into the saturated, aromatic and polar hydrocarbon fractions.

As an example, in an earlier investigation by Karlsen et. al. (1991) analysing oil samples, the Chromarods were developed in n-hexane (40 min., 95% rod length), air dried (3 min.) developed in cyclohexane (20 min.,

50% rod length), air dried (3 min.), developed in toluene (5 min., 25% rod length) and then dried at 60°C (90 sec.) to remove the solvents and for standardizing samples with a large $<C_{15}$ fraction. The four resolved peaks were identified as; saturated hydrocarbons, mono-/diaromatic hydrocarbons, polycyclic aromatic hydrocarbons and resins/asphaltenes (Karlsen *et al.*, 1991).

Effect of Hydrogen Detector Flow Rates

In this investigation, a hydrogen flow rate of approximately 120mL/min was used. Earlier investigations (Karlsen *et al.*, 1991) found that hydrogen flow rates must be higher than about 120ml/min to ensure quantitative removal of the polar fractions from the rod using 10-30 μ g of Ula, Fulmar, Ekofisk and Gullfaks oils, while oils very rich in polar compounds, e.g. samples from the Miocene Monterey Formation needed either a higher hydrogen flow or decreased amount of sample. For both hydrocarbons and resins/asphaltenes, there is a decrease in response with decreasing hydrogen flow rate, the decrease being more pronounced for the asphaltene/resin fraction.

Volume of Sample

It is very likely that the volume of sample applied to each Chromarod, i.e. 3 μ L was excessive, it is therefore recommended that for future work smaller volumes of samples be applied, e.g. 1 μ L (Iatroscan MK-5 manual). The sample spot should be kept as small and concentrated as possible. The larger the sample spot is spread at the origin, the poorer the separation performance.

Number of Repeat Specimens

As the Coefficient of Variation amongst the various fractions can be at least as high as 22%, care must be exercised when interpreting the results of a limited number of samples. A more thorough statistical approach to the number of test samples and data analysis needs to be adopted when using the Iatroscan.

Activation of Chromarods

Although in this investigation, reactivation and cleaning of the Chromarods was accomplished by performing a single Blank Scanning program on the Iatroscan. Nonetheless, it was clearly visible that the Chromarods were not clean enough for reliable results. This is most likely to be the result of the high asphaltene content of bitumen samples when compared to conventional oil samples, e.g. as shown in Table 9. Multi-Blank runs on the same Chromarods should have been carried out in an attempt to obtain cleaner rods and reduce interference during the Chromarod development stage.

Using Deasphalted Samples

According to the Norwegian Industry Guide to Organic Geochemical Analysis (Weiss *et al.*, 2000), TLC-FID analysis should not be carried out on whole (i.e. not deasphalted oil), only deasphalted oil samples (i.e. maltene fraction) should be analysed. It appears logical that any future TLC-FID work on bitumens should at least assess such a recommendation. This is not as straight forward as it may first appear, as regardless of the solvent type and operating conditions, there is a tendency for non-asphaltic n-pentane soluble and insoluble materials to be co-precipitated with asphaltenes. Gürgey (1998) showed that following n-pentane treatment, waxy material, probably consisting of high molecular weight n-alkanes, was co-precipitated with the asphaltenes of waxy crudes.

CONCLUSIONS

Four bitumen grades (vacuum residues of petroleum) which are used in the manufacture of road surfacing asphalts were selected for this investigation. The bitumens were classed as; 35, 40/60, 70/100 and 160/220 penetration grade bitumens. For each grade, bitumen samples from two origins were obtained, a Middle Eastern source and a Venezuelan source. Furthermore, a Kuwaiti 60/70 penetration grade bitumen was also analysed and compared with the Middle Eastern samples.

A review of the literature on the ageing properties of thin films of penetration grade bitumens showed that the proportion of hardening caused by volatilization and oxidation varies somewhat between bitumens from different sources. It was argued that the greater susceptibility of some bitumens to oxidation was possibly related to their higher asphaltene contents.

TLC-FID analysis of virgin bitumen samples showed that the asphaltene content did decrease as the penetration value of the bitumen increased. It was also found that the saturates content of both the Middle Eastern and Venezuelan bitumens, with the exception one sample, all increased as the penetration value increased.

The process of short term oven ageing of the bitumens caused an increase in the asphaltene content for all bitumen grades and types. In the majority of cases it was also observed that the recovered bitumens had an even greater percentage of asphaltenes than the oven aged bitumens.

Except for one sample, all the Middle Eastern virgin bitumens experienced an increase in the amount of saturates following short term oven ageing. On the other hand all Venezuelan virgin samples experienced a decrease in the amount of saturates following short term ageing.

There was some trend indicating that ageing of bitumens reduces the values of the coefficient of dispersion "X", though the data do show considerable scatter. The "X" values of the Middle Eastern virgin or oven aged bitumens were always higher than the "X" values of the Venezuelan virgin bitumens of equivalent grade.

With respect to change in composition as a result of ageing, a much improved trend was observed when considering the ratio "P" as opposed to the ratio "X". "P" was defined as the ratio of (resins + asphaltenes) / (saturates + aromatics + resins + asphaltenes). With a single exception, the "P" values increased as the condition of all bitumens changed from virgin to aged and finally to recovered.

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