THE MODIFICATION OF BITUMINOUS MATERIALS USING TALL OIL PITCH

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SEAN R. BEARSLEY

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Abstract

There are economic, occupational safety and health, and environmental advantages in using tall oil pitch (TOP) as a bitumen extender. However, before bitumen modified with TOP can be used commercially in New Zealand, it must meet the requirements of the national specification for roading bitumen. The rheological and chemical properties of TOP modified bitumen were assessed before and after ageing samples as 1 mm thick films for 3024 ± 8 hours in an oven at 60°C. An 80/100 bitumen was produced by blending 12% TOP with 40/50 bitumen. Similarly, 180/200 bitumen was produced by blending 25% TOP with 40/50 bitumen, 15% TOP with 80/100 bitumen or 6% TOP with 130/150 bitumen. The ageing index of the bitumen increased as the TOP content increased, which indicates that TOP modified bitumen is less durable than conventional bitumen. Increasing the TOP content caused both a decrease in the dispersability of the asphaltenes as measured by the Heithaus parameter P_a, and an increase in the quantity of asphaltenes after ageing. However, analysis of the bitumen using gel permeation chromatography and confocal laser scanning microscopy showed that the size of the asphaltene aggregates remains in the range of 2 – 7 μm and is not affected by the TOP content or by ageing. The acid value of the bitumen is proportional to the TOP content and is unaffected by ageing. TOP modified bitumen is compatible with kerosene and AGO in proportions commonly used during chipsealing. Although TOP had an adverse effect on the effectiveness of adhesion agents used during chipsealing, it improved the resistance of asphalt concrete to moisture damage. Because of its poor ageing characteristics, asphalt concrete manufactured using TOP modified bitumen is more likely to suffer from fatigue cracking and ravelling, but it less likely to rut or produce tender mixes. The use of TOP as a bitumen modifier in New Zealand is not recommended since it lacks both durability and compatibility with adhesion agents as required by the national bitumen specification. Future research should concentrate on improving the resistance of TOP modified bitumen to age hardening and improve its compatibility with adhesion agents.

Keywords: Tall oil pitch, bitumen, asphalt, asphaltenes, ageing, oxidation, durability, GPC, confocal laser scanning microscopy, interfacial tension, adhesion.

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Executive Summary

Bitumen has been used extensively in pavement construction throughout the twentieth century. Its highly desirable mechanical properties coupled with its chemical excellent adhesive and waterproofing properties and its resistance to chemical and microbiological degradation makes bitumen a very durable pavement construction material. However, increased demands that have been placed upon the roading networks have caused pavements to prematurely fail and roading asset managers and contractors alike are searching for cost-effective solutions for maintaining pavements in a serviceable condition.

Intense competition and increasing environmental pressures, especially in the civil construction industry, has forced companies in New Zealand to become more innovative, cost effective and environmentally friendly. As a result, tall oil pitch (TOP) has been identified as a by-product that can potentially be used as a bitumen extender. Being less expensive than bitumen, its use results in economic benefits while maintaining a high level of environmental awareness and occupational safety and health. However, before it can be used commercially in New Zealand, it must be shown that the TOP modified bitumen conforms to the requirements of the specification for bitumen and that TOP does not adversely affect the quality of the bitumen.

The primary aim of this research is to determine is TOP can be used as a bitumen modifier in New Zealand. More specifically, research is required to answer the following questions:

1. Is TOP compatible with diluents used during chipsealing such as kerosene and automotive gas oil?
2. Does TOP modified bitumen possess adequate resistance to oxidative ageing?
3. How does TOP affect the chemical composition and characteristics of the bitumen and what is the likely effect of TOP on the long-term performance of bitumen?
4. Is TOP compatible with the adhesion agents used in chipsealing?

A review of the literature indicates that TOP modified bitumen can be successfully used in pavement construction. By adding up to 50% TOP to hard grades of bitumen, softer grades can be produced that exhibit similar rheological properties to that of conventional bitumen.

Limited research also indicates that the temperature susceptibility and ageing potential of the TOP modified bitumen is similar to that of conventional bitumen. The moisture susceptibility of pavements constructed using TOP modified bitumen is significantly reduced, presumably because the carboxylic acids in the TOP have a high affinity for mineral aggregate. For all intents and purposes the mode of manufacture and construction is identical to that of hot mix asphalt pavements made using unmodified bitumen. Limited field data has shown that the performance of the TOP modified pavements is equal to that of conventional bituminous pavements.

Since the addition of TOP will affect the composition of the bitumen, a review of the literature was also undertaken to ascertain how bitumen composition and chemistry affects its physical performance.

Bitumen can be considered to be a dispersion of highly polar and aromatic asphaltene molecules in a solution of non-polar aromatic and saturate molecules. The asphaltene molecules contribute significantly to the rheological properties of the bitumen by associating together and forming micellar structures. They are 'peptised' by resin molecules, which orientate themselves at the interface between the asphaltene micelles and the dispersing phase. The resins are also polar and aromatic, but are less so than the asphaltenes. Resins are responsible for maintaining the asphaltenes in suspension and for preventing their precipitation.

Researchers have determined that bitumens with low and high asphaltene content are susceptible to rutting and cracking respectively. The resins are responsible for ductility of the bitumen and together with the aromatics keep the asphaltenes in a satisfactory state of dispersion. The aromatics and saturates act as plasticisers and impart fluidity to the bitumen. A high saturates content can cause excessive steric hardening which will lead to cracking. Most researchers agree that performance is determined by how the various molecules in the bitumen interact rather than the quantity of a particular fraction.

Ageing is the hardening of bitumen over time and is caused by volatilisation of lower molecular weight plasticising components, oxidation of the bitumen and steric hardening. The primary ageing mechanism is oxidation although steric hardening effects can be significant. The major oxidation products are carbonyl groups and sulphoxides from aliphatic sulphides, both of which can convert non-polar molecules into polar molecules. An increase in polarity causes an increase in interactions between bitumen molecules. This manifests itself as an increase in viscosity. The extent of oxidation is mainly dependent upon the reactivity of the bitumen and the temperature. Higher temperatures promote more oxidation and excessive oxidation can cause the bitumen to crack. It is widely believed that during oxidation aromatic and resin molecules are converted to asphaltenes, while the saturate molecules remain unreactive.

The adhesive properties of the bitumen appear to be governed by the polar molecules. Sulphoxides and ketones in the bitumen promote adhesion to mineral aggregate, although sulphoxides are also susceptible to displacement by water. Carboxylic acids, which are highly polar, serve to increase the viscosity of the bitumen and have also been implicated as a cause of stripping in some hot mix asphalts. The presence of nitrogen based functional groups are favoured because they promote excellent adhesion. They are found in the resins fraction and do not appear to take part in oxidation reactions.

TOP was blended with bitumen in various proportions as shown in Table 1 to produce 80/100 and 180/200 penetration grade binders. Standard rheological measurements, such as the penetration, softening point and viscosity, were recorded and the compatibility of TOP modified bitumen with kerosene and automotive gas oil (AGO) was determined using a storage stability test. The chemical properties were analysed by measuring the Heithaus parameters and acid value of the bitumen. An assessment of the composition of the TOP modified bitumen was conducted by determining the proportion of asphaltenes, resins, aromatics and saturates using the Corbett fractionation procedure. The Corbett fractionation together with gel permeation chromatography (GPC) and confocal laser scanning microscopy (CLSM) were used to investigate the colloidal properties. The adhesive properties of the TOP modified bitumen were measured using the Vialit test and by determining the tensile splitting ratio after soaking an asphalt concrete specimen manufactured using TOP modified bitumen in water. The interfacial tensions of the TOP modified bitumen in contact with both air and water were also measured.

Table 1 shows that TOP can be blended with bitumen to produce binders that conform to the rheological requirements of the New Zealand bitumen specification. The penetration, softening point and penetration index are all similar to that of conventional bitumen. The kinematic viscosity at 60°C of the TOP modified bitumen is typically slightly higher than that of conventional bitumen. No significant difference was found in the viscosity between the top and bottom portions of a blend of TOP modified bitumen and kerosene or AGO after storage for 7 days at 160°C. Although the fact that the storage vessels were not airtight interfered with the quality of the results, the data indicates that TOP modified bitumen is compatible with kerosene and AGO at levels typically used during chipsealing.

Table 1: Formulation of TOP modified bitumens.

Binder Designation	Grade of Bitumen used to Make Blend	Bitumen Content (%)	TOP Content (%)	Penetration Grade of TOP Modified Bitumen
B50-T12	40/50	88	12	80/100
B50-T25	40/50	75	25	180/200
B100-T15	80/100	85	15	180/200
B150-T6	130/150	94	6	180/200

TOP has an adverse effect on the ageing index of the bitumen. Samples of TOP modified bitumen were aged as 1 mm thick films for 4 months in an oven at 60°C and the penetration measured before and after ageing. An increase in the TOP content caused a linear proportional increase in the ageing index. In a separate study, the rate of age hardening of TOP modified bitumen was found to exceed that of the Safaniya bitumen that is typically used in New Zealand for paving operations. It is apparent that increasing the TOP content of the bitumen causes a reduction in the durability.

Since TOP is known to contain acidic species it is not surprising that the acid number of the bitumen increases linearly with the proportion of TOP in the bitumen. No significant change in the acid value of the bitumen was detected after ageing. No evidence was found to suggest that TOP affects the dispersability of the asphaltenes, the solvent power of the maltenes, or the overall compatibility of the bitumen in unaged samples. After ageing however, TOP was found to cause a reduction in the dispersability of the asphaltene fraction as measured by the Heithaus parameter, P_a. This implies that the asphaltene fraction tends to aggregate more readily in the presence of TOP after ageing and is consistent with the observed increase in ageing index with increasing TOP content. TOP also caused the solvent power of the maltenes (P_o) and overall compatibility of the bitumen (P) to increase after ageing.

The Corbett fractionation showed that TOP causes a significant increase in the proportion of asphaltenes in the bitumen after ageing. The colloidal index within a particular penetration grade was unaffected by the proportion of TOP in the bitumen both before and after ageing. For example, all the unaged 180/200 bitumens have a colloidal index of 0.29 regardless of the TOP content. The GPC analysis showed that the asphaltene aggregates all eluted at the same time, regardless of TOP content or whether the bitumen had been aged or not. This indicates that neither TOP nor ageing has any detectable effect on the size of the aggregated asphaltene molecules. The GPC results were confirmed using CLSM, which showed that the size of the asphaltene aggregates ranged from 2 – 7 μm regardless of the TOP content or the age of the sample.

An assessment of the adhesive properties of TOP modified bitumen showed mixed results. Firstly, TOP has a severe adverse effect on the adhesion agents used in chipsealing. Vialit test results showed that a bitumen containing more than ~4% TOP was likely to cause a failure in the Vialit test. On the other hand, TOP was found to improve the tensile splitting ratio of hot mix asphalt that had been soaked in water at 60°C for 24 hours. The interfacial tension measurements confirmed that TOP improved the adhesive properties of bitumen. The interfacial tension of bitumen in air at 23°C increased from ~28.5 mJ/m^2 to ~30.6 mJ/m^2 when 25% TOP was added to the bitumen. Similarly, the interfacial tension of bitumen in contact with water at 23°C decreased from ~31.4 mJ/m^2 to ~30.0 mJ/m^2 when 25% TOP was added to the bitumen. At 60°C the contact angle of bitumen on a microscope slide immersed in water improved from an average of 110° to 73°.

Using these results it is possible to speculate about the anticipated performance of TOP modified bitumen in practice. The rheological properties of the unaged bitumen suggest that TOP modified bitumen will behave in a similar manner to conventional bitumen during construction of the bituminous pavement. TOP modified bitumen is compatible with diluents such as kerosene and AGO, but should not be used with adhesion agents used in chipsealing. It is thought that the acid in the TOP quickly renders the adhesion agents ineffective.

The higher ageing index, together with the reduced dispersability of the asphaltenes and higher asphaltene content after ageing indicates that pavements constructed using TOP modified bitumen will be more susceptible to fatigue cracking and ravelling. On the

positive side, since TOP modified bitumen tends to have a higher viscosity than conventional bitumen, there will be a reduced risk of rutting or producing a tender asphalt mix. TOP also improves the resistance of hot mix asphalt to moisture damage.

TOP is not suitable for use as a bitumen extender in New Zealand in its current form. The lack of durability and incompatibility with adhesion agents means that TOP modified bitumen will not meet the requirements of the specification for bitumen. Further research in this area should focus on improving the resistance of the TOP modified bitumen to age hardening and to improve its compatibility with adhesion agents.

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SECTION I:

BACKGROUND AND LITERATURE REVIEW

1.0 Introduction

Throughout the years, bitumen has proven to be an economical and reliable pavement construction material. At ambient temperatures the visco-elastic nature of bitumen imparts both flexibility and strength to the pavement. These highly desirable mechanical engineering properties of bitumen, coupled with its excellent adhesive and water proofing properties and its resistance to chemical or microbiological degradation, makes bitumen a very durable pavement construction material (Roberts *et al*, 1991).

However, many bituminous pavements are now showing signs of distress due to increases in both the weight and volume of traffic throughout the latter half of the twentieth century. Many pavements are in excess of forty years old and are being subjected to loads in excess of their engineering capacity. Consequently, the bitumen used in pavements tends to crack, bleed or deform and engineers have been exploring ways of improving the performance and durability of pavements (Asphalt Institute, 1996). The most popular method of improving the engineering properties of the bitumen is to modify it using various additives including polymer, fillers and hydrocarbon oils (Bahia *et al*, 1998). However, recent research conducted by the Strategic Highways Research Program (SHRP) in the USA has shown that it is also important that the fundamental aspects of bitumen quality are not overlooked when considering pavement durability and performance (Petersen *et al*, 1994a).

The fate of pavements in New Zealand is similar to that of the rest of the world. An ageing transportation infrastructure, an increase in traffic loads and volumes caused by burgeoning populations, increased standard of living and deregulation of the land transport industry has placed a strain on the roading network. Consequently, road managers and contractors alike are looking for alternative means of cost-effectively maintaining pavements in a serviceable condition.

The pavement construction industry in New Zealand is highly competitive. In recent years deregulation, rationalisation and intense competition has seen the demise of several companies through take-overs and liquidation. The competition was intensified in 2000 by the fact that the cost of bitumen, which is one of the prime raw materials used by the industry, increased by approximately 45% in a twelve month period.

Increasing environmental awareness, especially in Europe and the USA, is forcing civil construction companies to assess the impact that they have on the environment. The use of recycled industrial waste in bituminous pavements, such as vehicle tyres, glass, fly ash and plastics, is becoming common place in the industry. Indeed, it is now common practise to use recycled asphalt concrete in new pavements.

Tall oil pitch (TOP) has been identified as an industrial by-product that can potentially be used as a bitumen extender (Ball *et al*, 1993). The use of TOP in bituminous pavements not only reduces the cost of the bitumen, but also adds value to an industrial by-product and substitutes a renewable resource for a non-renewable one. TOP is obtained from the forestry industry whereas bitumen is obtained from non-renewable crude oil.

Before TOP can be used as a bitumen extender it must be shown that it does not adversely affect the quality of the bitumen. In New Zealand, TNZ M/1 (1995) regulates bitumen quality through a national bitumen specification that sets limits for the physical properties of the bitumen. Therefore, although TOP can potentially reduce the cost of bitumen while improving the environmental performance of the industry, it must be shown that TOP modified bitumen complies with the national bitumen specification. It has also long been recognised that the composition and quality of the bitumen affects the pavement performance (Petersen, 1984). Therefore, any assessment of the use of TOP in bitumen must include an examination of its impact on bitumen composition, quality and anticipated performance. To do this it is necessary to gain an understanding of the chemistry of bitumen and how it affects long term durability.

2.0 The Manufacture and Use of Bitumen

2.1 Bitumen Production

Bitumen is obtained from the distillation of crude petroleum oil. It is essentially the non-volatile component of crude oil that remains after vacuum distillation of the lighter hydrocarbon fractions. Figure 1 shows a schematic representation of the production of bitumen. In many respects bitumen is a waste product, or at the very least a by-product of the distillation process. The primary products of the refinery are the more valuable, lighter hydrocarbon fractions such as volatile gases, naphtha, kerosene and gas oil that form the basis of the fuel and petrochemical industries. Consequently, the production of quality bitumen is usually subservient to that of the quality needs of the value added hydrocarbon fractions.

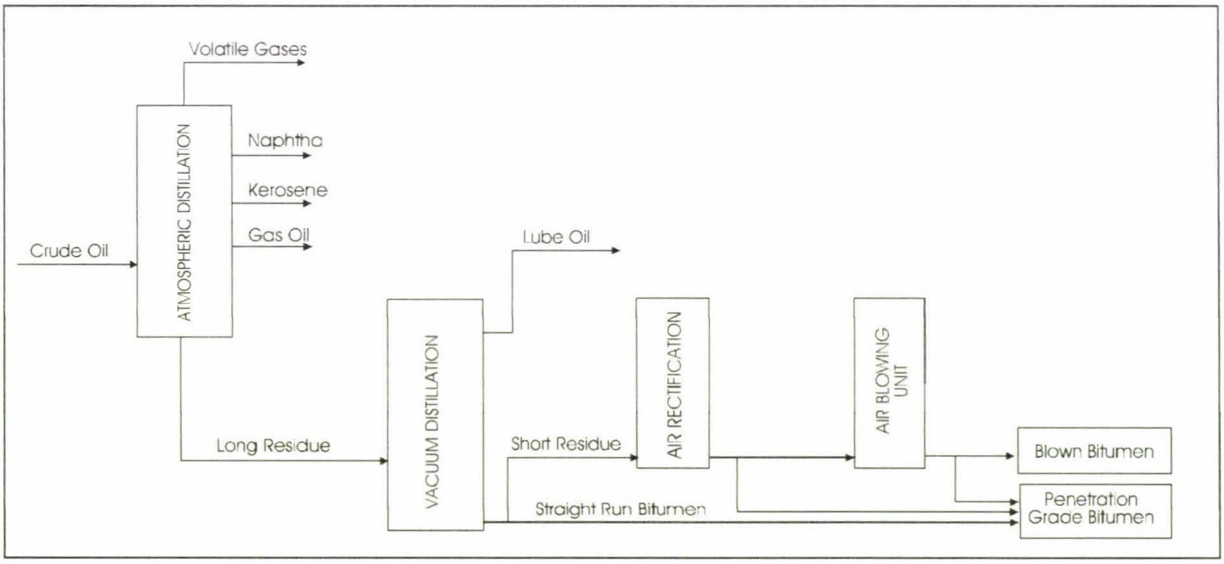


Figure 1: Schematic diagram of the manufacture of bitumen (adapted from Morgan and Mulder, 1995).

The residue from the vacuum distillation process is commonly referred to as 'straight-run' bitumen. It is typically a soft grade of bitumen and finds its primary use in the construction of chipseals. The 'straight-run' bitumen is often too soft for use in hot climates and is modified in the refinery to produce harder grades of bitumen. Modification traditionally involves oxidation by blowing air through the hot bitumen at 240 – 320°C (Morgan and

Mulder, 1995) until the desired hardness is achieved. It is possible to produce intermediate grades of bitumen by blending the hard, blown bitumen with the soft, straight-run bitumen.

An alternative to the use of air oxidation to produce a harder grade of bitumen is solvent refining (Holleran, 1994). A light aliphatic solvent such as propane or butane is used to separate the hard fractions from the bitumen in a process called propane deasphalting or butane deasphalting. The hard bitumen fractions are insoluble in the propane or butane solvent and are precipitated from the bitumen solution to give fractions known as propane precipitated asphalt (PPA) or butane precipitated asphalt (BPA). Bitumen of the correct consistency is then produced by re-blending the precipitate fraction with the stripped solvent soluble oils or with other refinery products such as straight-run bitumen. The advantage of this process is that is makes the deasphalted bitumen solution available for further processing into lube oils.

2.2 Bitumen Grading System

Bitumen is usually classified or graded according to either its viscosity at 60°C or its penetration at 25°C. The preferred classification system in New Zealand is to grade the bitumen according to its penetration value. In summary, a needle of specified dimensions and weighing 100 grams is allowed to fall under the influence of gravity into a sample of bitumen at 25°C for a duration of 5 seconds. The distance that the needle penetrates the bitumen sample is measured in deci-millimetres (dmm) and this value is the bitumen penetration result. For example, if the needle penetrates the bitumen sample to a depth of 19.3 mm, then the penetration is reported as being 193 dmm.

The bitumen classification system used in New Zealand specifies the lower and upper limits of the penetration allowed for a particular class. For example, two grades of bitumen are produced at the Marsden Point oil refinery near Whangarei. The soft grade is a straight-run bitumen that has a penetration of between 180 and 200 dmm. This bitumen is classified as 180/200 bitumen. Similarly, the hard grade of bitumen is an air blown grade and has a penetration of between 40 and 50 dmm. It is classified as 40/50 bitumen. By blending the 40/50 and 180/200 bitumen in the correct proportions, intermediate grades of 60/70, 80/100 and 130/150 can be produced.

2.3 Historical Use of Bitumen

Morgan and Mulder (1995) give an excellent overview of some of the known historical uses of bitumen. The first known use of bitumen occurred around 6,000 BC in Sumeria where it was used as a caulking agent for ships. Ancient civilisations were quick to realise the excellent waterproofing and adhesive properties of bitumen. The stone blocks used to construct a water tank that was found at Mohenjo Daro in the Indus Valley in modern day Pakistan are bonded with bitumen. The water tank dates from 3,000 BC. Biblical references describe the use of pitch for caulking Noah's Ark and for use in construction of the Tower of Babel. Some of the more abstract historical uses of bitumen are for the preservation of mummies in ancient Egypt, as a pigment in paints and as a component of a photographic process.

"The first documented use of rock asphalt as a sidewalk surfacing occurred in France in 1802 and later in Philadelphia in 1838" (Asphalt Institute, 1996). Whiteoak (1990) records that some of the first uses of bituminous binders as an asphaltic concrete paving material were in 1832 in Gloucestershire and 1835 in Paris. These pioneers of the asphalt industry used either tar or natural asphalts since it was not until the turn of the twentieth century that bitumen from the distillation of crude oil became available on a large scale.

2.4 Natural Occurrence

The ancient civilisations would have obtained bitumen from naturally occurring deposits similar to those available today. Two types of naturally occurring bitumen are known: lake asphalt and rock asphalt. As the names suggest, these naturally occurring bitumens are found in deposits as lakes or impregnated within porous rocks such as sandstone or limestone (Asphalt Institute, 1996).

Perhaps the largest modern deposit is the bitumen lake on the island of Trinidad. It is estimated to contain 10 – 15 million tonnes of material (Morgan and Mulder, 1995). Other naturally occurring lake asphalt deposits include the Bermudez Lake in Venezuela, the "Tar" Pits near Los Angeles (Asphalt Institute, 1996) and the "extensive tar sands throughout western Canada" (Roberts *et al*, 1991). Various deposits of rock asphalt occur throughout Italy, France and Switzerland. Deposits of the hard, friable bitumens known as

Gilsonite and Manjak can be found in the USA and Barbados respectively (Morgan and Mulder, 1995).

2.5 Modern Uses

Morgan and Mulder (1995) estimate that world bitumen consumption in 1994 was in the order of 75 million tonnes, 85% of which was consumed in road and pavement construction and maintenance. EAPA (2001) estimates that in 1999 the USA consumed ~ 27 million tonnes of bitumen in the roading industry, while the roading industry in Europe contributes ~ 18 million tonnes to world consumption. By comparison, New Zealand consumes approximately 150,000 tonnes annually (Higgins, 2003; Pidwerbesky, 1999).

Bitumen also finds important uses in other industrial applications including the manufacture of roofing shingles and bitumen impregnated building papers and felts. It forms the basis of various construction adhesives, grouts and putties and is used in some types of paints and coatings. Bitumen also finds agricultural uses as a preservative for preventing infection of trees after pruning and can be used as a mulching material or for erosion control. It is used in various waterproofing and hydraulic applications, has applications in acoustic dampers and is a good electrical insulator. Bitumen is also used as a pigmenting agent, is used in printing inks and has been employed as an extender or plasticiser in rubber and polymer compositions (Morgan and Mulder, 1995).

3.0 Tall Oil Pitch

Crude tall oil (CTO) "is a by-product of the Kraft pulping of resinous softwoods such as spruce and pine" (Johnson and Juristovski, 1995). The residue from the distillation of CTO is tall oil pitch (TOP). In many respects the production of TOP is analogous to the production of bitumen from the distillation of crude oil. In essence, it is a waste product that is produced in significant quantities and as such poses considerable disposal problems. World production of tall oil pitch was estimated in 1989 by Peltonen (1989a) to stand at 400,000 tonnes per annum. Approximately half of this is produced by the USA and approximately 10% is produced by Finland. In 1993, Mazuch (1993) reported that up to 10,000 tonnes of TOP was produced annually in British Columbia alone. New Zealand contributes approximately 4,000 tonnes per annum to the world total. TOP produced in New Zealand is usually disposed of as a low sulphur furnace fuel (Ball *et al*, 1993; Peltonen, 1989b). Besides being used as a furnace fuel or bitumen additive, TOP has found a number of other uses including the manufacture of printing inks and as a rubber compounding additive (Johnson and Juristovski, 1995).

3.1 TOP Recovery Process

"Crude tall oil (CTO) is a by-product of the Kraft pulping of resinous softwoods such as spruce and pine. ... Approximately 2% of a pine tree is recovered in the form of tall oil" (Johnson and Juristovski, 1995). The composition of TOP produced in each locality varies depending upon the species of tree that the TOP is derived from, the geographical area and the processing method.

During the Kraft pulping process, cellulose fibres are recovered from wood chips by digesting the chips in a solution of sodium hydroxide and sodium sulphide. The lignin material that binds the cellulose fibres together is degraded into neutral compounds and sodium salts of various carboxylic acids by the highly alkaline pulping chemicals. The spent digestion chemicals and degraded lignin material forms the 'black liquor', which is separated from the more valuable cellulose fibres using filtration. In order to minimise expense, reduce wastage and lessen any adverse environmental impact, the digestion chemicals are recovered from the black liquor for reuse in the Kraft pulping process (Johnson and Juristovski, 1995).

The black liquor is concentrated by evaporation and the degraded lignin material floats to the top of the concentrated black liquor where it is skimmed off to facilitate more efficient evaporation. The skimmed material is reacted with sulphuric acid to produce crude tall oil. In some cases, the skimmed material is first extracted with acetone and hexane for separation of the unsaponifiable material prior to acidification with sulphuric acid (Ball, 1992). The CTO then undergoes a distillation process to produce various useful materials such as tall oil fatty acids (TOFA), tall oil rosin (TOR) and distilled tall oil. TOFA is used in the manufacture of various types of surfactants and TOR is used to produce a sizing compound for use in manufacturing paper (Johnson and Juristovski, 1995). A schematic diagram of the process used to obtain TOP is given in Figure 2.

3.2 Properties of TOP

> "As in the case of asphalt, TOP is a very complex system containing numerous individual compounds. A typical representative of the fatty acids fraction are C_{18} linear and unsaturated compounds such as linoleic, oleic and stearic acids. Resin acids are represented by C_{20} abietic acid (rosin) and its homologues. The unsaponifiables and neutrals contain mostly high fatty alcohols, esters, sterols (β-sitosterol) and terpenes" (Mazuch, 1993).

Other compounds that have been identified in TOP are esterified fatty acids, rosin dimers and rosin anhydrides (Johnson and Juristovski, 1995). The properties of various tall oil pitches produced throughout the world are shown in Table 2. The ash in TOP is less than 1.0% by mass and has been identified as predominately being residual sodium sulphate from the recovery of the crude tall oil. TOP is soluble in benzene and chlorinated hydrocarbons but is not completely soluble in ethanol, methanol, hexane, or pentane (Smith, 1989).

Table 2: Properties of TOP produced in various countries.

Source	New Zealand [a]	Finnish [a] Hard Pitch	Finnish [a] Soft Pitch	Western [b] Canada	Florida, [c] USA
Chemical Properties					
Acid Number (mg KOH/g)	45	32 – 42	25 – 35	26	101
pH				4	
Rosin Acid	9%	5 – 15%	10 – 30%	6%	20%
Other Fatty Acids and Esters	10%			8%	46%
Unsaponifiables	40%	25 – 45%	25 – 35%	42%	34%
Neutrals				44%	
Saponification Number	106	45 – 80	90 – 110		0.6
Physical Properties					
Boiling Point				320°C	
Softening Point				< 30°C	
Viscosity (35°C)	80,000 cSt				
Viscosity (60°C)					3,732 cSt
Viscosity (80°C)				450 cSt	
Viscosity (99°C)					260 cSt
Viscosity (135°C)				40 cSt	59 cSt
Flash Point	240°C			255°C	216°C
Fire Point	270°C			275°C	
Specific Gravity (25°C)	1.02	0.95 – 1.05	0.95 – 1.05	0.96	
Vapour Pressure				< 1 mm Hg	

[a] Ball *et al* (1993)
[b] Mazuch and Jeffery (1995)
[c] Stroup-Gardiner *et al* (1993)

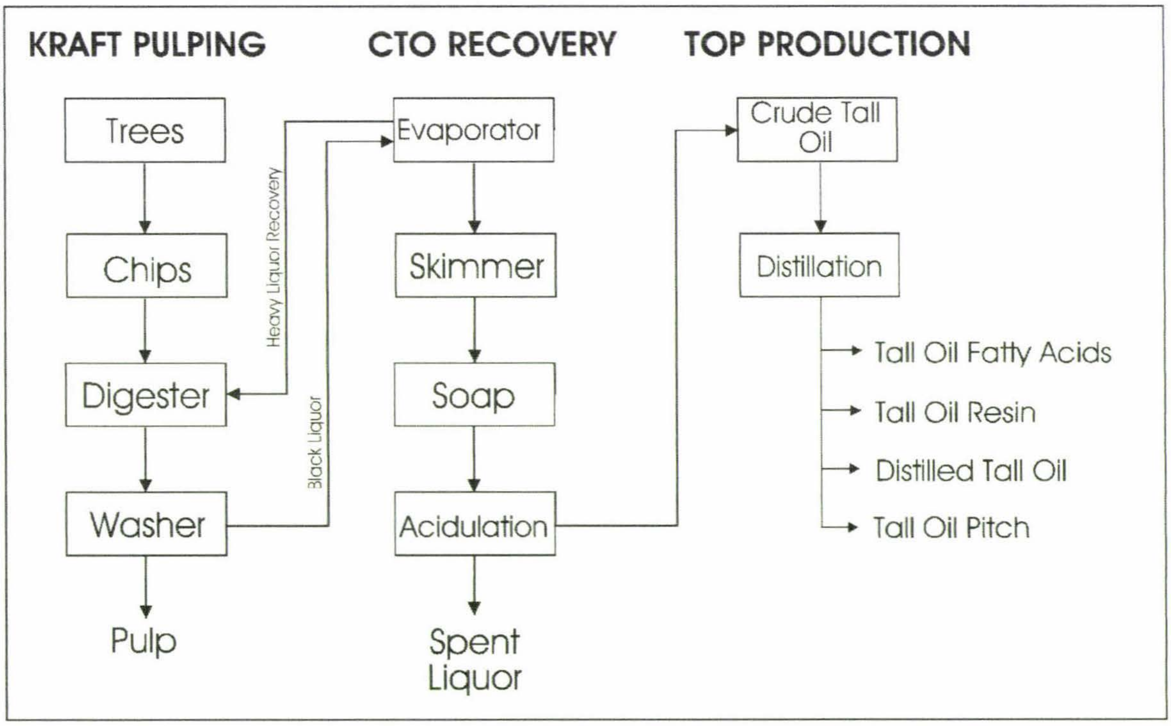


Figure 2: Schematic diagram of the recovery of TOP from pine and spruce.

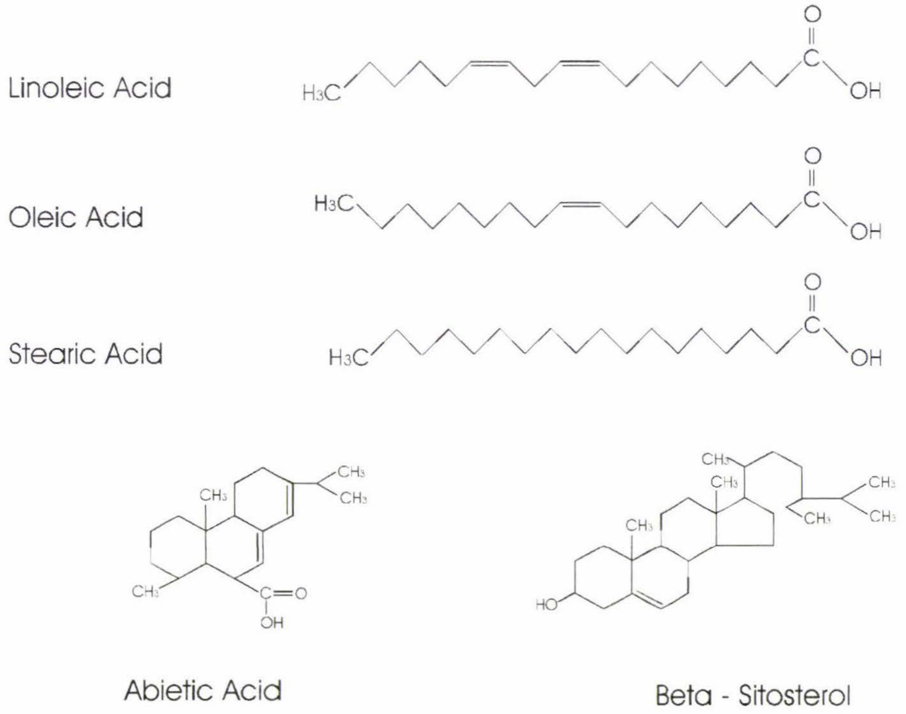


Figure 3: Some of the more important constituents of TOP.

3.3 Effect of TOP on Bitumen Properties

Not surprisingly, the majority of research into alternative uses for TOP has occurred in those countries that have a significant forestry industry such as Canada and Finland. Whilst the modification of bitumen with TOP is not practised extensively, some comprehensive, albeit minor, research into the effect that TOP has on bitumen properties has been undertaken in Finland (Peltonen, 1989a, 1989b), Canada (Mazuch, 1993; Mazuch and Jeffrey, 1995), USA (Johnson and Juristovski, 1995) and New Zealand (Ball *et al*, 1993).

3.3.1 Physical Properties

Several researchers that have studied the effect that TOP has on the physical properties of bitumen have all arrived at similar conclusions (Peltonen, 1989a, 1989b; Johnson and Juristovski, 1995; Mazuch, 1993). The TOP softens the bitumen, reduces age hardening and increases the temperature susceptibility and adhesion. An example of the properties of the TOP modified bitumen is shown in Table 3. Although these results are specifically for the modification of bitumen used in New Zealand, Finnish (Peltonen, 1989a), Canadian (Mazuch, 1993) and USA (Johnson and Juristovski, 1995) researchers observed similar trends. An examination of the data in Table 3 shows that TOP modified bitumens meet the specification for the physical properties of bitumens used in pavement construction in New Zealand. The specification for bitumen used in New Zealand has changed slightly since Ball *et al* (1993) undertook their research. The current New Zealand specification for bitumen is given by TNZ M/1 (1995). Table 4 is an exert from the current specification and shows that the TOP modified bitumen assessed by Ball *et al* (1993) still complies with the physical requirements for the bitumen.

Table 3: Properties of Safaniya bitumen modified with tall oil pitch (from Ball *et al*, 1993).

180/200 Bitumen				
Test	**Specification Limits**	**Control**	**15% TOP**	**31.5% TOP**
Proportion of Bitumen (%)	-	100% 180/200	85% 80/100	68.5% 40/50
Proportion of TOP (%)	-	0% TOP	15% TOP	31.5% TOP
Penetration (5°C, 100g, 5s, dmm)	-	20	19	19
Penetration (25°C, 100g, 5s, dmm)	180 – 200	184	186	185
Viscosity (70°C, mm^2/s)	14,000 – 49,000	18,100	24,300	20,900
Viscosity (135°C, mm^2/s)	140 – 350	233	278	253
Softening Point (°C)	37 – 43	40.6	41.9	41.8
Flash Point (°C)	218 min	302	296	282
Solubility in Trichloroethylene (%)	99.5 min	99.80	99.91	99.83
Ductility (25°C, m)	1.00 min	> 1.00	> 1.00	> 1.00
80/100 Bitumen				
Test	**Specification Limits**	**Control**	**12.1% TOP**	
Proportion of Bitumen (%)	-	100% 80/100	87.9% 40/50	
Proportion of TOP (%)	-	0% TOP	12.1% TOP	
Penetration (5°C, 100g, 5s, dmm)	-	16	16	
Penetration (25°C, 100g, 5s, dmm)	80 – 100	94	87	
Viscosity (70°C, mm^2/s)	40,000 – 140,000	55,600	64,500	
Viscosity (135°C, mm^2/s)	300 – 650	426	478	
Softening Point (°C)	45 – 52	47.8	48.9	
Flash Point (°C)	218 min	> 290	300	
Solubility in Trichloroethylene (%)	99.5% min	99.85	99.71	
Rolling Thin Film Oven Residue				
Retained Penetration (%)	50 min	58.5	58.2	
Ductility (25°C, m)	0.60 min	> 1.00	> 1.00	

Tall oil pitch mixes readily with bitumen at elevated temperatures and has been shown to be completely miscible at up to 50% w/w addition rates (Peltonen, 1989a, 1989b; Ball *et al*, 1993). Bitumen and TOP are completely compatible and do not undergo phase separation at elevated temperatures. It has also been observed that the density (Ball *et al*, 1993) and molecular weight distribution (Peltonen, 1989b) of bitumens and TOP are very similar. Both of these factors may assist in ease of mixing and stability and compatibility during storage.

Increasing the proportion of TOP causes a reduction in viscosity and softening point and an increase in penetration value of the bitumen (Johnson and Juristovski, 1995; Mazuch, 1993; Peltonen, 1989b). It is common practice to add TOP to hard grades of bitumen to obtain the desired softer grades typically used in pavement construction, for example 80/100 and 180/200 penetration grades.

Table 4: Physical properties of roading bitumens used in New Zealand.

Property	**Grade**	
	80/100	**180/200**
Penetration (25°C, 100g, 5s), dmm	80 – 100	180 – 200
Viscosity (70°C), mm^2/s	40,000 – 140,000	14,000 – 49,000
Viscosity (135°C), mm^2/s	300 – 650	140 – 350
Flash Point, °C	218 min	218 min
Solubility in Trichloroethylene, %	99.5 min	99.5 min
RTFOT		
Penetration after Test (25°C, 100g, 5s), % of original	50 min	50 min
Ductility of Residue (25°C), m	0.60 min	0.60 min

3.3.2 Age Hardening

Most of the data related to the hardening of the TOP modified bitumen with time was obtained using tests designed to simulate the ageing process due to the manufacture of hot mix asphalt and not the *in-situ* oxidative ageing that occurs during the service life of the binder. Consequently, very little data exists that relates the long-term age hardening potential of TOP modified bitumens to that of conventional bitumen. While studying the use of TOP as a alternative bitumen flux, Herrington *et al* (1996) aged a 10% TOP modified 180/200 bitumen for 3.3 years at 43°C. One of the conclusions from the study was that the rate of hardening of the TOP modified bitumen was similar to that of a conventional bitumen. Other studies used accelerated ageing tests such as the RTFOT and the TFOT and concluded that an increase in the proportion of TOP results in a decrease in the rate of hardening of the bitumen (Ball *et al*, 1993; Peltonen, 1989a, 1989b).

3.3.3 Adhesion

The addition of TOP causes a pronounced change in the contact angle of the bitumen on a granite surface (Peltonen, 1989b) and an improvement in the bitumen's adhesive properties (Peltonen, 1989a, 1992; Mazuch, 1993; Mazuch and Jeffery, 1995). Mixtures of aggregate and TOP modified bitumen showed resistance to water stripping when tested in mechanical water abrasion tests (Peltonen, 1989a, 1989b, 1992). Mazuch (1993) and Mazuch and Jeffery (1995) confirmed the finding of Peltonen (1989a, 1989b, 1992) by testing the stripping potential of asphalt concrete specimens manufactured using a bitumen modified with 11% TOP. The anti-stripping properties of TOP were found to be comparable, if not superior to that of conventional and popular anti-stripping additives such as hydrated lime and alkyl amines.

These observations are in contrast with what could be expected from Plancher *et al*'s (1977) studies of the adsorption of bitumen functional groups onto aggregate. Tall oil pitch contains a significant proportion of resin and fatty acids that give TOP a relatively high acid number (~ 40 mg KOH/g) compared to that of bitumen (usually less than 3 mg KOH/g). Consequently, the addition of TOP has a significant effect upon the acid number of the bitumen. Peltonen (1989b) suggests that the improvement in adhesion upon addition of TOP to bitumen is caused by interactions between the acidic components of the TOP and the mineral aggregate surface. However, according to Plancher *et al* (1977) and Robertson (1991) carboxylic acids are more susceptible to displacement by water.

It is possible that the improvement in adhesion of the TOP modified bitumen that was observed by Peltonen (1989b, 1992) is a result of improved wetting of the aggregate surfaces. Improved wetting would allow other bitumen species to interact with the aggregate over a larger interfacial area. If this is the case, the carboxylic acid species in the TOP modified bitumen may still be displaced by water, but the improved initial wetting of the aggregate surface means that other, more tenacious water resistant bonds were able to form between bitumen species and the aggregate surface.

During chipsealing work in New Zealand it is common practice to add amine based adhesion agents to the bitumen. Ball (1992) and Ball *et al* (1993) expressed concerns about the use of TOP as a bitumen extender when amine based adhesion agents are used. At the elevated temperatures employed during bitumen spraying operations, the carboxylic acids in the TOP can react with the alkyl amine adhesion agents to form salts. "Although the salts are still active as adhesion promoters, at binder storage and application temperatures (130 – 180°C) dehydration of the salt to give an inactive amide can occur" (Ball *et al*, 1993).

3.3.4 Temperature Susceptibility

Peltonen (1989b), Mazuch (1993) and Johnson and Juristovski (1995) have all reported that TOP modified bitumens are more temperature susceptible than the original bitumens that the blends were derived from. However, in an investigation undertaken by Ball (1992) the temperature susceptibility of TOP modified bitumen proved to be similar, if not identical to that of a neat bitumen of similar penetration value. The difference in results is in all likelihood related to the fact that Ball (1992) compared a straight run bitumen to a TOP modified oxidised bitumen, while the former researchers used only one grade of bitumen. Nonetheless, Ball (1992) has shown that the temperature susceptibility of TOP modified bitumen can be matched to that of conventional bitumen.

3.4 Commercial Use of TOP Modified Bitumen

Since the early 1980s, TOP has been added to bitumen used in pavement construction trials in amounts up to 20 % w/w in Finland and the former USSR (Peltonen, 1989b). However, the practice is not widespread and is sporadic. Approximately 150 km of pavements were constructed in 1988 in Finland utilising TOP modified bitumen. In British Columbia, Canada, several test sections were constructed using TOP in virgin hot mix asphalt and in recycled mixes between 1989 and 1992 (Mazuch, 1993). For all intents and purposes the mode of manufacture and construction is identical to that of hot mix asphalt pavements made using unmodified bitumen. After three years, the performance of the TOP modified pavements was equal to that of the control sections. No performance data later than three years has been found in the literature for the Canadian trial sections.

Mazuch (1993) presents data that indicates that the use of TOP in bitumen is unlikely to cause any occupational safety and health (OSH) concerns over and above what is normally experienced when handling conventional bitumen. Emissions of polynuclear aromatic hydrocarbons, phenols and acetaldehyde from the TOP modified bitumen are all within the permitted levels as specified by the relevant Canadian authorities. Tall oil and its derivatives have been used for many years without creating any known OSH problems. In all likelihood, the hazards and risks associated with handling TOP modified bitumen will be identical to those that present themselves when handling conventional bitumen.

A more recent use of TOP in roading bitumen has been in the area of polymer modified bitumen. Stroup-Gardiner *et al* (1993) showed that the use of TOP caused a reduction in the viscosity and ageing index of crumb rubber modified bitumen. Peltonen (1996) also mentions that the addition of TOP to crumb rubber modified bitumen improves the adhesion and elasticity of the blend. Korhonen and Kellomäki (1996) and Pinomaa *et al* (1996) used TOP as a dispersing agent while blending polyethylene and polypropylene plastics into bitumen. TOP was found to improve the dispersion and morphology of the blends. Various patents also mention the use of tall oil pitch or its derivatives as a means of improving the performance of the bitumen, especially with respect to polymer modification or emulsification (Schilling and Schreuders, 1989; Gaidas, 1991; Ostermeyer, 1993; Pinomaa, 1995).

4.0 Bitumen Chemistry

> "Differences in the quality of asphalts from different sources (different composition) and relationships between composition and performance properties have long been recognised ... Asphalts meeting the same specification often produce pavements with widely differing performance and serviceability. ... The importance of chemical composition to asphalt durability, although not well understood, cannot be disputed. Durability is determined by the physical properties of the asphalt, which in turn are determined directly by the chemical composition. An understanding of the chemical factors affecting physical properties is thus fundamental to an understanding of the factors that control asphalt durability" (Petersen, 1984)

It has long been recognised that two bitumens can have similar physical properties but have widely different chemical composition. Consequently, it is not unexpected that they possess different performance properties (Robertson *et al*, 1991). Therefore, to gain a complete understanding of the quality and expected performance of a particular bitumen, it is necessary to first know its chemical characteristics. Essentially it is the chemical composition of the bitumen that defines the level of performance and quality.

Most practitioners in the bitumen industry are interested solely in the physical properties of the bitumen. This seems logical since it is the physical performance of the bitumen that determines its suitability as an engineering material. Every bitumen specification in the world is based upon the physical performance characteristics of the bitumen. However, it has been only in the last few decades that practitioners have begun to realise that the chemical aspects of the bitumen dictate the physical attributes. In 1987, the US government initiated the Strategic Highways Research Program (SHRP), which was a US$150 million dollar research program with the aim of improving the performance and durability of US roads. US$50 million of this was dedicated for bitumen and hot mix asphalt research (Asphalt Institute, 1996). "The Strategic Highways Research Program (SHRP) was originally conceived in response to a perception within the highway industry that after the Arab oil embargo of 1972, the quality of paving grade asphalt had in many instances deteriorated to an unacceptable level" (Petersen *et al*, 1994a). Consequently, outputs from the program have led to an increased understanding of how chemical attributes affects the physical performance of the bitumen.

The quality and nature of the bitumen is dependent upon a number of factors, perhaps the most important being the crude oil source that the bitumen is derived from and the production route. Since the composition of each crude source is different, it is not surprising that the composition of the bitumen varies depending upon the crude source that it was obtained from. Similarly, the chemical composition will define the level of reactivity of the bitumen and consequently how it responds to various processing steps such as air blowing and solvent refining.

Bitumen is a black or dark brown coloured solid, semi-solid or viscous material. It has a slight, characteristic odour and is essentially non-volatile. Being thermoplastic in nature, it displays varying degrees of visco-elastic behaviour depending upon the temperature and rate of loading that is applied. That is to say, at high temperatures (typically above 60°C) and low loading rates the bitumen softens and becomes increasingly fluid. It has a low component of elasticity and is predominately viscous in nature. Under these conditions bitumen undergoes plastic deformation when a stress is applied to it. As the temperature decreases or the loading rate increases, the bitumen becomes more elastic in nature and can recover its original shape if deformed by a stress. At intermediate temperatures the bitumen is semi-solid. If the temperature is decreased further (typically less than 0°C) until it approaches the glass transition point (T_g) the bitumen behaves like a brittle solid.

4.1 Elemental Composition

Chemically, bitumen can be described as a complex hydrocarbon mixture that contains various minor proportions of the heteroatoms sulphur, nitrogen and oxygen. An elemental analysis of several bitumens is given in Table 5. Metal ions such as vanadium, nickel, iron, molybdenum, chromium and lead are also usually present in part per million (ppm) quantities. Unfortunately, an elemental analysis yields very little in the way of valuable information into the expected performance of the bitumen. It is the functional arrangement of the elements that gives the bitumen its particular performance attributes (Petersen, 1984).

Table 5: Elemental analysis of several bitumens (Petersen *et al*, 1994a; Herrington, 2000a).

MRL Reference		**AAA-1**	**AAC-1**	**AAG-1**	**AAK-1**
Source	**Arabian Heavy Safaniya**	**Canadian Lloydminster**	**Canadian Redwater**	**Californian Valley**	**Boscan**
Carbon (% wt)	83.7	84.1	85.5	85.7	81.0
Hydrogen (% wt)	10.8	10.0	10.6	9.9	9.6
Nitrogen (% wt)	0.5	0.6	0.7	1.1	0.7
Sulphur (% wt)	5.5	5.5	1.9	1.3	6.4
Oxygen (% wt)	< 0.5	0.6	0.9	1.1	0.8
Vanadium (ppm)	65	174	148	37	1498
Nickel (ppm)	18	86	63	95	141

Roberts *et al* (1991) groups bitumen into three distinct classes depending upon the abundance of a particular type of hydrocarbon structure in any given bitumen.

Paraffinic bitumens tend to have a predominance of straight or branched chain, aliphatic hydrocarbon molecules.

Naphthenic types of bitumen contain significant quantities of simple or complex saturated hydrocarbon rings.

Aromatic bitumens are characterised by the abundance of aromatic rings in the hydrocarbon molecules. The molecules may contain one or more aromatic rings, which are often fused together.

Paraffinic and naphthenic bitumens tend to be more common than aromatic bitumens. Petersen (1984) reports that typically 25 – 35% of the carbon is contained in aromatic structures, 15 – 30% is naphthenic and 35 – 60% is paraffinic in nature. It may be of interest to note that unsaturated double or triple carbon bonds are not usually found in significant amounts, if at all in bitumen (Petersen, 1984). In fact, Herrington (1993) and Herrington *et al* (1994) did not observe the presence of any olefinic protons while studying the proton NMR spectra of Safaniya and Boscan bitumens that had previously been used in New Zealand.

The individual molecules in the bitumen are themselves complex structures and usually possess a variety of chemical characteristics. For example, Figure 4 shows a hypothetical bitumen molecule that contains aromatic, naphthenic and paraffinic structures as well as heteroatoms. Often the aromatic and naphthenic ring structures are substituted with straight or branched paraffinic chains.

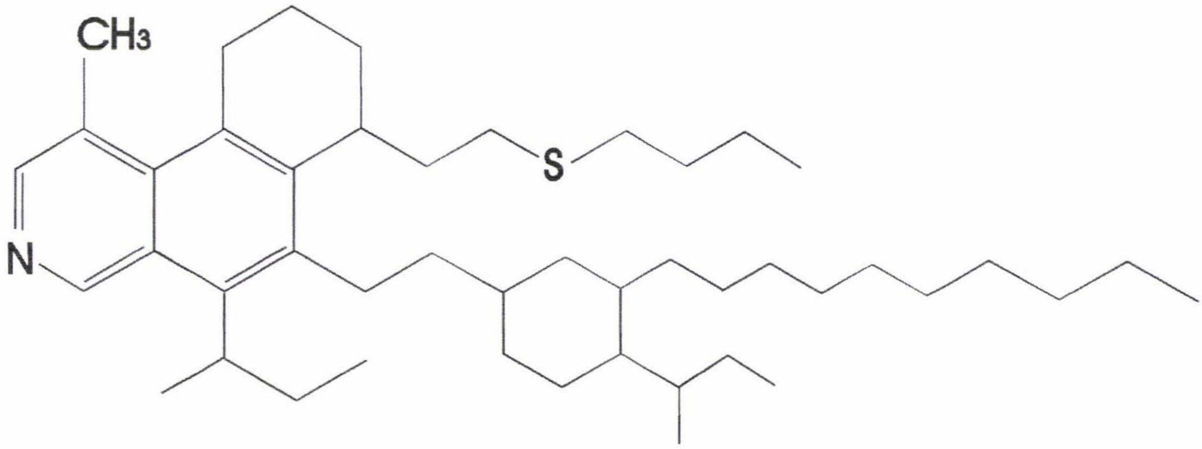
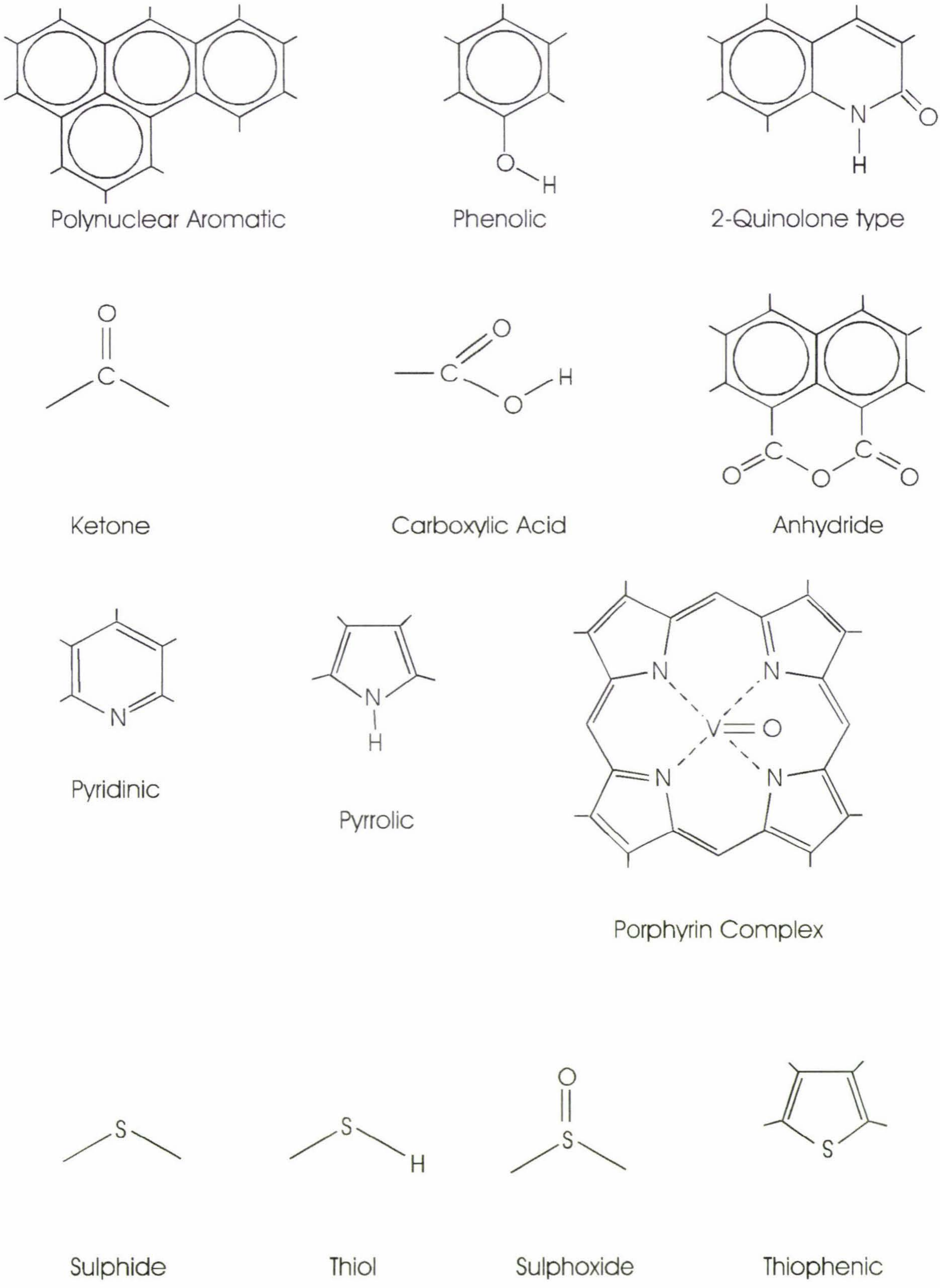


Figure 4: Structure of a hypothetical bitumen molecule.

The heteroatoms, nitrogen, sulphur and oxygen give the bitumen its polar characteristics. They are responsible for promoting molecular interactions and contribute to the visco-elastic nature of the bitumen. Examples of some of the functional groups that have been identified in bitumen are given in Table 6 and Figure 5. It is thought that the transition metals are retained in condensed porphyrin complexes (Petersen, 1984; Robertson, 1991) and are residues from the decomposition of plant and animal material that contained the likes of chlorophyll and haemoglobin. Morgan and Mulder (1995) state that the metallic constituents of bitumen may also be present in colloidal form, as carboxylic salts, or as other, non-porphyrin metal complexes.

Table 6: Sulphur, nitrogen and oxygen containing functionalities identified in bitumen.

Sulphur	Polysulphides Sulphides Thiols Thiophenes Sulphoxides
Nitrogen	Pyridinic Pyrrole, indole, carbazole Porphyrins
Oxygen	Carboxylic Acids Phenols Ketones Anhydrides



Polynuclear Aromatic

Phenolic

2-Quinolone type

Ketone

Carboxylic Acid

Anhydride

Pyridinic

Pyrrolic

Porphyrin Complex

Sulphide

Thiol

Sulphoxide

Thiophenic

Figure 5: Functional groups found in bitumen molecules (adapted from Jeon and Curtis, 1991; Robertson, 1991).

4.2 Fractional Composition

While possessing an understanding of the functional groups present in bitumen and how they might affect the performance properties is useful, it is not until bitumen is viewed on a micro-structural level that a more realistic understanding of its rheological behaviour becomes apparent. The behaviour of most bitumens can be better understood if it is realised that bitumen can be fractionated into four generic fractions: asphaltenes, resins, aromatics and saturates.

4.2.1 Asphaltenes

Asphaltenes are black or dark brown friable solids that are composed of complex, highly polar, high molecular weight molecules. A major portion of the nitrogen, oxygen and sulphur that occurs in bitumen is present in the asphaltene fraction (Morgan and Mulder, 1995). Consequently, the asphaltene fraction contains a significant proportion of acidic, basic and amphoteric molecules. The asphaltenes contain fused aromatic ring systems and can associate into micelles through polar interactions between its acid and base functionalities or *pi-pi* interactions between aromatic structures. It has been claimed that the predominant association mechanism in asphaltene micelles is stacking of the polynuclear condensed aromatic sheets prevalent in asphaltene molecules (Petersen *et al*, 1994a). The condensed aromatic sheets are 8 – 15Å in size and typically have an intermolecular gap of 3.55 – 3.70Å between each sheet (Dickie *et al*, 1969; Brûlé *et al*, 1986). Electron microscopy studies have shown that the individual asphaltene molecules have a diameter of only 20 – 30Å (Dickie *et al*, 1969) but the asphaltenes readily form micelles that are typically 5 – 30 nm in size (Morgan and Mulder, 1995). The molecular weight of the individual asphaltenes molecules is thought to be in the order of 1,000 g/mol, but since they have a strong tendency to associate and form micelles, the molecular weights of asphaltenes have been reported as being up to 500,000 g/mol (Dickie and Yen, 1967). Holleran (1994) reports that when mass spectroscopy was used to analyse a sample of Boscan bitumen, no material with a molecular weight greater than 1,000 g/mol was found. Any method that reports molecular weights greater than this are more than likely measuring the molecular weight of associated molecules. Asphaltenes contribute significantly to the rheological properties of the bitumen and are insoluble in non-polar solvents. Bitumens used in road construction generally contain 5 – 25% asphaltenes (Holleran, 1994; Morgan and Mulder, 1995; Roberts *et al*, 1991; Stroup-Gardiner, 1996).

4.2.2 Resins

The resin fraction is chemically similar to that of the asphaltenes. They contain significant proportions of heteroatoms, but are not as polar or interactive as the asphaltenes. Resin molecules tend to be comprised of polycyclic saturated, aromatic and heteroaromatic ring systems and reportedly have a molecular weight range of 500 – 50,000 g/mol. They are soluble in non-polar solvents and are thought to act as dispersing agents, or 'peptisers' for the asphaltene fraction. They are dark coloured, brittle solids at low temperatures, but become fluid when heated. Resins typically constitute 9 – 51% of the bitumen depending upon the method of analysis (Holleran, 1994; Morgan and Mulder, 1995; Roberts *et al*, 1991; Stroup-Gardiner, 1996).

4.2.3 Aromatics

The aromatic fraction is comprised of neutral, weakly polar and weakly polarisable molecules in which the aromatic and naphthenic ring systems dominate. They typically have a molecular weight of 300 – 2,000 g/mol and may contain significant quantities of sulphur, but only minor amounts of nitrogen and oxygen. Aromatics are highly effective solvents for the asphaltenes and resins and together with the saturates form the dispersing phase of the bitumen. They are dark brown viscous liquids that are soluble in non-polar solvents and usually comprise 29 – 62% of the bitumen depending upon the method of analysis (Holleran, 1994; Morgan and Mulder, 1995; Roberts *et al*, 1991; Stroup-Gardiner, 1996).

4.2.4 Saturates

The last of the four generic fractions is the saturates. "Saturates comprise straight and branch-chain aliphatic hydrocarbons, together with alkyl-naphthenes and alkyl-aromatics. They are straw or white in colour. The average molecular weight range is similar to that of aromatics …" (Morgan and Mulder, 1995). Minor amounts of sulphur can frequently be found in the saturate fraction, but nitrogen and oxygen are usually not present in appreciable quantities. The saturates, together with the aromatics form the dispersing phase and constitute 2 – 20% of the bitumen (Holleran, 1994; Morgan and Mulder, 1995; Roberts *et al*, 1991; Stroup-Gardiner, 1996).

4.3 Methods of Analysis

> "Because the number of molecules in asphalt with different chemical structures and reactivity is extremely large, chemists have not seriously considered attempts to separate and individually characterise them. Considerable progress, however, has been made in the study of asphalt composition by separation or characterisation of asphalt based on the reactivity or polarity, or both, of the various molecular types present. The molecules in asphalt can be conveniently separated or grouped into classes of molecular types or fractions based on their chemical functionality. This separation and classification of molecular types has been useful to provide simpler component fractions that permit further characterisation and has aided in determining how different molecular types affect the physical and chemical properties of the whole asphalt" (Petersen, 1984).

The various fractionation techniques for characterising bitumen are not ideal, but have proven both useful and practical. Although the various fractions are more homogenous than the whole bitumen, it must be remembered that "the 'generic' fractions are still complex mixtures and not defined chemical species; thus the same generic fraction from different asphalt cements may have a quantitatively different effect on the physical properties" (Roberts *et al*, 1991).

Petersen (1984), Roberts *et al* (1991), Goodrich *et al* (1986) and Holleran (1994) all reviewed various fractionation and analytical techniques that have been used to characterise bitumen. Some of the more important techniques used in the past are:

- Chemical Fractionation
  - Rostler/Sternberg Precipitation
  - Traxler Partitioning with Partial Solvents
- Chromatographic Techniques
  - Simple Fractionation

  - Corbett Adsorption-Desorption
  - Clay-Gel Fractionation
  - HPLC and GPC Methods
- SHRP Methods
  - Size Exclusion Chromatography
  - Ion Exchange Chromatography
  - Supercritical Fluid Chromatography

Other techniques have been used but are considered to be either less important or less popular. The SHRP methods of fractionating bitumen are essentially chromatographic techniques, but are given special mention since the development of the latest models and predictors of performance are based on the fractions obtained using these separation techniques. A summary of the various techniques used to separate bitumen and the comparative fractions obtained are given in Figure 6.

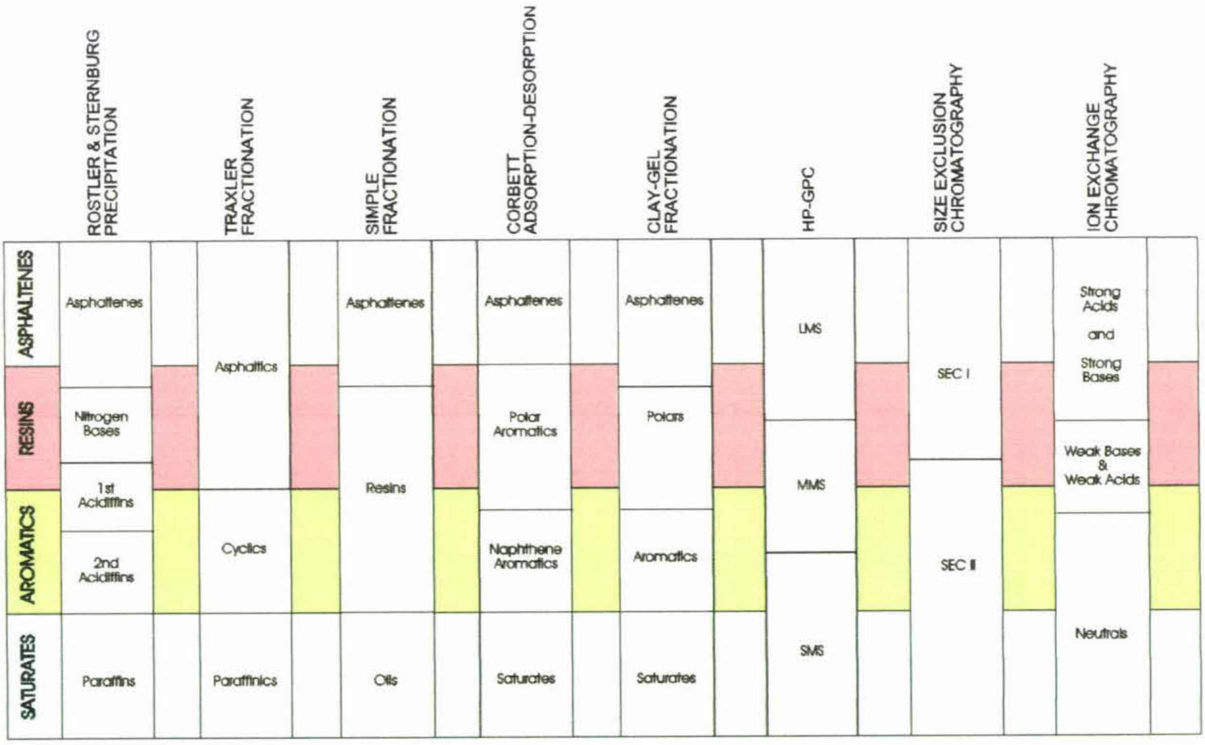


Figure 6: Simplistic comparison between different methods of fractionating bitumen (partially based on Goodrich *et al*, 1986).

4.3.1 Rostler/Sternberg Precipitation

The Rostler/Sternberg precipitation method has proven to be relatively popular in the past although it is destructive and does not allow subsequent analysis of the bitumen fractions to be made (Petersen, 1984). This method of analysis separates the bitumen components of the basis of their reactivity with sulphuric acid. As shown in Figure 7, Scheme 1, the asphaltenes are first precipitated using n-pentane. Sulphuric acid (85%) is then added to the resulting maltenes fraction and the nitrogen bases fraction of the bitumen is partitioned into the sulphuric acid phase. A fraction of lower reactivity, the 1st acidaffins, is then removed by reaction with 98% sulphuric acid. A fraction called the 2nd acidaffins is subsequently removed by reaction with H_2SO_4 containing SO_3. The remaining bitumen fraction, which is essentially unreactive towards sulphuric acid, is called the paraffins.

4.3.2 Traxler Partitioning using Partial Solvents

The Traxler method separates the bitumen into three fractions: asphaltics, cyclics and paraffinics. The bitumen is dissolved in n-butanol and the asphaltics fraction is removed by precipitation. The butanol is removed from the remaining two fractions by evaporation before they are redissolved in acetone. The acetone solution is chilled to –23°C at which point the paraffinic fraction precipitates, leaving the cyclics in solution (Petersen, 1984; Goodrich *et al*, 1986). This method is shown as Figure 7, Scheme 2.

4.3.3 Simple Fractionation

In its simplest form, bitumen can be considered to be made up of two fractions: asphaltenes and maltenes (or petrolenes) (Roberts *et al*, 1991). Figure 7, Scheme 3 gives a representation of the most basic of the chromatographic separation methods. Asphaltenes are insoluble in non-polar solvents such as pentane, hexane, or heptane. When bitumen is dissolved in pentane the asphaltenes are precipitated from the solution. The components retained in the solution are referred to as maltenes and can be further separated into two groups, resins and oils. The resins present in the maltene solution are absorbed on alumina and are recovered by elution with a mixture of 90% benzene and 10% methanol (Holleran, 1994). The oils are not absorbed by the alumina and can be recovered by evaporation of the pentane.

4.3.4 Corbett Adsorption-Desorption

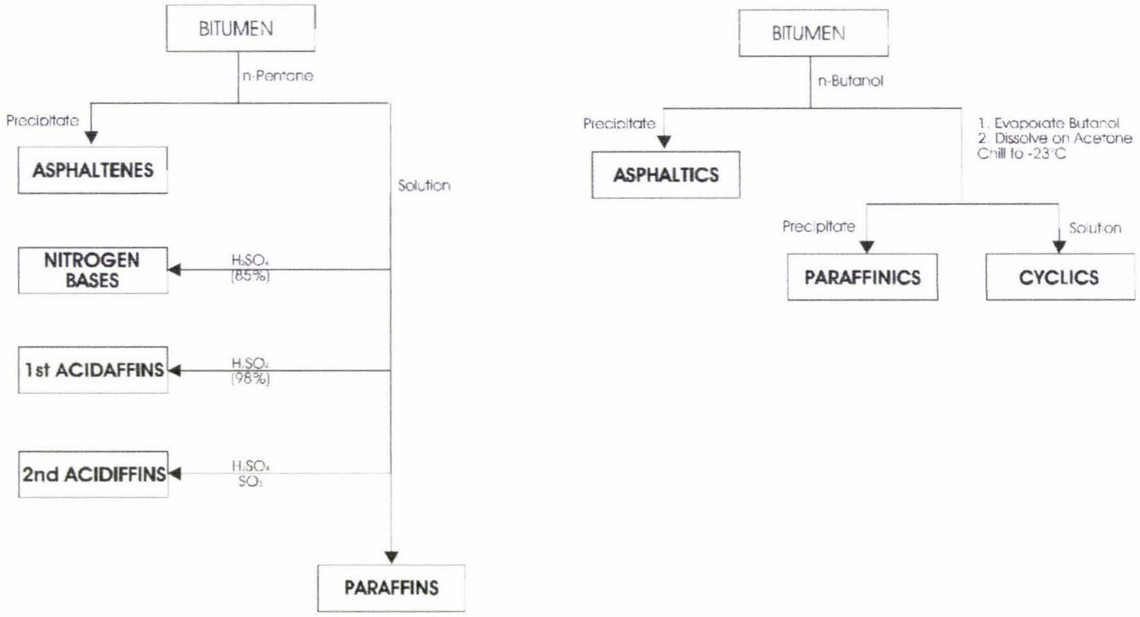
The Corbett fractionation is more sophisticated than the 'Simple Fractionation' method, but is also more popular because it provides more information about the composition of the bitumen. The four individual bitumen fractions can also be recovered for further analysis. Essentially the method involves absorbing the maltene fractions onto alumina before removing each fraction with successive elutions of increasingly polar solvents. A schematic of the Corbett fractionation is shown in Figure 7, Scheme 4. Bitumen is dissolved in n-heptane and the asphaltenes are allowed to precipitate before being separated by filtration. The filtrate is then adsorbed onto an alumina column. The column is first eluted with n-heptane to remove the non-polar, saturates fraction of the bitumen. Elution with benzene removes the naphthenic aromatic fraction, which is weakly absorbed onto the alumina. Finally, the polar aromatics, which are strongly absorbed onto the surface of the alumina are removed by elution with a 50/50 mixture of methanol and benzene followed by elution with trichloroethylene (Petersen, 1984; ASTM D4124, 1996). Evaporation of the solvents allows a quantitative determination of the bitumen composition to be made.

4.3.5 Clay-Gel Fractionation

The clay-gel fractionation is a chromatographic method similar to the Corbett method described in Section 4.3.4. The asphaltenes are first precipitated from the whole bitumen using n-pentane in a similar manner to the Rostler/Sternberg method (see Section 4.3.1). The remaining maltenes fraction is adsorbed onto attapulgus clay before being firstly eluted with n-pentane to remove the oil fraction, which contains the aromatics and saturates. The clay is then eluted with a mixture of benzene and acetone to desorb the polar fraction. The oil fraction is adsorbed onto a mixture of attapulgus clay and silica gel where it is eluted with n-pentane to remove the saturates fraction. The aromatics fraction is determined by difference (Goodrich *et al*, 1986).

Scheme 1: Rostler/Sternberg Precipitation

Scheme 2: Traxler Partitioning with Partial Solvents



Scheme 3: Simple Fractionation

Scheme 4: Corbett Adsorption-Desorption:

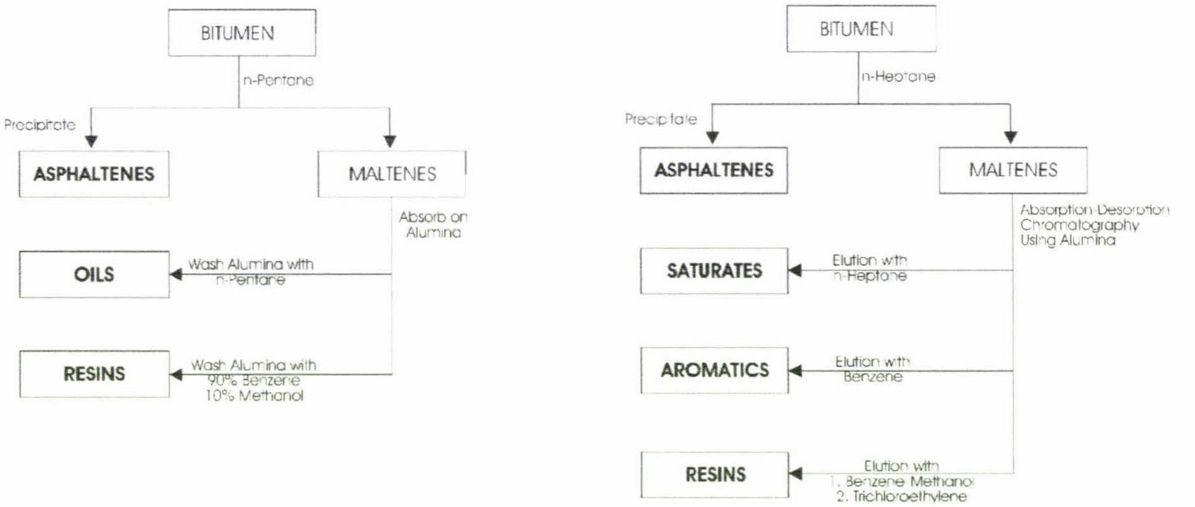


Figure 7: Schematic diagrams of four bitumen fractionation methods.

4.3.6 HPLC and GPC Methods

Yapp *et al* (1991) provides an excellent review of various researchers who have used high pressure liquid chromatography (HPLC) and gel permeation chromatography (GPC) techniques to characterise bitumen. Hattingh (1984) describes the use of both HPLC and GPC to characterise bitumen. The HPLC method chosen by Hattingh (1984) to fractionate the bitumen firstly involved dissolving the whole bitumen in methylene chloride before injecting it directly onto a silica gel column. The adsorbed bitumen was then successively eluted with 9 solvents of progressively greater polarity ranging from n-hexane to a mixture of pyridine and 3% ethanol. This allowed the bitumen to be fractionated into 9 different fractions corresponding to different polarities.

When GPC columns are combined with HPLC equipment the technique has become known as HP-GPC. Since Bynum and Traxler (1970) applied GPC techniques to the study of bitumen in 1970, it has become apparent that the shape of the chromatogram obtained from the HP-GPC techniques is very dependent upon the conditions under which the bitumen is analysed. Some of the factors found to influence the nature of the chromatogram obtained are:

- Test temperature
- Bitumen concentration in solvent
- Solvent type
- Flow rate through the HPLC
- The type of packing, packing particle size, length and porosity of the GPC columns
- The type and response of the detection system.

The use of HP-GPC has been likened to a molecular sieve analysis for bitumens, in a similar way that the particle size distribution of aggregates are determined (Stroup-Gardiner, 1996; Roberts *et al*, 1991; Jennings *et al*, 1993). A popular method of analysing the GPC chromatogram is to divide it into three sections of equal elution volume and to measure the corresponding area under each section. The higher molecular weight, more associative molecules are eluted first and are termed the large molecular size (LMS) fraction. The second section corresponds to the medium molecular size (MMS) fraction and the last section relates to the small molecular size (SMS) material. In an ideal world, the larger bitumen molecules are eluted first since they cannot enter pores in the column packing and so tend to take the shortest path through the column. Smaller sized bitumen molecules are absorbed into the pores in the packing medium and therefore have a longer retention time. They are therefore eluted after the large molecular sized (LMS) molecules.

The determination of the molecular size distribution of a bitumen using HP-GPC is complicated by several factors. Firstly, the highly polar, predominately larger sized molecules that are typically represented as the asphaltenes and resins fractions have a tendency to aggregate. Therefore, what appears to be a single molecule with a mass of several thousand or tens of thousands of daltons, may in fact be an agglomeration of dozens of smaller sized, polar molecules.

Also, the HP-GPC technique separates the bitumen according to the hydrodynamic volume of the molecule and not the molecular weight. Therefore, aliphatic molecules, which tend to occupy a larger volume than their aromatic counterparts, will be eluted before aromatic molecules of a similar mass.

The nature of the GPC column also influences the chromatograph. Polar and aromatic molecules can become absorbed onto the column to various degrees and consequently, may display an extended retention time. Therefore, larger polar molecules may be eluted and detected along with smaller more neutral molecules. It has also been found that the use of GPC columns with a finer porosity tends to increase the retention time and allows disassociations to develop amongst the polar LMS material. This will cause asphaltene aggregates to break up and will allow a more accurate representation of the molecular size distribution to be obtained, but at the expense of understanding the extent of the associations.

Similarly, the type of solvent and concentration of bitumen also affect the degree of intermolecular associations. Aromatic solvents such as toluene disrupt the *pi-pi* associations that are thought to be a major contributor to asphaltene associations. Similarly, tetrahydrofuran (THF) affects the polar interactions amongst the molecules. Higher concentrations of bitumen in the solvent allow many of the intermolecular associations to be retained whereas low bitumen concentrations tend to provide a more complete separation of the bitumen molecules. High column temperatures are also thought to disrupt intermolecular association caused by polar and *pi-pi* interactions.

The type of detector also influences the chromatogram. UV-vis detectors are ideal for detecting aromatic compounds present in bitumen but the response varies depending upon the wavelength that the detector is set to. They can also give misleading results. Jennings *et al* (1993) reported that up to 19 minutes retention time the detector response is "proportionally 'too large' for the percentage of asphalt responsible; after that time, the opposite is true." This phenomenon is attributed to the fact that asphaltenes and resins, which are eluted first, contain a disproportionately high aromatic content, which is easily detected by the uv-vis detector. The smaller, neutral fraction, which is eluted later, is predominately aliphatic in nature and the detector response is poor. Aliphatic materials do not tend to absorb or emit light in the UV spectrum. The refractive index detector suffers similar problems. Bitumen components that change the refractive index the most will cause a greater detector response, which may not be proportionate to the mass of sample being detected.

HP-GPC is proving to be a useful research and analysis tool for examining the effect that the material in the LMS region of the chromatogram has on bitumen performance. Unfortunately its usefulness is limited when it comes to examining the smaller, simpler hydrocarbons in the small molecular size (SMS) region.

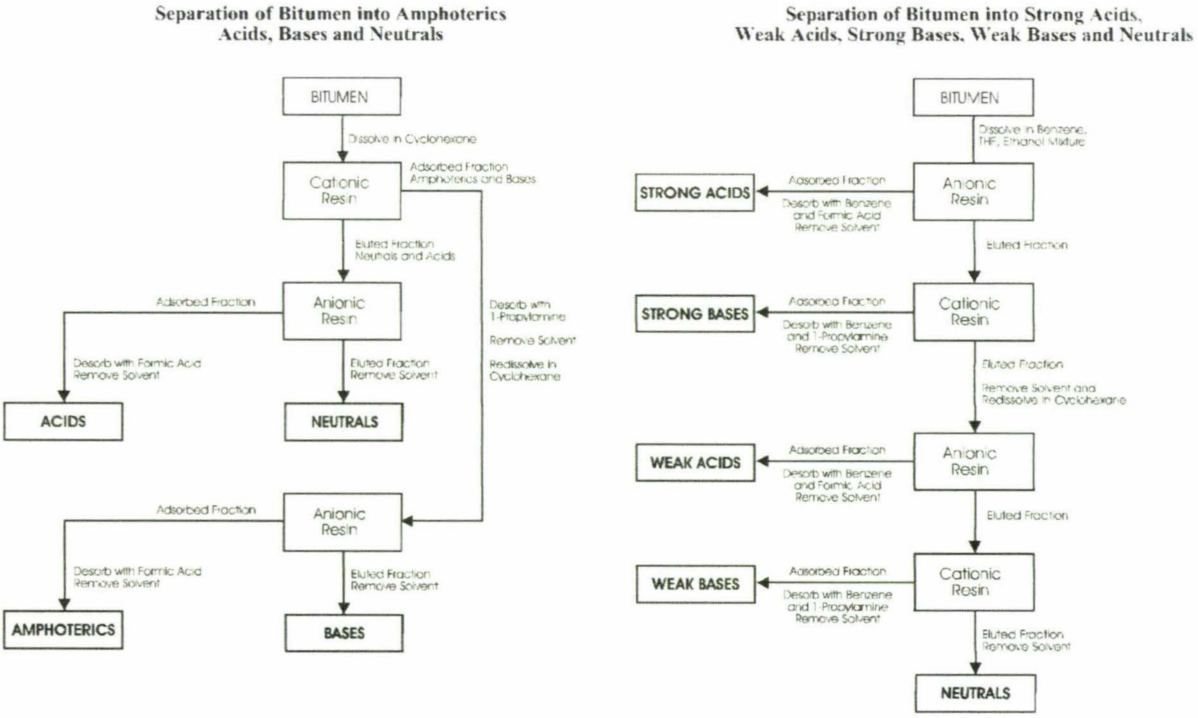
4.3.7 Size Exclusion Chromatography (SEC)

SEC is essentially a GPC technique and is currently used to obtain bitumen fractions for further analysis. The eluants are divided into two fractions: SEC I and SEC II. The SEC I fractions are predominately asphaltene and resin materials and are characterised by high molecular weight, highly polar, aromatic material. The SEC II fraction largely consists of the oil phase of the bitumen and is characterised by neutral or weakly polarisable aliphatic and aromatic compounds (Petersen *et al*, 1994b).

4.3.8 Ion Exchange Chromatography (IEC)

IEC has become increasingly popular in recent years as a method for separating and analysing bitumen fractions based on their acid and base properties. Petersen *et al* (1994b) describes two similar techniques for separating the bitumen into different fractions. Schematic diagrams of each separation technique is shown in Figure 8. In the first method, the bitumen is separated into acids, bases, amphoterics and neutrals. The bitumen is dissolved in cyclohexane and contacted with a cationic resin in a column. The base and amphoteric fractions are absorbed while the acid and neutral fractions pass freely through the column. The eluted fractions are then contacted with an anionic resin whereby the acid fraction is absorbed and the neutral fraction passes through the resin column. The acid fraction can then be recovered by desorbing from the anionic resin using formic acid. The amphoterics and bases are separated by desorbing them from the cationic resin using a solution of 1 part 1-propylamine and 2 parts benzene. The desorbed amphoterics and bases are then stripped of solvent and 1-propylamine, redissolved in cyclohexane and passed through a column of anionic resin. The amphoterics are absorbed while the base fraction passes through the column. Formic acid is used to desorb the amphoterics.

The second technique described by Petersen *et al* (1994b) separates the bitumen into five fractions: strong bases, strong acids, weak bases, weak acids and neutrals. The bitumen is dissolved in a mixture of benzene, THF and ethanol in the ratio 45:45:10. The solution is passed through an anionic resin column and a cationic resin column in series. The strong acids and strong bases are adsorbed onto the respective resins while the weak acids, weak bases and neutrals are eluted. The eluted fractions are stripped of solvent and re-dissolved in cyclohexane before being passed through two different columns, the first containing anionic resin and the second containing cationic resin. The weak acids and weak bases are adsorbed onto the respective columns while the neutral fraction is eluted. The adsorbed species are desorbed using similar procedures to those described before and the fractions recovered by removal of the solvents.


Separation of Bitumen into Amphoterics Acids, Bases and Neutrals

Separation of Bitumen into Strong Acids, Weak Acids, Strong Bases, Weak Bases and Neutrals

Figure 8: Separation of bitumen using ion exchange chromatography.

4.3.9 Supercritical Fluid Chromatography (SFC)

The neutral, saturate fraction of the bitumen has in recent years been analysed using the relatively new technique of supercritical fluid chromatography (SFC). Until the development of this technique it has only been possible to provide a limited analysis of the bitumen saturate fraction. "Near their critical points, fluids have the solvent power of a liquid but the mobility of a gas. In most SFC separations, carbon dioxide is the mobile phase, which limits application of the method to analysis of relatively non-polar molecules" (Petersen *et al*, 1994b).

SFC allows the quantification and analysis of non-polar hydrocarbon species in bitumen with a carbon number between 18 and 110. The SEC II fractions that are recovered using size exclusion chromatography (see Section 4.3.7) are dissolved in toluene and injected into the SFC column. The column temperature is increased at a rate of 2°C per minute from 125°C to 150°C. The column pressure is simultaneously increased from 2,000 psi to 5,500 psi at a rate of 140 psi per minute. The principle of supercritical fluid chromatography is that molecules with different molecular weights and with varying degrees of aromaticity possess varying degrees of solubility in the supercritical fluid at different conditions of temperature and pressure. As less soluble species in the neutral bitumen fraction approach their critical temperature and pressures they are precipitated. Hence the neutral fraction is separated on the basis of molecular size and also on the basis of the aliphatic and aromatic nature of the molecule (Petersen *et al*, 1994b; Holleran, 1994).

4.3.10 Microscopy Techniques used for Bitumen.

Optical microscopy, electron microscopy and scanning probe microscopy have all been used to observe the structure of the asphaltene phase. Simple reflected or transmitted light microscopy has generally not been successful due to the nature of the bituminous samples. Because bitumen is dark coloured it prevents any contrast between the asphaltene and maltene phase from being observed. However, Li and Wan (1995) mention that they used optical microscopy to observe the particle size of asphaltenes that had been precipitated from bitumen using a light solvent.

Scanning electron microscopy (SEM) and environmental scanning electron microscopy (ESEM) have both been used to successfully image the structure of the asphaltene phase. Although the resolution of electron microscopes is excellent, they do suffer from shortcomings. For example, SEM and ESEM can only image surface topography, whereas the rheological properties of the bitumen are determined by the internal structure in the bulk of the sample. SEM requires the use of depressed temperatures and low vacuums, which can cause the asphaltene structure to differ from that at ambient temperatures. Although transmission electron microscopes (TEM) have been used to examine the dispersion of polymer in bitumen, no literature was found that disclosed the use of TEM for examining the structure of the asphaltene phase.

Electron microscopy techniques also require extensive sample preparation. Consequently, the preparation step may introduce artefacts into the imaging process. For example, the observation of the asphaltene structure using SEM or ESEM requires removal of the oily maltene phase from the sample. Loeber *et al* (1996, 1998) fixed the bitumen to filter paper before leaching the maltenes from the sample using a solvent. The remaining asphaltene structure could then be observed using SEM. Michon *et al* (1998) and Rozeveld *et al* (1997) used the electron beam to vaporise the lower molecular weight, less associated maltene phase from the bitumen sample in an ESEM. The asphaltene structure was revealed, which could then be observed in the usual way. Schalek and Drzal (2000) used the same technique to observe the structure of the polymer phase in a modified bitumen.

Atomic force microscopy (AFM) is gaining in popularity for examining bitumen samples. Unfortunately, AFM can only image surface features that may not be representative of the internal structure of the bitumen. Loeber *et al* (1996, 1998, 1999) and Pauli *et al* (2001) all used AFM to observed structures in a film of bitumen that they attributed to asphaltene networks. The advantage of AFM is that it requires no sample preparation that may influence the asphaltene structure. However, since AFM only images the surface of the bitumen, it may be better suited to investigating interfacial properties rather than the internal asphaltene structure.

Like AFM, fluorescence microscopy requires no sample preparation that may affect the asphaltene structure. The bitumen is observed as a neat sample under ambient conditions. Fluorescence microscopy has proven popular for examining the dispersion of polymer in a bitumen matrix. The polymer is easily observed because it fluoresces strongly under UV light (Rozeveld *et al*, 1997; Loeber *et al*, 1996). In contrast it has been claimed that bitumen does not exhibit much fluorescence (Loeber *et al*, 1996; Collins *et al*, 1991). The bitumen appears dark while the polymer is light coloured.

The current literature on the fluorescence properties of bitumen is contradictory. Collins *et al* (1991) notes that under blue and UV light with a wavelength of 400 – 440 nm, the aromatic and resin constituents of the bitumen fluoresce while the asphaltenes and saturates do not. The fluorescent light was filtered so that only wavelengths greater than 470 nm were observed. Loeber *et al* (1996) states that "oil exhibits autofluorescence when irradiated with shorter wavelength light such as UV light, but for asphalt there is little fluorescent light emission because the oil phase is mixed with an asphaltene and a resin phase which do not exhibit any autofluorescence." However, Loeber *et al* (1996) managed to observe the presence of dark "round forms" with a diameter of 2 – 50 μm using fluorescence microscopy. The "round forms" were attributed to asphaltene aggregates dispersed in a slightly fluorescing bitumen matrix. Newman (1998) observed that bitumen appears dark grey or black under UV light at 50 times magnification. It may be worthwhile noting that neither Loeber *et al* (1996) or Newman (1998) mention the use of filters for screening out reflected light when undertaking fluorescent microscopy. It may be that the reflected image obscured any fluorescence that occurred in the bitumen.

Contrary to the results published by Collins *et al* (1991) and Loeber *et al* (1996), Li and Wan (1995) used the fluorescence properties of asphaltenes to observe their particle size against a dark bituminous background. The incident light source had a wavelength of 568 nm. They mention that "since highly conjugated aromatic structures are a major part of asphaltene components, fluorescent excitation by visible light is a distinct possibility" (Li and Wan, 1995).

Guibault (1990) notes that aromatic hydrocarbons, especially polyaromatic hydrocarbons (PAH), generally exhibit fluorescence in the UV or visible spectrum. The wavelength at which maximum absorbance and fluorescence occurs tends to increase as the level of conjugation increases. Figure 9 gives the wavelength of maximum fluorescent emission for a series of conjugated aromatic molecules.

Figure 9: Maximum wavelength of fluorescence emission of some conjugated aromatic molecules (from Guibault, 1990).

Mikula and Munoz (2000) used confocal laser scanning microscopy (CLSM) operating in the fluorescent mode to investigate the processing and extraction of bitumen from oil sands. Bitumen and oil were found to exhibit fluorescence when irradiated with 488 nm wavelength light. With the use of appropriate filters, the fluorescent image was detected in the green part of the spectrum (514 nm wavelength). Furthermore, Rost (1995) mentions the use of fluorescence in the petrological examination of bituminous materials such as coal or shale oils. "Natural petroleum and asphalt usually fluoresce blue, green or yellow under UV excitation" (Rost, 1995).

Consequently, the use of various microscopy techniques for examining bitumen can lead to an improved understanding of how that bitumen fractions, especially the asphaltenes, interact with each other. It is likely that future advances in the field of microscopy will provide researchers with an improved visual understanding of the composition and structure of bitumen.

4.4 Structural Models of Bitumen

4.4.1 Colloidal Model

An understanding of the chemistry and interaction of the four generic fractions of bitumen: asphaltenes, resins, aromatics and saturates, can be used to build a structural model of bitumen. For any model to be useful, it must be able to infer and predict the likely rheological behaviour of the bitumen in practice. The traditional model of the structure of bitumen is most commonly referred to as the 'colloidal model'. The colloidal model considers bitumen to consist of the highly polar, high molecular weight asphaltenes, dispersed in an oily medium made up of the neutral aromatic and saturate fractions. Resins, which are soluble in the aromatic and saturate continuous phase, are absorbed at the interface of the asphaltene micelles and oil phase. The resins act as dispersing agents for the asphaltenes, which are otherwise insoluble in the aromatics and saturates fraction.

> "Asphalt cement is not a true solution, but is considered a colloidal or micellar system. Nellensteyn first recognised its colloidal nature by stating that it has a dispersion of micelles in an oily medium. The relative amounts and characteristics of asphaltenes, resins and oils present in an asphalt cement influence its physical properties and performance in a HMA mixture. These influences make the asphalt act as a 'sol', 'sol-gel' or 'gel'" (Roberts *et al*, 1991).

By their very nature asphaltenes tend to associate with each other through *pi-pi* or polar interactions. Highly compatible bitumens exhibit a high degree of dispersion of the asphaltenes and are termed 'sol' bitumens. Sol bitumens are said to possess a sufficient quantity of high quality resins that can act as dispersing agents for the asphaltenes. In addition, the maltene phase tends to be more aromatic, which provides an effective solvent for the dispersed phase.

A decrease in compatibility within the bitumen is characterised by a decrease in the quantity and quality of the resin fraction and a reduction in the aromaticity of the maltene phase. Effectively, the maltenes become a poorer solvent for the dispersed phase. Reduced compatibility will cause the individual asphaltene molecules to associate forming micellar structures. Eventually, these asphaltene micelles will flocculate to form what is termed 'aggregates'. Such highly associated bitumens are known as 'gel' bitumens. Figure 10 is a schematic representation of the structure of sol and gel bitumens. Sol bitumens tend to exhibit Newtonian flow characteristics whereas gel type bitumens tend to exhibit non-Newtonian rheological behaviour. Sol-gel type bitumens are intermediate in rheological characteristics between sol and gel bitumens.

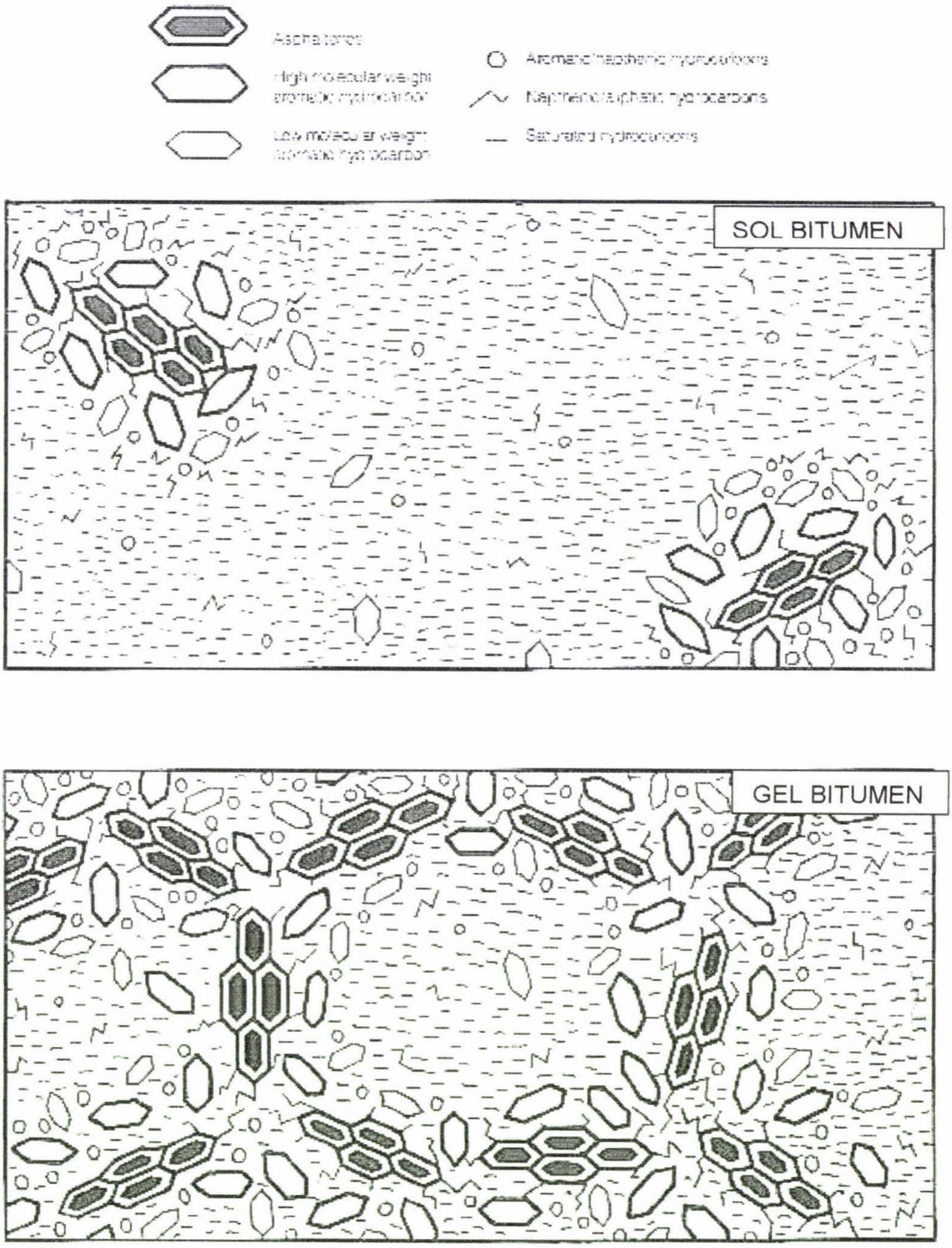


Figure 10: Schematic representation of the structure of 'sol' and 'gel' bitumens (from Morgan and Mulder, 1995).

Brûlé *et al* (1986) postulates that an equilibrium exists in bitumen that describes the degree of association between asphaltene species:

$$\text{Molecules} \leftrightharpoons \text{Micelles} \leftrightharpoons \text{Aggregates}$$

Brûlé *et al* (1986) and Yapp *et al* (1991) both refer to a model of asphaltene association proposed by Dickie and Yen (1967). Figure 11 is a pictorial representation of Dickie and Yen's (1967) model and of the above equilibrium relationship. Of course, the extent of the association between asphaltene molecules is not only a function of the dispersing power of the resins and solvent power of the oils, but is also a function of the quantity and quality of the asphaltenes (Holleran, 1994).

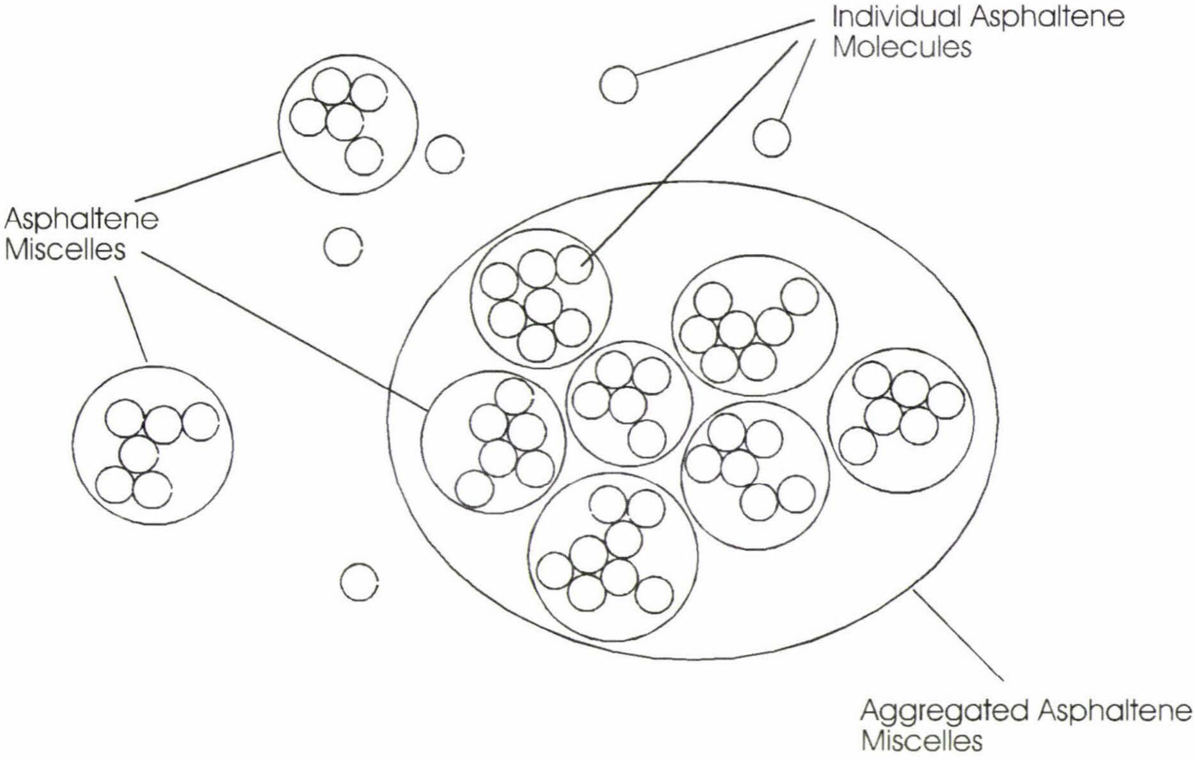


Figure 11: Dickie and Yen's (1967) model of the structure of asphaltene micelles (adapted from Dickie and Yen, 1967; Brûlé *et al*, 1986).

The more asphaltenes in the bitumen, and the higher the polarity or greater the *pi-pi* interactions, the greater is the tendency to associate. Asphaltenes of a higher molecular weight are also more likely to associate than lower molecular weight asphaltenes. Also, Lesueur *et al* (1997) maintains that the structure of the bitumen changes with temperature.

> "In the colloidal picture, a solvation shell made of resins surrounds the asphaltene core of the dispersed particles; so the resins are either liquid (dissolved in the maltene matrix) or solid (peptising the asphaltenes) and the following reversible process occurs:

$$[Resin]_{liquid} \overset{T}{\leftrightharpoons} [Resin]_{solid}$$

> This equilibrium is of course temperature dependent. Thus, the amount of total solid phase (asphaltenes + solid resins) is also temperature dependent" (Lesueur *et al*, 1997).

Therefore, the extent of association of the asphaltenes is influenced by the temperature as is illustrated in Figure 12. At higher temperatures, the solvating shell of resins surrounding the asphaltenes is smaller and consequently the volume of dispersed phase is less. The association of asphaltene particles is also less since higher temperatures disrupt the *pi-pi* and polar interactions. As the temperature cools, the solubility of the asphaltenes decreases and the solvating shell of resins increases in size as more resins become orientated at the interface of the asphaltene particle with the maltene phase. As the temperature varies the association between the asphaltene particles will also vary, and so too will the sol-gel characteristics of the bitumen.

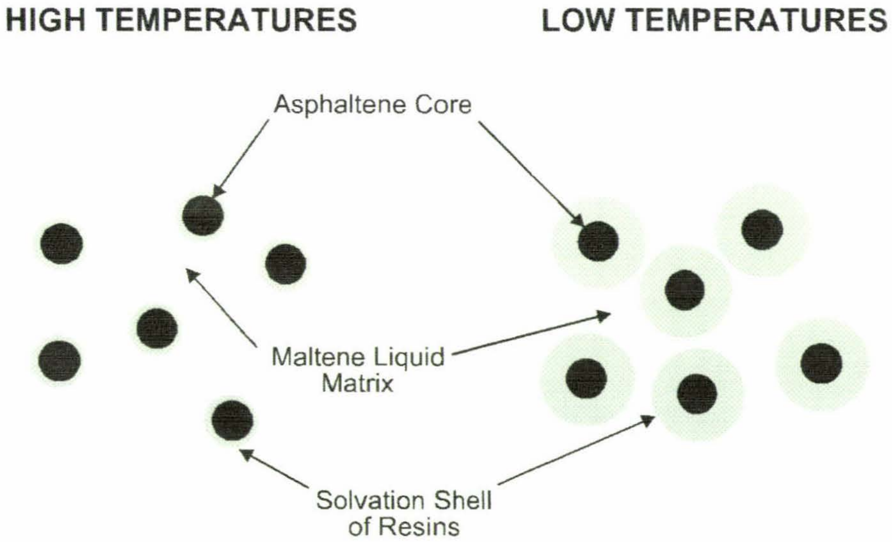


Figure 12: Structure of the bitumen dispersed phase as a function of temperature (from Lesueur *et al*, 1997).

Although the colloidal model has withstood many challenges to its accuracy over time, it is not without its drawbacks. Petersen *et al* (1994a) reviewed the literature regarding association of asphaltene molecules. Various researchers presented compelling evidence both for and against the colloidal nature of bitumen. While it is apparent that colloidal models explain the behaviour of bitumens some of the time, not all of the rheological behaviour of bitumen can be satisfactorily explained using colloid theory. Hence, the jury is still out regarding the extent of interaction between the asphaltene molecules in bitumen.

Petersen *et al* (1994a) identified some of the colloidal models that are more applicable to bitumens as:

- Lyophobic sols
- Gel
- Micellar solutions
- Emulsions

A critical review of the various colloidal models and how bitumen relates to each yields the following analysis:

> "Lyophobic sols typically contain only 1 or 2 percent of the dispersed phase. Asphalts contain a much higher percentage of asphaltenes, so this structure is unlikely. Additionally, such a small amount of a dispersed phase would be unlikely to greatly affect the properties of the asphalts. Although the gel-type structure seems plausible, there are several contradictions in this classification. Gels typically exhibit a high degree of rubber elasticity. Upon heating, a gel liquefies at a well-defined temperature, and when cooled, solidifies at another well-defined temperature. Asphalt cements do not exhibit rubber elasticity and show no well-defined melting or solidification points. Emulsions are three phase systems consisting of a dispersed liquid, a continuous liquid, and a dispersing agent. In this classic model of asphalt structure the asphaltenes are the dispersed phase, the oils the continuous phase, and the resins the dispersant. There are however, several problems with this model. Asphaltenes, except at very high temperatures, are solids, not liquids, and probably agglomerate as small (less than 50 nm) discrete particles showing semi-crystalline characteristics. Also, although many attempts have been made to explain the properties of asphalt cement through the relative proportions of asphaltenes and

> resin, none has been successful. The dispersed droplets in emulsions tend to flocculate into larger, spherical droplets, not into three-dimensional networks. Thus, the apparent structure in some asphalts is not explained by this model."
>
> "Micellar solutions may be a more appropriate colloidal model for asphalt cement. Micellar solutions are similar in some respects to emulsions, but the primary dispersed phase consists of amphipathic molecules arranged in micelles, either of the normal type or reversed. In asphalt cement, the micelles would be reversed and in many or all cases would be centred around asphaltene particles. This theory is, unfortunately, similar to the emulsion theory and has many of the same drawbacks. An important question here is whether amphipathic molecules are present in asphalt cement in large enough amounts to produce enough micelles to account for the level of structure present in asphalt. Additionally, there is no evidence that the micelles in micellar solutions can coalesce into a three-dimensional network. Such coalescence would probably be necessary to explain the steric hardening and oxidative hardening seen in most asphalts" (Petersen *et al*, 1994a).

4.4.2 The Microstructural Model.

Therefore, due to the inability for the colloidal model to explain specific properties of the bitumen, the microstructural model was proposed. The microstructure model has its basis in the colloidal model but is also noticeably different. In this model the interface between the dispersed asphaltene phase and the solvent oil phase is less defined and bitumen is described as "a continuum of polar and non-polar material. It is a homogenous, self-compatible mixture consisting of a variety of molecular species that are mutually dissolved or dispersed" (Holleran, 1994). The more polar molecules are able to form 'microstructures' to varying degrees depending upon the quantity and chemistry of the asphaltenes and resins.

The microstructural model hypothesises that the bitumen is composed of two phases: a solvent phase and an associated phase. The solvent phase consists of "relatively aliphatic, non-polar molecules that are low in heteroatoms ... and that this phase disperses microstructures (structural units formed from molecular associations) consisting of more polar, aromatic, asphaltene-like molecules" (Petersen *et al*, 1994a).

4.4.3 The Dispersed Polar Fluid Model

A third though less popular model of bitumen structure is the dispersed polar fluid model. This model considers bitumen to consist of a single phase of completely homogenous, mutually soluble non-polar and polar hydrocarbon molecules. The observed rheological behaviour of bitumen is caused by random interactions between polar molecules. This model does not provide any structure for bitumen and as such is contradictory to structural effects observed in some bitumens, especially the gelled types. Therefore, while it may explain some of the behaviour of certain bitumens, the dispersed polar fluid model is inadequate for providing a complete model of bitumen structure.

In effect, the three models are variants of each other and form a continuum from high to low order and structure. The colloidal model provides the highest degree of structure, through to the microstructural model giving an intermediate level of structure and finally the dispersed polar fluid model providing next to no structure and order at all.

4.5 Ageing of Bitumen

The failure of many bituminous pavements can be partially attributed to ageing of the bitumen during service. In a similar manner to plastics that become brittle after long-term exposure to the atmosphere and sunlight, bitumen undergoes oxidation and age hardening. Ageing of bitumen increases the modulus and reduces its flexibility and fatigue life, which leads to cracking of the pavement. Continued use by vehicular traffic subsequently causes a rapid deterioration of the pavement surface.

In the literature related to the ageing of bitumen, the terms bitumen oxidation and bitumen hardening tend to be used interchangeably. However, there are subtle differences between the two terms. For example, while all bitumen oxidation causes the bitumen to harden, not all hardening is attributed to bitumen oxidation. Hardening processes are generally physical in nature, while oxidative ageing usually involves chemical reactions.

While Bell (1989) reports that some researchers have identified up to 15 processes that contribute to ageing, it is generally recognised that "three fundamental composition-related factors govern the changes that could cause hardening of asphalts in pavements:

1. Loss of oily components of asphalt by volatility or absorption by porous aggregates,
2. Changes in the chemical composition of asphalt molecules from reaction with atmospheric oxygen, and
3. Molecular structuring that produces thixotropic effects (steric hardening)" (Petersen, 1984).

4.5.1 Volatilisation and Exudation

Because bitumen is composed of high boiling point fractions obtained from the vacuum distillation of crude oil, the loss of oily components by volatilisation at ambient temperatures is probably not a significant factor in age hardening of the bitumen (Petersen, 1984; Herrington *et al*, 1994). The lower molecular weight, less associated, oily components act as plasticisers and impart a softening effect to the bitumen. It is also possible that some aggregates may absorb the oily fraction of the bitumen. The net effect of this is to reduce the amount of solvent available for dispersion of the asphaltenes and consequently, the bitumen will harden. Another process that will reduce the amount of plasticising components in the bitumen is exudation. Exudation of the solvating saturates and aromatics fraction can occur in some bitumens that are low in compatibility. The asphaltenes are poorly solvated by the saturates and aromatics, and the oily phase exudes from the bulk of the bitumen during service.

4.5.2 Oxidative Ageing

The oxidation of bitumen has been the most extensively studied area amongst bitumen and hot mix asphalt researchers since it is perhaps the most significant contributor to age hardening. During ageing the aromatic fraction is converted to resins and the resin fraction is converted to asphaltenes. Saturates remain largely unaffected by oxidation. Petersen (1984) reports that the relative reactivity towards oxidation of the saturate, aromatic, polar aromatic and asphaltene fractions of a Californian bitumen were 1:7:32:40 respectively.

This indicates that the polar fractions of the bitumen are the most susceptible to oxidation. The increased molecular weight that occurs upon oxidation, coupled with increased polarity, which promotes hydrogen bonding and inter-molecular associations, causes a general increase in the viscosity and modulus of the bitumen.

It has been observed that the hydrogen to carbon ratio decreases upon oxidation (Herrington *et al*, 1994) This indicates that aromatic ring structures are increasing, presumably by dehydrogenation of naphthenic structures. It may be possible that saturate side chains of some molecules may be converted to cyclic structures. The cyclic structures can undergo subsequent dehydrogenation to form aromatic species. Herrington *et al* (1994) reports that the average number of aromatic rings per molecule, as determined from ^{13}C NMR studies, increases upon oxidation. Aromatization probably occurs at the expense of alkyl substituted naphthenic ring systems (Herrington *et al*, 1994).

4.5.2.1 Free-Radical Theory

It has traditionally been thought that the formation of carbonyl groups in bitumen occurs through a free-radical mechanism involving molecular oxygen and benzylic carbon atoms (Petersen, 1984; Robertson, 1991). "Benzylic hydrogens are approximately 100 times more reactive towards peroxy radicals than aliphatic hydrogens" (Herrington *et al*, 1994), presumably because the radical intermediate can be resonance stabilised by the aromatic ring system. However, Herrington *et al* (1994) did not detect any change in the benzylic hydrogen concentration during oxidation experiments with Safaniya bitumen. Benzylic hydrogen atoms are hydrogens attached to a saturated carbon atom that is located α to an aromatic ring. These results "suggest that carbonyl formation at other than benzylic sites is a more significant process during bitumen oxidation than usually supposed" (Herrington *et al*, 1994).

Most hydrocarbon materials undergo oxidation via a free-radical mechanism involving peroxy, alkoxy or phenoxy free-radical intermediates (Branthaver *et al*, 1993). The absence of a free-radical oxidative ageing mechanism in the case of bitumen is supported by the fact that bitumen contains naturally occurring free-radical inhibitors such as phenolic and pyrrole type compounds (Branthaver *et al* 1993). Also, studies involving the addition of free-radical inhibitors to bitumen, such as phenols and zinc dithiocarbamates, have shown that the rate of oxidation appears to be unaffected by the addition of these compounds (Branthaver *et al*, 1993). It is suggested that "the [oxidation] process must proceed by some other pathway, perhaps involving complexes of oxygen with aromatics, peroxide reactions with metals, or even spontaneous reaction of oxygen with reactive pyrrole-like structures" (Branthaver *et al*, 1993).

Herrington *et al's* (1994) observation that there was no discernible change in benzylic hydrogen concentration upon oxidation, together with the knowledge that bitumen contains naturally occurring free-radical inhibitors, throws doubt on the traditional mechanism of bitumen oxidation involving free-radical attack on the benzylic carbon. However, Branthaver *et al* (1993) describes experiments that indicate that free-radical oxidation occurs in bitumen. These experiments involved measuring the chemiluminescence emissions from thin bitumen films undergoing oxidation. Chemiluminescence is caused by peroxy free-radical interactions with organic compounds and polymers and "is due to conversion of a carbonyl triplet (R=O*) excited state to a ground state with production of a blue photon" (Branthaver *et al*, 1993).

Therefore, while it has been shown that free-radical oxidation does occur during the reaction of bitumen with oxygen, the significance of this reaction mechanism has yet to be established. What is known, is that although peroxy radicals are involved in bitumen oxidation, carbonyl formation involving free radical oxidation of benzylic carbons may not be as significant as previously thought.

4.5.2.2 Carbonyl and Sulphoxide Formation

The oxidation of bitumen typically involves the formation of sulphoxide and carbonyl groups. IR spectrophotometry has been used to show that there is an increase in the ketone, carboxylic acid, anhydride and sulphoxide concentration in bitumen after oxidative ageing (Petersen, 1984). The sulphur in unaged bitumen is predominately in the form of aliphatic, alicyclic and aryl sulphides, or thiophenes. Aliphatic and alicyclic sulphides are susceptible to oxidation and readily form sulphoxides. By comparison aryl sulphides and thiophenes are not very reactive (Branthaver *et al*, 1993; Green *et al*, 1993; Herrington *et al*, 1994). For all intents and purposes, sulphoxide is the only oxidised form of sulphur that has been detected to any significant level in bitumen (Branthaver *et al*, 1993). Green *et al* (1993) did not detect any sulphonic acids, sulphones or thiols in SHRP bitumens. An examination of the IR spectra of oxidised Safaniya bitumen did not show the presence of sulphones (Herrington *et al*, 1994).

From various sulphide oxidation experiments involving model aliphatic sulphide compounds, Branthaver *et al* (1993) "concluded that sulphoxide formation in asphalts does not arise from direct reaction of asphalt sulphides with oxygen." It was suggested that the reaction of aliphatic sulphides with oxygen probably occurs via an intramolecular hydroperoxy intermediate. This suggestion is in accordance with the assertion by Petersen (1984) that sulphides are hydroperoxide scavengers.

The amount, type and distribution of sulphur compounds in bitumen partially determine its susceptibility to oxidation. Aliphatic sulphides do not contribute significantly to the polarity and rheology of unaged bitumen. Yet upon ageing, the aliphatic sulphides prove to be one of the more reactive constituents and are readily converted to polar sulphoxides. Branthaver *et al* (1993) reported that sulphoxide formation from aliphatic sulphides in Californian Coastal bitumen was responsible for a ten-fold increase in the viscosity of the bitumen.

In recent years, researchers have paid an interest in the abundance of aliphatic sulphur in the acidic fraction as recovered using IEC. Acidic molecules are predominately resident in the resin and asphaltene fraction of the bitumen. Upon oxidation however, acidic molecules that contain aliphatic sulphur are converted to amphoteric molecules since sulphoxide is slightly basic (Green *et al*, 1993). Amphoteric molecules are highly associative and are resident in the asphaltene fraction of the bitumen. Consequently, a possible mechanism for the conversion of resins to asphaltenes during oxidation has been postulated.

Green *et al* (1993) separated four different bitumens into their strong acid, strong base, weak acid, weak base and neutral fractions using a non-aqueous ion exchange liquid chromatography (NIELC) technique. The neutral fraction was further separated into polar-neutral, sulphide, non-sulphide, saturated hydrocarbon and neutral aromatic fractions. Each of the 9 fractions were analysed for sulphur content. It appears that sulphur is evenly distributed throughout each of the bitumen fractions, with the exception of the saturate neutral fraction, which is essentially sulphur free. Whiteoak (1990) presents similar data that shows that the saturate fraction is essentially sulphur free, while the asphaltene, resin and aromatic fractions all contain similar proportions of sulphur.

The ratio of thiophenic sulphur to sulphide sulphur (aliphatic, alicyclic and aryl sulphides) in whole, unaged bitumens is typically of the order of 72:28 to 60:40 (Branthaver *et al*, 1993; Green *et al*, 1993). However, variations occur between bitumen from different sources. Thiophenic and aryl sulphides are more abundant in the strong acid, weak acid and strong base fractions. This is to be expected since these species typically form the asphaltene and resin fraction and are more aromatic in nature than the saturate fraction. Notwithstanding this, aliphatic sulphur is still detectable in these fractions. The weak base and neutral fraction typically contain a greater proportion of sulphide sulphur compared to the strong acid, weak acid and strong base fractions (Green *et al*, 1993).

The research conducted by Green *et al* (1993) provides a mechanism for the observed conversion of aromatic and resin fractions to asphaltenes during bitumen oxidation. Aliphatic sulphur is readily converted to the polar sulphoxide form, which makes the molecule more associative. The increase in polarity converts an aromatic or resinous molecule into an asphaltene molecule. This is especially true in the case of molecules containing both aliphatic sulphur and acidic groups since the oxidised molecule becomes amphoteric.

Being polar and slightly basic, sulphoxides exhibit a stronger interaction with aggregates than aliphatic sulphur does. However, Green *et al* (1993) indicates that sulphoxide-aggregate bonds are more susceptible to displacement by water compared to nitrogen-aggregate bonds. By implication, bitumen that contains a significant proportion of sulphoxides, or oxidisable sulphur, may be susceptible to moisture damage and stripping. Green *et al* (1993) reports "that the bulk of sulphoxides removed via water displacement are probably those within the neutral fraction which lack other polar functionalities to enhance adhesion to aggregate in the presence of water."

Sulphoxide formation occurs at a faster rate than carbonyl formation, but tends to reach a plateau relatively quickly whilst carbonyl formation continues to occur as the bitumen is progressively aged (Herrington and Ball, 1996; Herrington *et al*, 1994). Sulphoxides also tend to decompose at temperatures above 113°C, while carbonyls do not (Branthaver *et al*, 1993; Herrington, 1995). This is a good reason to artificially age bitumen at lower temperatures in the laboratory to ensure that the oxidation products are consistent with those produced in the field.

Oxidation of carbon atoms in the bitumen predominately forms ketones with only minor amounts of carboxylic acids and anhydrides being formed. No esters have been detected in paving grade bitumens (Petersen, 1984). While evidence has been provided that refutes the traditional view that carbonyl formation occurs at the benzylic carbon, Petersen (1984) notes "that ketones are formed in the highest concentration in the asphaltene and polar aromatic fractions; lesser amounts are formed in the aromatic fraction, and considerably less in the saturate fraction." Petersen (1984) goes on to point out that the asphaltene and polar aromatic fraction contains the highest proportion of benzylic carbons.

Carbonyl formation continues to occur after depletion of all the reactive sulphide in bitumen and is responsible for further increases in the viscosity of the bitumen. Herrington (1998) has determined that the change in viscosity of Safaniya bitumen can be modelled by the Equation 4-1:

Equation 4-1: $\Delta \log \eta = k\, \Delta ([CO] + [SO])$

where η = viscosity
k = rate constant
$[CO]$ = concentration of carbonyl groups
$[SO]$ = concentration of sulphoxide groups

This indicates that changes in the bitumen viscosity are significantly affected by carbonyl and sulphoxide formation. Studies by Herrington (1998) show that "bitumen oxidation can be generalised as consisting of a group of 'fast' reactions obeying approximately first order kinetics, and involving carbonyl and sulphoxide formation and a much slower process involving carbonyl formation which is approximately constant over the experimental time frame."

To date, researchers have not been able to account for all the oxygen consumed during oxidation experiments with bitumen. The concentration of carbonyl and sulphoxide groups usually accounts for only 20 – 60% of the oxygen (Branthaver *et al,* 1993). Measurements by Branthaver *et al* (1993) did not detect any CO or CO_2 formation, so it can be assumed decarboxylation is not occurring. It is possible that the unaccounted for oxygen is present in bitumen as peroxy radicals or as H_2O. Alternatively, the oxygen may be present as alcohols, which are difficult to detect using IR methods (Branthaver *et al,* 1993). Another consideration is the fact that the uncertainty in the measurements of O_2, sulphoxide and carbonyl concentrations can be significant.

4.5.3 Steric Hardening

Steric hardening, "although elusive and difficult to quantify, may also be a significant contributor" to the age hardening of bitumen (Petersen, 1984). Steric hardening refers to the phenomenon of isothermal reversible age-hardening that occurs in bitumen and is distinctly different from the irreversible hardening that is a result of oxidation. It is believed to be a result of the self-rearrangement of molecules in the bitumen film to achieve a more thermodynamically stable conformation. Over a period of several months and even years, the molecules in the bitumen re-orientate themselves to achieve a type of internal structuring that results in an increase in the viscosity, modulus and elastic properties of the bitumen (Branthaver *et al*, 1993).

Steric hardening was originally thought to be governed by the asphaltene molecules and was a result of molecular structuring of polar molecules resident in the bitumen. However, it has been shown that steric hardening also occurs in bitumen that has had the polar fractions removed. Branthaver *et al* (1993) reports that even neutral bitumen fractions recovered by IEC exhibit an increase in modulus over time. Therefore, the phenomenon of reversible age hardening is a result of molecular structuring of various types of bitumen molecules and is likely to be caused by a variety of mechanisms, such as hydrogen bonding amongst polar molecules, *pi-pi* associations amongst aromatic molecules and crystallisation amongst aliphatic, wax like molecules.

Steric hardening is only observed at temperatures below 60°C. Heating above this temperature results in a reduction of the bitumen's mechanical properties to its original value before steric hardening occurred. This can be explained by the fact that steric hardening involves weak intermolecular bonds such as hydrogen bonds and van der Waals forces that are easily disrupted by heat. The extent of steric hardening within a specific bitumen is dependent upon several factors including ambient temperature, rate of cooling and bitumen composition.

The ambient temperature influences the rate at which the bitumen molecules can re-orientate themselves and the extent of the bonding involved. It has also been observed that bitumens that are cooled slowly from temperatures above 60°C harden at a faster rate than a bitumen that is cooled quickly. This is thought to be because the molecules in a bitumen that is cooled slowly have enough time to begin the orientation process whilst the bitumen is still sufficiently fluid. Rapidly cooled bitumen become viscous very quickly thereby trapping the individual molecules in the conformation they possessed whilst the bitumen was in a fluid state.

In studies reported by Branthaver *et al* (1993), steric hardening was found to cause an increase in the rheological properties of three different bitumens as shown in Table 7. The bitumens had all been cured at 25°C in an inert gas atmosphere to prevent any interference that may be caused by oxidative hardening. The bitumens were all cured in their respective test assemblies to avoid damaging any inter-molecular structuring that had occurred that would otherwise be destroyed by annealing or mechanically moulding the bitumens during test specimen preparation.

Table 7: Change in rheological properties of three bitumens caused by steric hardening.

Bitumen	Cure Time (Hrs)	Increase in Elastic Modulus (%)*	Increase in Viscosity (%)*
AAD-1	1,958	111%	64%
AAK-1	5,138	86%	57%
AAM-1	2,031	74%	39%

* Calculated from data given in Branthaver *et al* (1993).

4.5.4 Alternative Ageing Mechanisms

While loss of volatile components, oxidative ageing and steric hardening are thought to be by far the most common causes of age hardening in bitumen, other factors that may affect the rheological properties of the bitumen during service have also been discussed in the literature. These other factors include the influence of water, aggregates and sunlight. The study of the effects of water on bituminous pavements is usually limited to its effect on the adhesion between the bitumen and the aggregate. However, although bitumen is hydrophobic, Robertson (1991) explains that water can be incorporated into bitumen by attraction to the more polar resin and asphaltene fractions. It may also be possible that low molecular weight polar molecules (e.g. some carboxylic acid species) may be solvated by water molecules and be subsequently washed from the bitumen resulting in a change in the rheological properties.

It has been suggested (Kennedy *et al*, 1990) that when bitumen is mixed with aggregates an ordered inter-phase region develops between the polar aggregate and the bitumen. The inter-phase region extends from the interface with the mineral aggregate up to 100 μm into the bulk of the bitumen. The polar aggregates cause polar molecules in the bitumen to orientate themselves and create a structured phase that affects the rheological, ageing and adhesive properties of the bitumen. While examining this hypothesis, Curtis *et al* (1993) found no evidence for the formation of an inter-phase region, thereby casting doubt upon Kennedy *et al*'s (1990) hypothesis.

While it has been shown that ultraviolet radiation can cause significant age hardening (Bell, 1989) of the bitumen, the overall influence of UV radiation on the ageing process is minimal. This is because UV radiation can only penetrate a few microns into the bitumen film (Button, 1996). Since asphalt concrete is typically laid 20 – 200 mm thick the overall effect of UV radiation is minimal. Similarly, the bitumen film thickness in chip seals is typically in the order of 1 – 5 mm and consequently approximately 99.9% of the bitumen film is unaffected by UV radiation.

4.5.5 Laboratory Ageing of Bitumen

Because the ageing characteristics of the bitumen are directly related to its durability and long-term *in-situ* performance, many attempts have been made to accelerate the ageing of bitumen in the laboratory so as to ascertain its likely long-term durability. Bell (1989) describes several of the procedures and studies used to examine the phenomenon of age hardening in bitumen and asphalt concrete. The vast majority of these accelerated ageing procedures have relied upon the use of elevated temperatures although there are differences in the conditions employed. For example, Table 8 gives a summary of the conditions employed by various researchers using some of the more popular, standardised ageing procedures.

Table 8: Conditions reportedly used for the accelerated ageing of bitumen (Bell, 1989).

Method	Film Thickness (nominal)	Duration of Ageing	Ageing Temperature
Thin Film Oven Test (TFOT)	100 – 3000 μm	5 – 24 hrs	163°C
Shell Microfilm Test	5 – 20 μm	2 – 24 hrs	99 – 107°C
Rolling Thin Film Oven Test (RFTOT)	1250 μm	75 min – 8 hours	163°C
Rolling Microfilm Oven Test (RMFO)	20 μm	24 hrs	99°C
Tilt Oven Durability Test (TODT)	1250 μm	100 – 168 hrs	113 – 115°C
Thin Film Accelerated Ageing Test (TFAAT)	15 μm	72 hrs	113°C
Air Blowing (9.1 L/min)	-	15 min	204 – 229°C
Pressure Oxidation Vessel (100 – 300psi O_2)	3000 μm	20 – 2000 hrs	60 – 110°C

The extent of ageing is usually evaluated by comparing the physical properties of the bitumen, such as viscosity, penetration or modulus, before ageing to the same property after ageing. However, it is accepted that the different ageing procedures give different degrees of age hardening. This can be explained by considering that the extent of oxidation is dependent upon several different factors such as the film thickness, the temperature and the duration of ageing. Firstly, oxidation is dependent upon the rate of diffusion of oxygen into the bitumen film. Obviously thicker films will require a longer ageing time to allow oxygen to come into contact with reactive bituminous species that may be resident in the centre of the film. It must also be considered that the diffusion rate varies depending upon the temperature and the viscosity of bitumen.

Secondly, the rate of oxidation is temperature dependent. Recent research has complicated the matter by proving that the temperature of the ageing procedure not only affects the rate of oxidation, but it also affects the mechanism and the oxidation products formed (Herrington *et al*, 1994; Herrington and Ball, 1996). Higher temperatures result in a greater rate of age hardening but this does not necessarily correlate to observed field performance. The oxidation products formed at different temperatures vary, which gives rise to variations between the degree of hardening observed in the laboratory and that observed in the field.

The extent of oxidation of bitumen is also dependent upon the duration of ageing. Obviously, a longer duration of ageing will result in a greater degree of oxidation. Like all chemical reactions, the oxidation of bitumen is rate dependent. The oxidation rate has been found to be a first order reaction but varies depending upon the rate of oxygen diffusion and the reactivity of the bitumen in question. Pressure does not appear to affect the rate of oxidation in the range of 100 – 2,000 kPa.

SHRP recently standardised the protocol for ageing bitumen in the laboratory (Asphalt Institute, 1996). It divided the procedure into two parts. The first part consists of the Rolling Thin-Film Oven Test (RTFOT), which simulates the short-term ageing of bitumen as it passes through an asphalt plant. Films of bitumen (1250 μm thick) are aged for 85 minutes at 163°C in rotating bottles in an oven. The rate of air flow is fixed at 4.0 L/min (ASTM D2872, 1996).

The second part of the ageing procedure consists of oxidising the bitumen in a pressure oxidation vessel (POV) at 90, 100 or 110°C depending upon the grade of bitumen and the expected climate it will be used in. The bitumen is oxidised at a pressure of 2,070 kPa (300psi) O_2 for 20 hours. The film thickness is nominally 3000 μm. The pressure oxidation vessel is intended to simulate the effects of long term ageing on the bitumen.

Some researchers have used UV or IR radiation to age the bitumen. As noted in Section 4.5.4, the effect of UV radiation on bitumen is usually not appreciable. While UV radiation does cause severe oxidation and polymerisation of the bitumen, this effect is limited to the first 2 – 5 microns near the bitumen surface, where the radiation is incident (Button, 1996; Bell, 1989). Since asphalt concrete is usually laid more than 20 mm thick and bitumen used in chip sealing is more then 1000 μm thick, the bulk of the bitumen remains unaffected by UV radiation. Infra-red radiation (IR) also causes the bitumen to age but is not as effective as UV radiation.

Another promising technique for ageing bitumen is the use of microwave radiation. In recent years, various researchers (Bell, 1989; Bishara and Reynolds, 1996) have identified the use of microwave radiation for the ageing of bitumen in the laboratory. Very little is known about the effects and mechanism of ageing using a microwave oven except that bitumen can be hardened to levels comparable with those achieved using more conventional techniques such as RFTOT and POV.

Numerous researchers have also studied the effect of age hardening on the bitumen in hot mix asphalt. The procedures involve mixing aggregate and bitumen together, ageing them in a similar fashion to that already discussed for bitumen and then comparing the properties of the mix before and after ageing.

Herrington *et al* (1994) studied the oxidation of Safaniya bitumen, which has been the main source of bitumen in New Zealand over the past 15 years. Herrington *et al's* (1994) studies indicate that the oxidation products formed at 60°C and the mechanism of oxidation may be different from those at temperatures of 100°C and 130°C. The implication for this is that the durability indicated by accelerated ageing procedures at elevated temperatures may be incorrect. Herrington (1998) concluded that accurate indications of the durability of bitumen can only be achieved at lower (60°C) temperatures.

Another variable that has been identified as affecting the rate of oxidation in bitumen is molecular structuring (Branthaver *et al*, 1993; Herrington and Wu, 1999). The asphaltenes are not only the most reactive fraction in bitumen but are also the most associative. Therefore at lower temperatures they exhibit a higher degree of association, which may serve to sterically hinder sites that are susceptible to oxidation. In bitumen that has been artificially aged at higher temperatures, the association of asphaltenes is broken down and it is feasible that previously unavailable reactive sites may become available for oxidation. Therefore, it is possible that the reaction products obtained by oxidation at higher temperatures are not necessarily representative of the oxidation products formed at typical pavement temperatures.

Branthaver *et al* (1993) suggests that the rate of oxidation is also subject to a 'quenching' reaction due to molecular structuring. The more polar molecules are more susceptible to oxidation, which would increase their polarity even further. An increase in polarity causes an increase in molecular association and therefore an increase in steric hindrance of the most reactive sites. Consequently, the more a bitumen is oxidised, the stronger the driving force for molecular association and quenching of the oxidation reaction. Bitumens that possess a maltene phase that is not very effective at dispersing the asphaltenes are more susceptible to quenching than those that possess a maltene phase with good solvent power. Interestingly, Herrington and Wu (1999) concluded that intermolecular associations did not significantly affect the rate of oxidation in the bitumens they studied.

5.0 Effect of Bitumen Composition on Performance

Most national specifications for paving grade bitumen specify the bitumen on the basis of measurable physical properties such as penetration, viscosity and susceptibility to ageing. It has been observed that two bitumens of the same grade, as determined by measurement of a physical property such as viscosity, can in fact have vastly different performance in terms of fatigue and rutting resistance, moisture sensitivity and durability. Since the composition of bitumen varies widely between sources, it is not unreasonable that the performance of bitumens from different sources has been observed to vary also.

5.1 Performance Indices

The physical properties of the bitumen are not necessarily related to the quantity of any particular fraction of the bitumen, but is rather an artefact of how the individual molecules and fractions interact (Roberts *et al*, 1991; Petersen, 1984). This has led to the development of several indices that attempt to relate bitumen composition to physical performance.

5.1.1 Rostler Indices

Roberts *et al* (1991) describes two parameters determined using data obtained from the Rostler and Sternberg fractionation of bitumen (see Section 4.3.1). Equation 5-1 describes the compatibility ratio, which compares the nitrogen base fraction to the paraffin fraction. The nitrogen base fraction is responsible for the dispersion of the asphaltenes while the paraffin fraction promotes flocculation of the asphaltenes. The Rostler Durability Ratio (RDR) is described by Equation 5-2 and compares the most reactive components of the bitumen against the least reactive. Roberts *et al* (1991) reports that "a compatibility ratio of more than 0.5 is considered good. ... A durability parameter of less than 0.40 is considered poor and more than 1.00 is considered good."

Equation 5-1: $$\text{Compatibility Ratio} = \frac{\text{Nitrogen Bases}}{\text{Paraffins}}$$

Equation 5-2:

$$\text{Rostler Durability Ratio} = \frac{\text{Nitrogen Bases} + 1^{\text{st}}\ \text{Acidaffins}}{\text{Paraffins} + 2^{\text{nd}}\ \text{Acidaffins}}$$

One study that related the RDR to the performance of the bitumen "indicated that asphalts with RDR less than 1.14 had excellent abrasion resistance" Bell (1989). A second study "concluded that for pavements with less than 2% air voids there was a direct relationship between the RDR and ageing as measured by the viscosity of the recovered asphalt. For higher air voids the RDR was overshadowed by other effects, but the ratio for minimum hardening appears to be in the range 1.0 to 1.4" (Bell, 1989). A study conducted in South Africa "concluded that there was good correlation between the RDR and road performance and that appropriate limits for coastal South Africa would be 1.0 to 1.7..." (Bell, 1989). High and low values of the Rostler Durability Ratio are indicative of bitumens that are likely to suffer from temperature susceptibility problems and poor resistance to oxidative ageing.

Petersen (1984) and Goodrich *et al* (1986) are critical of the use of the Rostler Durability Ratio since it does not consider the influence of the most reactive bitumen component, the asphaltenes. They also suggest that as a general rule the RDR does not correlate well with observed field performance.

5.1.2 Gotolski Ratio

The Gotolski Ratio also uses data obtained from the Rostler and Sternberg procedure for the fractionation of bitumen and is described by Equation 5-3. The main improvement that the Gotolski Ratio offers over the Rostler Durability Ratio is that it includes the influence of the asphaltenes in the equation.

Equation 5-3:

$$\text{Gotolski Ratio} = \frac{\text{Nitrogen Bases} + 1^{\text{st}}\ \text{Acidaffins} + 2^{\text{nd}}\ \text{Acidaffins}}{\text{Paraffins} + \text{Asphaltenes}}$$

Bell (1989) explains that the Gotolski Ratio is related to the susceptibility of the bitumen to ageing and that a high Gotolski Ratio is an indicator of poor performance. Suggested limits of the Gotolski Ratio for satisfactory performance of the bitumen are 1.3 to 2.6 (Holleran, 1994).

Once again the Gotolski Ratio attracts its share of critics: Bell (1989) and Goodrich *et al* (1986) both reviewed studies that suggest that there is no significant relationship between the Gotolski Ratio and field performance of the bitumen.

5.1.3 Gaestel Index

An alternative indicator of performance to the Rostler or Gotolski Ratios, is the Gaestel Index, or the 'Colloidal Instability Index (I_c)' as it is sometimes known. The Gaestel Index is described by Equation 5-4 and is similar to the Rostler and Gotolski Ratios, but uses data obtained from the fractionation of bitumen using the Corbett procedure (see Section 4.3.4) instead of the method of Rostler and Sternberg.

Equation 5-4:

$$\text{Gaestel Index } (I_c) = \frac{\text{Asphaltenes} + \text{Saturates}}{\text{Polar Aromatics} + \text{Naphthene Aromatics}}$$

Tuffour *et al* (1989) found a definite relationship between the Gaestel Index and the viscosity of the bitumen. It was also observed that the Gaestel Index increased as the bitumen was progressively aged. The relationship between viscosity and Gaestel Index did not hold for purely propane-precipitated bitumens, which are characterised by a high level of polar aromatics. In another study, Ishai *et al* (1988) observed that bitumens with a high Gaestel Index had a higher ageing index (increased susceptibility to ageing) than bitumens with a low Gaestel Index.

Gaestel notes that all the properties of the bitumen including softening point, ductility, temperature susceptibility, elastic recovery and shear susceptibility vary considerably depending upon the value of the Gaestel Index (Brûlé *et al*, 1986; Holleran, 1994). While the Gaestel Index is a popular and useful tool for analysing the colloidal behaviour of bitumen, Brûlé *et al* (1986) points out that the Gaestel Index only takes into account the quantity of the asphaltene fraction. It does not account for any effect that the type or quality of the asphaltenes has on the colloidal nature of the bitumen.

High values of the Gaestel Index indicate that the bitumen has a lower colloidal stability than if it had a low Gaestel Index. Serfass *et al* (1992) used the Gaestel Index as a measure of compatibility between bitumen and SBS polymer. It was concluded "that no precise borderline between 'compatible' and 'incompatible' bitumen can be drawn. Bitumen with I_c higher than 0.25 are definitely incompatible; those with I_c lower than 0.15 are generally compatible. In between, other factors govern the compatibility, e.g. SBS structure and molecular weight, maltenes solvent power and molecular weight" (Serfass *et al*, 1992).

Loeber *et al* (1998) used a parameter called the Colloidal Stability Index (CI) while studying the colloidal nature of bitumen. The Colloidal Stability Index is in fact the inverse of the Gaestel Index. Higher values of the Colloidal Stability Index, which correspond to lower values of the Gaestel Index, indicate an improved dispersion of asphaltenes in the maltene phase.

5.1.4 HP-GPC Studies

Yapp *et al* (1991) provided a review that showed that various researchers have attempted to correlate the GPC chromatograms of bitumen to the observed performance in the field. The results have been inconsistent with some researchers finding correlations and others finding none. The results are likely to have been confounded by variations in methodology and equipment.

Yapp *et al* (1991) reviewed a study by Zenewitz and Tran that concluded that a greater proportion of SMS material in the bitumen may cause rutting in asphalt mixes, while a greater proportion of LMS material (and a correspondingly lower proportion of SMS material) may cause cracking. Branthaver *et al* (1992) came to a similar conclusion. They found that bitumens that contained more than 85% SEC-II fraction were more likely to rut than bitumens containing lesser amounts of SEC-II fraction. The SEC-II fraction comprises the non-associative phase of the bitumen and is akin to the MMS and SMS fractions obtained from other GPC studies.

Goodrich *et al* (1986) and Yapp *et al* (1991) observed that the temperature susceptibility of a bitumen can be related to its particular GPC chromatograph. Bitumens with a broad range of molecular sizes, i.e. bitumens that are polydisperse, are moderately temperature susceptible. Bitumen that has a narrow range of molecular sizes typically has a very high or very low temperature susceptibility depending upon the location of the peak.

Garrick and Wood (1986) observed that the viscosity and penetration of bitumen was related to the HP-GPC profiles. However the relationship was complex and it was apparent that the penetration and viscosity is determined by the overall interaction between molecules of varying molecular size and polarity.

Yapp *et al* (1991) reviewed two different studies that developed regression equations that related the GPC chromatograph to various physical properties of the bitumen such as specific gravity, indirect tensile strength, resilient modulus and temperature susceptibility. Each regression equation had a correlation coefficient of greater than 0.75. Interestingly, these latter studies could not find any correlation between the GPC profile and the penetration or viscosity. This is in direct conflict with the findings of Garrick and Wood (1986).

Kim *et al* (1993) managed to establish relationships between the GPC chromatogram of bitumen and the mechanical strength of asphalt mixtures as measured by tensile strength and resilient modulus. The correlation coefficient was greater than 0.90.

5.1.5 Heithaus Parameters

Heithaus (1960) defined three parameters that can be used to define the compatibility of a bitumen: P, P_a and P_o. The overall system compatibility is defined by the parameters 'P'. The parameter 'P_a' measures the peptisability of the asphaltene fraction and P_o, measures the solvent power of the maltenes phase. An increase in any of these parameters indicates an increase in the compatibility of the bitumen. A higher P_a suggests that the asphaltenes are more readily dispersed and an increase in P_o indicates that the maltenes are more efficient at solvating or peptising the asphaltenes. The values of P_a, P_o and P can be calculated using Equation 8-4, Equation 8-5 and Equation 8-6 respectively in Section 8.3.2.3.

Heithaus (1960) and Pauli and Branthaver (1998) have related the three parameters to the relative viscosity of the bitumen. An increase in the Heithaus parameters tends to lead to a decrease in viscosity. Heithaus (1960) also suggests that P_a and P_o influence the durability and colloidal stability of the bitumen.

A study undertaken in 1987 by Glover and co-workers (Yapp *et al*, 1991) indicates that bitumens that are too compatible, i.e. have high values of P_a and P_o, may be susceptible to tenderness problems in hot mix asphalt. That is to say, the asphaltenes do not associate sufficiently for the bitumen to reach a minimum necessary modulus value for satisfactory performance.

5.2 Effect of Fractional Components

5.2.1 Asphaltenes

It is generally acknowledged that the asphaltenes are the viscosity building, or thickening agents in bitumen (Roberts *et al*, 1991; Petersen, 1984). The rheological and mechanical properties of the bitumen, such as penetration, viscosity, softening point and modulus are strongly influence by the amount and type of asphaltenes present. Increasing the amount or the association potential of the asphaltenes will lead to an increase in the softening point and viscosity and a decrease in the penetration (Morgan and Mulder, 1995).

Finn *et al* (1990) summarised data from numerous field trials and concluded that high asphaltene contents promoted cracking and low asphaltene contents promoted rutting in asphalt concrete pavements. In a review of the literature pertaining to GPC analyses of bitumen, Yapp *et al* (1991), Roberts *et al* (1991) and Tarrer and Wagh (1994) note that bitumens with a low asphaltene content can cause tenderness problems in asphalt mixes.

Because the asphaltene fraction contains the highest proportion of heteroatoms (including metal atoms) and is high in substituted, polynuclear aromatic ring systems, it is also the fraction that is most susceptible to oxidative ageing (Petersen, 1984). Therefore, the quantity and type of asphaltenes present in the bitumen contribute to the durability of the asphalt concrete with respect to age hardening behaviour.

5.2.2 Resins

The resins fraction of bitumen has been found to be a major contributor to the ductility of the bitumen (Corbett, 1970). Being polar in nature, the resins contribute to the adhesive properties of the bitumen and are thought to be a determinant of the degree of asphaltene dispersion in the bitumen. Consequently, the quantity and nature of the resins influences the rheological properties of the bitumen. Upon oxidation resins are readily converted to asphaltene molecules (Morgan and Mulder, 1995).

5.2.3 Aromatics

The aromatic fraction of the bitumen is not as susceptible to oxidation as the resin and asphaltene fractions. However, it does undergo some oxidation and is converted to resin and asphaltene type molecules. In general, the aromatic fraction, along with the saturates, is responsible for the fluid nature of the bitumen and acts as a solvent for the dispersed phase (Petersen, 1984). Higher levels of aromatics molecules results in less agglomeration of asphaltene molecules and consequently lower viscosity and reduced elasticity (Petersen *et al*, 1994a). A field trial conducted in Montana, USA that was reviewed by Finn *et al* (1990) concluded that the "resistance to cracking is associated with relatively lower concentrations of naphthene aromatics."

Both Petersen (1984) and Branthaver *et al* (1993) note that the ability of the non-associated phase (such as the aromatic fraction) to effectively disperse the associated oxidation products is a determinant of the age hardening potential of the bitumen. Highly compatible bitumens usually possess a non-associated phase that is an effective solvent for the associated phase and consequently exhibit a lower viscosity after oxidation.

5.2.4 Saturates

Full scale road trials in Utah concluded that the saturates fraction adversely affected the temperature susceptibility, ductility and cracking resistance of bitumen (Finn *et al*, 1990). Another study undertaken by the Federal Highway Administration concluded that higher levels of saturates resulted in less hardening of the bitumen (Finn *et al*, 1990). However, while summarising a review of various studies, Finn *et al* (1990) states that the Federal Highway Administration study concluded that high saturate contents tend to promote a higher amount of age hardening. This apparent contradiction is probably due to the loose use of the term 'hardening'. Saturates and aromatic type molecules act as plasticisers in the bitumen (Corbett, 1970) and as a general rule an increase in the saturate and aromatic fractions causes the bitumen to become softer. However, it should also be noted that saturates are poor solvents for the asphaltenes (Petersen, 1984) and therefore have a tendency to flocculate the asphaltene molecules. Consequently, in the absence of sufficient aromatic and resin type molecules, which can occur after oxidative ageing, the associated asphaltenes will cause the bitumen to have a higher viscosity and modulus.

The presence of wax type materials in the saturate fraction is deleterious (Petersen, 1984). Waxes have been implicated in causing tenderness problems in hot mix asphalt (Crawford, 1986). Waxes lower the modulus of the bitumen at high service temperatures and cause excessive steric hardening at low temperatures. Consequently, bitumens with a high wax content tend to have a poor temperature susceptibility and are prone to low temperature cracking caused by a high modulus at cooler temperatures (Petersen *et al*, 1994a).

5.3 Role of Specific Functional Groups

5.3.1 Carboxylic Acids and Anhydrides

Being highly polar, carboxylic acids and anhydrides are predominately found in the asphaltene fraction (Petersen, 1986). Petersen (1984) reports that lime treatment has been used to remove excessive amounts of carboxylic acids from bitumen. The resultant effect is a reduction in the age hardening of the bitumen and consequently a lower viscosity. The implication from this research is that carboxylic acids groups present in the bitumen increase the viscosity through molecular interactions. “Separate studies showed that the introduction of carboxylic acid functional groups into asphalt molecules greatly increased asphalt viscosity” (Petersen, 1984).

Herrington *et al* (1999) studied the effect of modifying bitumen with dicarboxylic acids and anhydrides. Dicarboxylic acids and anhydrides increased the modulus and reduced the temperature sensitivity of the bitumen. It is thought that the dicarboxylic acids and anhydrides act as cross-linking agents that interact with neighbouring bitumen molecules through hydrogen bonding and dipole-dipole interactions. It was noted that the addition of a mono-carboxylic acid such as decanoic acid had a plasticising effect on the bitumen. However, this may be more due to the low molecular weight (172 g/mol) of decanoic acid compared to the average molecular weight of bitumen molecules (600 – 1000 g/mol).

The role of carboxylic acids, anhydrides and carboxylic acid salts in the adhesion of bitumen to mineral aggregates was investigated by Plancher *et al* (1977). Carboxylic acids and anhydrides display a high affinity for mineral aggregates and are readily adsorbed from bitumen onto the aggregate surface. They are also the functional groups found in bitumen that are most readily desorbed from aggregate surfaces by water. Often the carboxylic acid is displaced by water as a salt after cation exchange has occurred at the mineral aggregate surface (Plancher *et al*, 1977). Because carboxylic acids are readily removed from the aggregate surface by water they are thought to play a significant role in water stripping in asphalt mixtures.

Amongst the carboxylic acid salts there exists a range of affinity for displacement from the aggregate surfaces. Robertson (1991) suggests that the practitioner ensures that any carboxylic acid salts at the aggregate interface be present as salts of divalent cations such as calcium, since these are less readily displaced than the salt of monovalent sodium or potassium cations.

5.3.2 Ketones

Ketones are formed during oxidation of the bitumen and can transform a non-polar aromatic bitumen molecule into a polar resinous molecule. Being polar they can engage in intermolecular associations and consequently an increase in bitumen viscosity accompanies and increase in ketone formation (Branthaver *et al*, 1993; Herrington *et al*, 1994).

Plancher *et al* (1977) observed that ketones were not as strongly adsorbed onto aggregate surfaces as nitrogen containing functional groups, quinolones, sulphoxides and carboxylic acids. However, ketones were found to be very resistant to displacement by water, which indicates that they would promote strong adhesion at the bitumen and aggregate interface.

5.3.3 Sulphur and Sulphoxide

The presence of sulphides in bitumen has negligible impact upon its physical and performance properties. Sulphides are non-polar and as such do not contribute to the rheological properties in the same manner as the more polar molecules. They show no appreciable adsorption onto aggregate surfaces and consequently do not contribute to the adhesive nature of the bitumen (Green *et al*, 1993; Plancher *et al*, 1977).

"The oxidised (sulphoxides) and oxidisable (aliphatic sulphides) sulphur probably impacts asphalt performance to a much greater extent than the more inert forms (aromatic sulphides, thiophenes)" (Green *et* al, 1993). While the aliphatic sulphides do not impact the performance of the bitumen to any great extent, their ability to be readily oxidised to sulphoxides means that the aliphatic sulphide content of the bitumen is a major contributor to bitumen durability. Sulphoxides are polar and as such contribute to intermolecular associations and consequently an increase in sulphoxide content usually causes an increase in viscosity (Branthaver *et al*, 1993; Herrington *et al*, 1994).

Green *et al* (1993) suggest that a negative correlation exists between the pavement performance and the concentration of aliphatic sulphides and sulphoxides in the bitumen. Goodrich *et al* (1986) commented "that asphalts with higher sulphur content tend to be less temperature susceptible." No rational was given for this comment although it undoubtedly relates to the effect of sulphur compounds on intermolecular interactions over the service temperature range of the bitumen. It is assumed that Green *et al's* (1993) comments relate to the age hardening and moisture susceptibility of the bitumen, while Goodrich *et al's* (1986) comments relate to the effects of sulphur compounds on the rheological properties of the bitumen. Hence, while the two comments may seem contradictory they may in fact be referring to different aspects of bitumen performance.

Sulphoxides are readily absorbed onto mineral surfaces, which indicates that they improve the adhesion between the aggregate and the bitumen. Unfortunately, Plancher *et al* (1977) observed that sulphoxides were also readily displaced from the aggregate surface by water. This suggests that bitumen with a high sulphoxide content may be susceptible to water stripping. However, it was also noted that the type of aggregate influenced the amount of sulphoxide that was displaced.

5.3.4 2-Quinolones, Pyridine and Nitrogen Structures

The nitrogen containing functional groups found in bitumen are 2-quinolones, pyrrole and pyridines. Being polar these structures are associated with the resin and asphaltene fractions of the bitumen. No evidence has been found to suggest that the nitrogen structures take place in oxidation reactions, but it is still possible that they influence the rate of oxidation. The nitrogen structures present in bitumen can take part in acid-base interactions and presumably have an affect on the rheological properties. Pyridine is basic and can form complexes with metal ions such as vanadium and nickel. Pyrrole is acidic and 2-quinolones are amphoteric.

The functional groups containing nitrogen exhibit a tenacious adsorption to aggregate surfaces and are resistant to the stripping action of water (Plancher *et al*, 1977).

5.3.5 Condensed Aromatic Structures

The majority of the condensed aromatic structures are contained in the asphaltene and resin fractions. Condensed aromatic structures can undergo intermolecular *pi-pi* interactions to form the associated micellar structures typical of asphaltene molecules. In this way they promote structuring and contribute to the viscosity of the bitumen.

Plancher *et al* (1977) also observed that condensed aromatic structures such as 1,2,3,4 – dibenzanthracene showed measurable adsorption onto mineral aggregates. The amount of adsorption was considerably less than that observed with polar molecules such as carboxylic acids, quinolines and sulphoxides. However, considering the fact that polar functional groups are typically found in the same molecules that possess condensed aromatic ring systems, such molecules are expected to contribute significantly to the adhesive properties of the bitumen. "The surfaces of minerals are known to contain OH groups and other electron deficient centres that could co-ordinate with the polarisable *pi* electrons in aromatic ring systems" (Plancher *et al*, 1977).

5.3.6 Metal Ion Content

Ishai *et al* (1988) states that the vanadium content can be related to the age-hardening behaviour of bitumen. A high vanadium content may be associated with a high degree of sensitivity to ageing and low vanadium contents may be associated with bitumen with a low sensitivity to ageing. However, some evidence has also been produced that indicates that the form of the metal in the bitumen may affect its ability to facilitate age hardening. The metal ions in bitumen are present as porphyrin structures, but may also occur as carboxylic acid salts or in colloidal form (Morgan and Mulder, 1995). Metal ions are usually found in the asphaltene fraction of bitumen (Ishai *et al*, 1988).

Goodrich *et al* (1986) state that "the significance of metals in the behaviour of asphalts is not yet well understood or defined." The correlation between the metal content and sensitivity to ageing is generally not good. Metal ions are thought to catalyse the bitumen oxidation reactions. In studies conducted by Branthaver *et al* (1993), the extent of oxidation of bitumen was found to increase when vanadyl acetylacetonate was used as a catalyst.

6.0 Literature Review Summary

Studies conducted in New Zealand, Finland, Canada and USA have shown that TOP can be successfully used to modify bitumen. TOP has a similar density and molecular size distribution to bitumen and the two are completely miscible. By blending hard grades of bitumen with TOP, it is possible to produce TOP modified bitumen having similar physical properties to conventional bitumen. Limited data also indicates that TOP modified bitumen may possibly be slightly more temperature susceptible, but it also has an improved resistance to age hardening. Commercial use of TOP modified bitumen has been limited, but what results are available indicate that TOP has no adverse effect on the performance of bituminous pavements.

One of the major benefits of using TOP as an additive is that it shows a marked improvement in the adhesive properties of the bitumen. However, TOP is known to contain appreciable quantities of carboxylic acids and previous research has shown that carboxylic acids were the cause of stripping in bituminous pavements. The improved adhesion observed when using TOP modified bitumen might be a result of improved wetting of the substrate. An improvement in wetting would bring bitumen molecules into closer contact with the substrate and consequently could improve the strength of the adhesive bond.

Bitumen can be considered to be a dispersion of asphaltene molecules in a solution of aromatic and saturate molecules. The asphaltene molecules can associate and form micellar structures and three dimension networks, which contribute significantly to the rheological properties of the bitumen. Resin molecules in the bitumen orientate themselves at the interface between the asphaltene micelles and the dispersing phase, forming a solvation shell around the micelles. The resins are responsible for maintaining the asphaltenes in suspension and preventing their precipitation.

The unsaturated fatty acids and resins present in TOP are likely to have an impact upon the performance of the bitumen. These acids are highly polar and as such will be involved in intermolecular interactions that may either increase or decrease bitumen viscosity depending upon whether they act as a part of the dispersed phase or the dispersing phase.

TOP is not expected to contain an appreciable quantity of asphaltene type molecules although the presence of some carboxylic acid micelles is likely. Consequently, the addition of significant quantities of TOP may have a diluting effect upon the concentration of asphaltenes in the bitumen. It is important that the asphaltene concentration does not undergo excessive dilution as a low asphaltene content has been implicated in causing rutting and tenderness problems in asphalt concrete.

TOP also contains an appreciable quantity of unsaponifiable neutral compounds that are likely to be partitioned into the saturates or aromatics fraction of the bitumen. Excessive proportions of saturates can cause cracking problems in bituminous pavements because of the phenomenon of steric hardening. Saturates are also flocculents for the asphaltenes and may cause increases in viscosity, especially upon ageing.

Bitumen ages over time by three main mechanisms: volatilisation, oxidative ageing and steric hardening. Volatilisation is not considered very significant since bitumen is produced by the distillation of crude oil under vacuum, which removes any potentially volatile components. Bitumen undergoes oxidative ageing through reaction of aliphatic sulphides and benzylic carbons with atmospheric oxygen to form sulphoxides and ketones. TOP is not known to contain any aliphatic sulphides although it is possible that it does possess some benzylic carbon sites that may be susceptible to oxidation. Although TOP contains conjugated ring systems in the form of β-sitosterol and abietic acid, these are not aromatic and the proportion of aromatic carbon is expected to be low. Consequently, the mechanism of oxidation and the oxidation products formed are likely to be different from that of conventional bitumen. TOP does contain significant quantities of unsaturated carbon bonds that are susceptible to oxidation, but are not normally present in bitumen. In addition, it is not known how the presence of carboxylic acid species in the TOP will affect the rate of oxidation of the bitumen. Neither is it known how the TOP will affect the steric hardening of the bitumen.

TOP contains up to 1% ash, which may or may not affect the properties of the bitumen. The major component of the ash is expected to be sodium sulphate. Since the quantity is low, any effect will probably be minimal. It is possible that the ash could cause some moisture susceptibility problems although previous researchers have found that TOP improved the adhesive properties of the bitumen. Nonetheless, the ash could form the nucleus of acidic micelles or alternatively donate sodium ions to carboxylic acids, allowing them to be readily stripped from the bitumen.

Obviously there are many avenues for further research into the use of TOP modified bitumen. While a first step would be to ascertain commercial viability by ensuring the TOP modified bitumen conforms fully to the requirements of TNZ M/1 (1995), the need also exists for research into the mechanism of oxidative ageing and steric hardening of TOP modified bitumen.

SECTION II:

MATERIALS, RESULTS AND ANALYSIS

7.0 Research Objectives

Previous research conducted in Finland (Peltonen, 1989a, 1989b) and Canada (Mazuch, 1993; Mazuch and Jeffery, 1995) has concluded that the use of TOP in bituminous pavement has no detrimental effect on the performance of the bitumen. Consequently, it is believed that there is sufficient evidence to evaluate the use of TOP in the Safaniya bitumen that is used in New Zealand. However, before TOP can be used to modify bitumen in New Zealand it must meet the national specification for bitumen (TNZ M/1, 1995). Ball *et al* (1993) has already shown that TOP modified bitumen meets the physical requirements of the specification with respect to penetration, viscosity, flash point, solubility in trichloroethylene, ductility and retained penetration and ductility after ageing in the rolling thin film oven test (RTFOT). However, there is a gap in the knowledge pertaining to the chemical requirements of the specification and how the TOP modified bitumen is expected to perform when used in the construction of chipseals or asphalt concrete surfaces.

The primary aim of this research is to determine if TOP can be used as a bitumen modifier in New Zealand. More specifically, research is required to answer the following questions:

1. Is TOP compatible with diluents used during chipsealing such as kerosene and automotive gas oil?
2. Does TOP modified bitumen possess adequate resistance to oxidative ageing?
3. How does TOP affect the chemical composition and characteristics of the bitumen and what is the likely effect of TOP on the long-term performance of bitumen?
4. Is TOP compatible with the adhesion agents used in chipsealing?

Answers to these four questions will allow an informed decision to be made about the suitability of the use of TOP as a bitumen modifier in chipseal and asphalt concrete. TOP modified bitumen must be compatible with diluents such as kerosene, AGO and adhesion agents that are routinely added to the bitumen during chipsealing operations. It is necessary to assess the ageing behaviour of the bitumen to ensure that TOP does not have an adverse effect on the durability and service life of the bituminous surface. It is also understood that the physical properties of the bitumen are partially derived from how the chemical constituents interact with each other. Consequently, the chemical properties of the TOP modified bitumen will need to be determined so that predictions regarding the physical performance can be made.

Before the new research is undertaken, it is proposed to validate the findings of other researchers using the materials available in New Zealand. The fact that the use of TOP in pavements in other parts of the world has been successful does not automatically mean that it will be successful in New Zealand. The composition of the bitumen, TOP and aggregates used in New Zealand are highly likely to differ from those used in, say, Finland and Canada.

8.0 Materials and Methodology

8.1 Experimental Procedure

Tall oil pitch was blended in various proportions with hard grades of bitumen to produce softer grades, which conformed to the TNZ M/1 (1995) specification for 80/100 and 180/200 bitumen. Table 9 gives the proportions of TOP added to the harder grades of bitumen and the resulting classification of the blend produced.

Table 9: Formulations of TOP modified bitumen used during the investigation.

Bitumen Designation	Original Bitumen Grade	Bitumen Proportion (%)	TOP Proportion (%)	TOP Modified Bitumen Grade
B200-T0	180/200	100	0	180/200
B150-T6	130/150	94	6	180/200
B100-T0	80/100	100	0	80/100
B100-T15	80/100	85	15	180/200
B50-T0	40/50	100	0	40/50
B50-T12	40/50	88	12	80/100
B50-T25	40/50	75	25	180/200

The test methods used to characterise and analyse the bitumens are given in Section 8.3. All the bitumens in Table 9, except for B50-T0, were aged in a 60°C oven for 4 months. A sample of TOP was aged to provide a comparison. The effect that ageing had on the bitumen was determined by comparing the rheological and colloidal properties of the bitumen before and after ageing. A bitumen durability test was also used to investigate the resistance of the TOP modified bitumen to ageing.

The rheological properties of each of the unaged and aged bitumens were measured for penetration, softening point and penetration index. Kinematic viscosity and dynamic viscosity measurements of the unaged bitumens were taken to ensure that the TOP modified bitumen conformed to the requirements of its appropriate grade. The compatibility between the TOP modified bitumen and kerosene and automotive gas oil (AGO) was investigated using a storage stability test.

The Heithaus parameters, acid number and Corbett fractions were measured to assess the chemical properties of the TOP modified bitumen. Confocal laser-scanning microscopy

(CLSM) and gel-permeation chromatography (GPC) were used to investigate the bitumen's colloidal properties.

The compatibility of TOP modified bitumen with adhesion agents used in chipsealing was determined using the Vialit test. Further investigations into the adhesive nature of TOP modified bitumen included measuring the moisture susceptibility of asphalt concrete manufactured using TOP modified bitumen. Measurements of the interfacial tension of bitumen in the presence of air and distilled water were also used to explore the adhesive properties of TOP modified bitumen.

8.2 Materials

All the bitumen was supplied by Belspray Bulk Bitumen Co., Ltd of Napier. The bitumen was originally manufactured by New Zealand Refining Co., Ltd from Safaniya crude oil. Two grades of bitumen were obtained: 40/50 and 180/200, from which intermediate grades of 80/100 and 130/150 were produced by blending in the appropriate proportions. Kerosene and AGO were supplied by Shell Oil (NZ) Ltd.

Tall oil pitch was manufactured and supplied by Eka Chemicals (NZ) Ltd. The manufacturer reported that the acid number of the TOP was 41.7 mg KOH/g and the rosin content was 14.9%. The adhesion agent used for adhesion testing was Diamine OLB. Diamine OLB is a commercial adhesion agent that is manufactured by Akzo Nobel Ltd and can be described as a blend of oleyl 1,3-diaminopropane and diethylene glycol.

The aggregate used for Vialit testing was obtained from Higgins Aggregates Ltd, Te Matai Road Quarry, Palmerston North. It is an alluvial graywacke won from the Manawatu River bed. Aggregate used to assess the moisture susceptibility of hot mix asphalt was obtained from three regions: Auckland, Hawkes Bay and Manawatu. The Auckland aggregate was obtained from Brookby Quarries and can be described as a basaltic type of material that was quarried from a rock face. The Hawkes Bay aggregate is an alluvial graywacke won from the Ngaruroro River and was supplied by Fraser Shingle Ltd. The Manawatu aggregate was supplied by Te Matai Road Quarry.

Toluene, methanol and iso-propanol, with a minimum purity of 99.5, 99.8 and 99.7% respectively, were supplied by BDH Laboratory Supplies. ChromAR HPLC grade n-heptane was supplied by Mallinckrodt Baker Inc. Tetrabutylammonium hydroxide (TBAH) was supplied as a 1.0M solution in methanol by Aldrich Chemical Co., Inc. Methylene chloride was supplied by INEOS Chlor Ltd and was used as received. All solvents and reagents were used as received.

Chromatographic grade, activated aluminium oxide was obtained from Aldrich Chemical Co., Inc. The aluminium oxide was acidic, Brockmann I, standard grade and had a porosity of 58Å, an average mesh size of ~150 µm and a surface area of 155 m^2/g. The aluminium oxide was calcined at 413°C for a minimum of 16 hours before being stored in an airtight container until used.

8.3 Test Methods

8.3.1 Physical Properties

8.3.1.1 Penetration

The penetration test was conducted using the method described by ASTM D5 (1996). A 100g needle of specified dimensions was allowed to penetrate into a sample of bitumen under the influence of gravity at 25°C for a period of 5.0 seconds. The depth to which the needle penetrated was measured in deci-millimetres (dmm). The penetration was recorded as the average of three measurements.

8.3.1.2 Softening Point

The softening point of the bitumen was determined using the ring and ball method described by ASTM D36 (1996). A small stainless steel ball is placed on top of a small disc of bitumen, which is suspended in a beaker of water. The water is heated at a rate of 5.0 ± 0.5°C per minute. The temperature at which the bitumen softens sufficiently for the stainless steel ball to fall a set distance through the disc of bitumen is defined as the softening point.

8.3.1.3 Penetration Index

The penetration index of the bitumen was calculated using the formula given by Morgan and Mulder (1995) and is reproduced in Equation 8-1.

Equation 8-1:

$$\text{Penetration Index} = \frac{1952 - 500.\log(P_{25}) - 20.(SP)}{50.\log(P_{25}) - SP - 120}$$

Where P_{25} = penetration value at 25°C (see Section 8.3.1.1)
SP = ring and ball softening point (see Section 8.3.1.2)

8.3.1.4 Kinematic Viscosity

The kinematic viscosity of the bitumen was measured using the method described by AS2341.3 (1993). Bitumen was allowed to flow through Cannon-Fenske capillary viscometer tubes and the time taken to flow between two points on the tube was used to calculate the viscosity. Testing was conducted at either 60°C or 70°C depending upon the estimated viscosity of the bitumen.

8.3.1.5 Dynamic Viscosity

A Brookfield RVT Syncro-Lectric dial viscometer coupled to a Brookfield Thermosel was used to measure the dynamic viscosity of the bitumen. Temperature was controlled to within ± 2°C using a Brookfield Model 75 temperature controller. The dynamic viscosity was recorded at a shear rate of 18.6 s^{-1} (20rpm) using an SC4-21 spindle.

8.3.1.6 Storage Stability Procedure

The compatibility between the bitumen and TOP, and the compatibility between the TOP modified bitumen and kerosene and AGO was determined using a storage stability test. Blends of bitumen and TOP were heated to 140°C before the kerosene or AGO were added at levels of 0, 5 and 10% v/v. The blends of bitumen, TOP and diluent were mixed using an overhead stirrer for at least 5 minutes before being placed in 350 ml aluminium beverage cans. The cans were covered with tin foil and were stored undisturbed in an oven for 7 days at 160°C. After 7 days the cans were removed from the oven and were allowed to cool to room temperature before being cut in half. The top and bottom halves of the bitumen were tested using the kinematic viscosity test described in Section 8.3.1.4. The percentage difference in viscosity between the two halves is the storage stability.

8.3.2 Chemical Properties and Ageing Resistance

8.3.2.1 Accelerated Ageing Procedure

Bitumen was artificially aged in air in a forced draft convection oven at 60 ± 2°C. The bitumen was spread onto stainless steel plates to give a nominal film thickness of 1 mm and stored in the oven for 3024 ± 8 hours.

8.3.2.2 Bitumen Durability Test

The resistance of the TOP modified bitumen to oxidative ageing was assessed using the bitumen durability test as described by Herrington (2000b). Essentially, bitumen was aged as 1mm thick films at 60°C in a pressure oxidation vessel charged with 2069 ± 35 kPa oxygen for up to 1500 hours. The change in modulus at a temperature of 5°C and a shear rate of 9 Hz was used as a measure of the rate of oxidation.

8.3.2.3 Heithaus Procedure

The Heithaus procedure was used to determine the internal compatibility of the bitumen using a method based on that described by Petersen *et al* (1994b), with the exception that the flasks were left to stand overnight after the toluene had been added. Heptane was added to each of four flasks containing 1 gram of bitumen and 1, 2, 4, and 6 mls of toluene respectively until flocculation of the asphaltenes occurred. The minimum volume of heptane required to promote flocculation was used to calculate three parameters, the peptisability of the bitumen (P), the peptisability of the asphaltenes (P_a) and the solvent power of the maltenes (P_o).

Equation 8-2: $FR = V_T / (V_T + V_H)$

Equation 8-3: $X = (V_T + V_H) / W_A$

Where V_T = Volume of toluene in flask (mls)

V_H = volume of heptane required for flocculation (mls)

W_A = weight of bitumen in flask.

Titration of the four flasks yielded four values of FR and X from which a plot of FR versus 1/X was prepared. The plot gave a straight line, which is extrapolated to both axes. The intercept with the y-axis gave the parameter FR_{max} and the intercept with the x-axis gave the parameter $1/X_{min}$ from which the Heithaus parameters were calculated using Equation 8-4 to Equation 8-6.

Equation 8-4: $P_a = 1 - FR_{max}$

Equation 8-5: $P_o = FR_{max}\,(X_{min} + 1)$

Equation 8-6: $P = P_o / (1 - P_a) = X_{min} + 1$

8.3.2.4 Acid Number

A non-aqueous potentiometric titration procedure based on those described by Petersen *et al* (1994b) and ASTM D664 (2001) was used to determine the acid number of the bitumen. The titration solvent was a solution of 1% pyridine in methylene chloride and the titrant was a 0.1M solution of tetrabutylammonium hydroxide (TBAH). The 0.1M TBAH solution was prepared by mixing 10mls of 1.0M TBAH in methanol, with 4mls of 2-propanol in a 100ml volumetric flask and diluting to the mark with toluene. An Orion 210A pH meter and Hanna HI1053B pH probe coupled to a Mettler Toledo ATC probe were used to measure changes in pH.

The end-point of the titration was chosen as the point of inflexion on a plot of titre versus pH, or in the case were no inflexion point was apparent, the end-point was chosen as the titre required to achieve a pH of 13.0. All of the titrations that displayed a point of inflexion, and the acids used to standardise the TBAH solution, possessed a point of inflexion that approximately corresponded to a pH of 13.0. Although the acid value was determined by titration with TBAH, all acid values were reported as a mg KOH/g equivalent.

8.3.2.5 Corbett Fractionation

Bitumen was fractionated into four components using the procedure described by ASTM D4124 (1996), with the exception that methylene chloride was used in place of trichloroethylene. The four fractions obtained are described as asphaltenes, resins, aromatics and saturates. Asphaltenes were separated from the bitumen by precipitation from n-heptane. The n-heptane soluble fractions were adsorbed onto an alumina column before being eluted with n-heptane to remove the saturate fraction. The aromatic fraction was recovered by elution with toluene. Some difficulty was encountered removing all the resins from the alumina column as explained in Section 10.5. Consequently, the resin fraction was recovered by elution with a 50:50 mixture of toluene and methanol, followed by methylene chloride and a mixture of 5% acetic acid in methylene chloride. The proportion of resins was calculated as being the difference between the whole bitumen and the sum of the asphaltene, aromatic and saturate fractions.

8.3.3 Colloidal Properties

8.3.3.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed using a 7.8mm x 300mm Ultrastyragel® 10^3 Å column manufactured by Millipore Corporation, USA. The particle size of the column packing was 7μm. The GPC column was coupled to a Jasco PU-980 HPLC pump and a Jasco UV-975 UV/vis detector. The operating conditions used for the GPC analysis are as follows:

Column Type: Ultrastyragel® 1000 Å, 7μm particle size.
Solvent: Toluene
Bitumen Concentration: 2%
Flow Rate: 2.0 ml/min
Temperature: Ambient
Pressure: 30 psi
Detection: UV absorbance at 400nm wavelength.

8.3.3.2 Confocal Laser Scanning Microscopy

A Leica DMRBE Microscope and Leica TCS4D Scanning Head were used to obtain confocal laser scanning microscopy (CLSM) images of the bitumen. The bitumen was irradiated with 488nm wavelength light and a BP-FTIC filter was used to observe the fluorescence in the 515 – 545nm wavelength range. All images were captured in 512 x 512 TIFF format. The magnification level was 1000 times.

Microscope slides were prepared by heating the bitumen to a fluid state and placing a small drop in a small concave well in the slide. A cover slip was placed over the drop of bitumen before the slide was placed in a 105°C oven until the bitumen was fluid enough to allow the cover slip to be pressed flat against the slide. The bitumen underwent no pre-treatment and was observed as neat samples at ambient temperature.

8.3.4 Adhesive Properties

8.3.4.1 Vialit Test

The Vialit test was used to measure the adhesion between a damp aggregate and bitumen in the presence of an adhesion agent. The method used is described by TNZ B301-89T (1989). Adhesion agent was added to the bitumen, which was spread onto stainless steel plates (200mm x 200mm) at a rate of 1.0 L/m^2. The bitumen films were soaked in distilled water before 100 clean, but damp, grade 3 aggregate chips were placed on the bitumen film in a 10 x 10 matrix. The chips were rolled into the bitumen using a roller of defined weight before being placed in distilled water at 25°C for 2 ½ hours. After 2 ½ hours the plates of bitumen were inverted and struck three times on the back with a 500g stainless steel ball, which was dropped from a set height. The retained aggregate chips were counted and used as a measure of the adhesion between the bitumen and aggregate.

8.3.4.2 Moisture Sensitivity

The moisture sensitivity of the asphalt concrete specimens was measured using the procedure described by ASTM D4867 (1996). The asphalt concrete specimens were compacted using the procedure outlined in Section 8.3.4.3 before being conditioned in a water bath at 60°C for 24 hours. After this time the tensile strength was measured and compared to that of a control set of specimens. Asphalt mixtures that retained less than 75% of their tensile strength after moisture conditioning were considered to be susceptible to moisture damage during service.

8.3.4.3 Asphalt Concrete Compaction Procedure

The asphalt concrete used for moisture sensitivity measurements (see Section 8.3.4.2) was mixed at 150 – 155°C and compacted at 140 – 145°C. Compaction was achieved using a Servopac gyratory compactor manufactured by Industrial Process Controls Ltd of Melbourne, Australia. The asphalt concrete specimens were compacted to a height of 65 ± 0.1 mm in a 100 mm diameter mould so that each specimen had similar dimensions. The Servopac was operated with a 2.0° angle of gyration, an air pressure of 240 kPa and a gyration rate of 60 gyrations per minute.

8.3.4.4 Air Voids

The air voids in the asphalt concrete used for moisture sensitivity testing (see Section 8.3.4.2) were measured using the procedure described by ASTM D3203 (1996). Equation 8-7 was used to calculate the percentage air voids in the asphalt concrete. This method requires the maximum theoretical density (MTD) and bulk specific gravity (BSG) to be measured using the procedures described by ASTM D2041 (1996) and ASTM D2726 (1996) respectively.

Equation 8-7: $$\text{Air Voids} = 100\,(1 - (\text{BSG} / \text{MTD}))$$

8.3.4.5 Interfacial Tension

The interfacial tension of the TOP modified bitumens were determined using a similar method to that used by Vargha-Butler *et al* (1988). Bitumen films were prepared by heating the bitumen until fluid before spreading it on a microscope slide. The slides were placed in a 105°C oven for ½ hour to allow the bitumen films to find their own level and create a visibly smooth surface. The films were cooled to room temperature before a drop of distilled water was placed on the film. Each drop had a volume of 0.03 – 0.06 mls. The contact angle of the drop on the bitumen was measured by photographing the drop with a digital camera and measuring the angle on the resulting photograph. Each measurement was repeated 10 – 24 times to obtain a statistically representative sample.

An equation of state relationship (Neumann *et al*, 1974) was used to calculate the interfacial tension between the bitumen and air from the contact angle measurements. The interfacial tension between bitumen and distilled water was then calculated using Young's equation.

In a separate experiment, microscope slides were cleaned by rinsing in methylene chloride and drying in an oven at 105°C for ½ hour. They were then boiled in distilled water for 20 minutes followed by drying in an oven at 105°C for another ½ hour. Bitumen was heated until fluid before drops of bitumen were placed on the microscope slides. The slides were left in a 60°C oven to allow the bitumen to spread on the slide until the contact angle between the bitumen and slide was less than 90°. Each slide was immersed in distilled water and left for 24 hours in the oven at 60°C. The contact angle between the bitumen, slide and water was photographed and measured.

9.0 Physical Properties

9.1 The Effect of TOP on Rheological Properties

Peltonen (1989), Ball *et al* (1993), Mazuch (1993) and Johnson and Juristovski (1995) previously published results of experimentation with blends of TOP and bitumen. These results show that the addition of TOP has a softening effect on the bitumen as indicated by an increase in the penetration value and a decrease in the softening point and viscosity of the blends. The results given in Table 10, Table 11, Figure 13 and Figure 14 verify that TOP does soften the Safaniya bitumen used in New Zealand.

9.1.1 Penetration

Ball *et al* (1993) gives some indication as to the amount of TOP to add to 40/50 and 80/100 Safaniya bitumen to produce the softer, 80/100 and 180/200 grades respectively. The proportions used by Ball *et al* (1993) were used as starting formulations. However, it was soon discovered that Ball *et al's* (1993) formulations produced a softer bitumen than was anticipated. This can be seen in Table 10 for the 40/50 bitumen modified with 15% and 30% TOP which produces a bitumen with a penetration of 106 dmm and 245 dmm respectively. It was anticipated that the respective penetrations would fall in the range of 80 – 100 and 180 – 200 dmm. This indicates that since Ball *et al* (1993) undertook their research the composition of either the TOP or the bitumen, or both has changed significantly. This is not unlikely since both TOP and bitumen are refined natural products and the composition and production methods are subject to change.

Table 10: Physical properties of 40/50 bitumen modified with TOP.

Sample ID	**B50-T0**	**B50-T12**	**B50-T15**	**B50-T25**	**B50-T30**
Formulation					
Bitumen 40/50 (%)	100	88	85	75	70
Bitumen 180/200 (%)	0	0	0	0	0
TOP (%)	0	12	15	25	30
Properties					
Penetration (dmm)	45	89	106	190	245
Softening Point (°C)	55.7	47.2	45.6	39.7	37.3
Penetration Index	-0.12	-0.48	-0.43	-0.41	-0.30
Kinematic Viscosity (70°C, mm^2/s)	-	62600	-	21100	-
Dynamic Viscosity (120°C, mPa.s)	2113	975	825	513	438
Dynamic Viscosity (135°C, mPa.s)	813	438	375	250	225
Dynamic Viscosity (150°C, mPa.s)	388	225	200	150	113
Dynamic Viscosity (165°C, mPa.s)	205	125	115	80	70
Dynamic Viscosity (180°C, mPa.s)	120	80	70	50	45

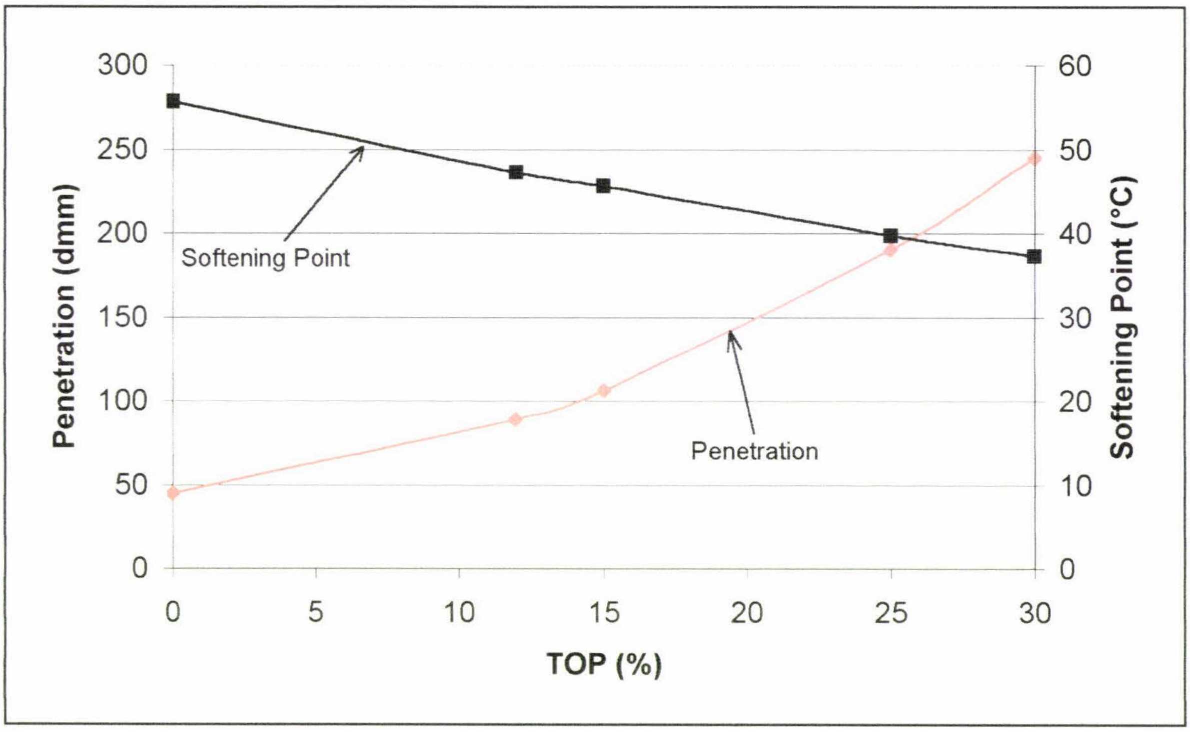


Figure 13: Effect of TOP on penetration and softening point of 40/50 bitumen.

The intention of the current research was to produce a TOP modified bitumen that conformed to the requirements of TNZ M/1 (1995). Therefore, TOP was added to bitumen in various proportions to produce a blended bitumen that met the specification for 80/100 or 180/200 bitumen. The required physical properties of the bitumen from TNZ M/1 (1995) have been reproduced in Table 12. Previous research undertaken by Ball *et al* (1993) has shown that the TOP modified bitumen already meets the specification for flash point, solubility in trichloroethylene and retained penetration and ductility after ageing in the rolling thin film oven. Therefore the penetration and viscosity tests were used to determine the appropriate proportion of TOP to add to the bitumen to ensure that the blend met the rheological requirements of the specification.

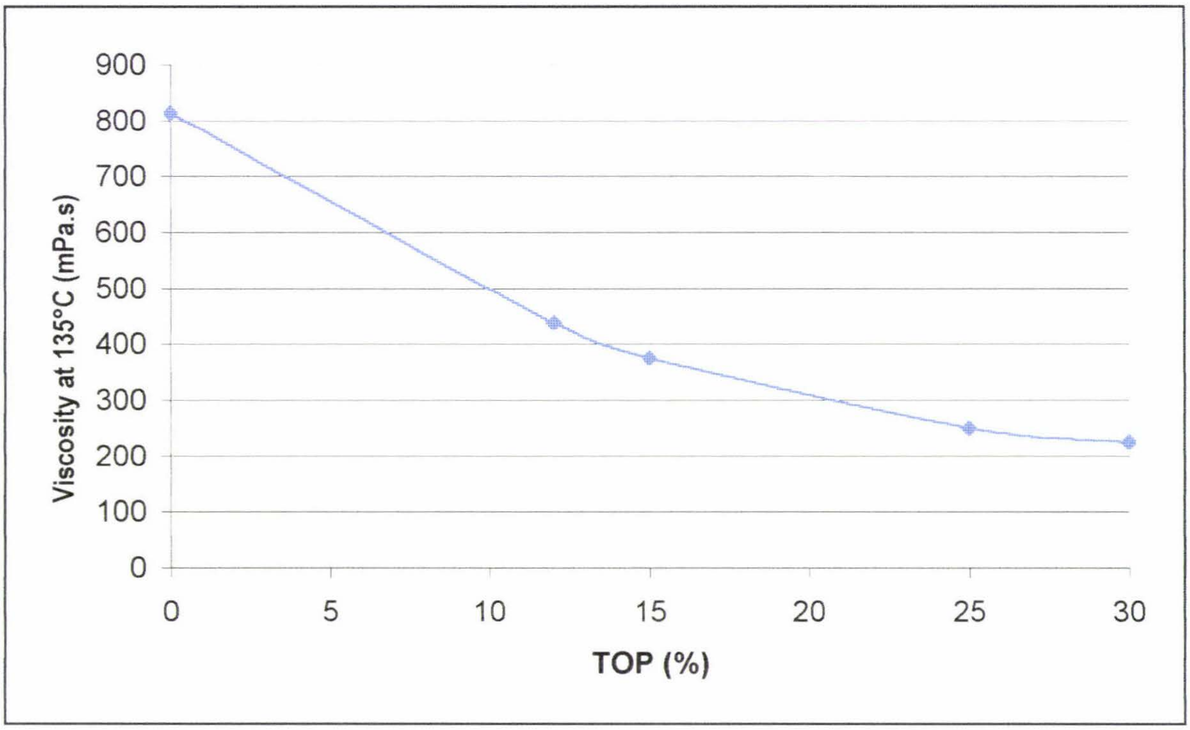


Figure 14: Effect of TOP on viscosity of 40/50 bitumen.

Table 11: Physical properties of 80/100 and 130/150 bitumen modified with TOP.

Sample ID	**B100-T0**	**B100-T15**	**B150-T0**	**B150-T6**	**B200-T0**
Formulation					
Bitumen 40/50 (%)	50	42.5	20	75.5	0
Bitumen 180/200 (%)	50	42.5	80	18.5	100
TOP (%)	0	15	0	6	0
Properties					
Penetration (dmm)	90	193	141	185	189
Softening Point (°C)	47.0	39.5	42.6	39.1	39.5
Penetration Index	-0.50	-0.43	-0.46	-0.80	-0.52
Kinematic Viscosity (70°C, mm^2/s)	58900	19800	-	19100	17600
Dynamic Viscosity (120°C, mPa.s)	850	488	563	475	463
Dynamic Viscosity (135°C, mPa.s)	388	238	263	283	225
Dynamic Viscosity (150°C, mPa.s)	200	138	150	125	125
Dynamic Viscosity (165°C, mPa.s)	115	75	85	75	75
Dynamic Viscosity (180°C, mPa.s)	70	50	55	45	50

By comparing the data contained in Table 10, Table 11 and Table 12 it can be seen that 80/100 grade bitumen can be produced by adding 12% TOP to 40/50 bitumen. Similarly, 180/200 bitumen can be produced by blending 25% TOP with 40/50 bitumen, 15% TOP with 80/100 bitumen, or 6% TOP with 130/150 bitumen.

Table 12: Physical properties of bitumen specified in TNZ M/1 (1995).

Property	Test Method	Grade			
		60/70	**80/100**	**130/150**	**180/200**
Penetration (25°C, 100g, 5sec, dmm)	ASTM D5	60 – 70	80 – 100	130 – 150	180 – 200
Viscosity (mm²/s) (a) 70°C	AS 2341.3 ASTM D2170	60,000 min 210,000 max	40,000 min 140,000 max	21,000 min 73,500 max	14,000 min 49,000 max
Viscosity (mm²/s) (b) 135°C		450 min 850 max	300 min 650 max	190 min 450 max	140 min 350 max
Flash Point (Cleveland Open Cup, °C)	ASTM D92	218 min	218 min	218 min	218 min
Solubility in Trichloroethylene (%)	ASTM D2042	99.5 min	99.5 min	99.5 min	99.5 min
Rolling Thin Film Oven Test (3.2mm)	M/1 (1995) Section 1.1				
Penetration after test (25°C, 100g, 5sec), % of original	ASTM D5	50 min	50 min	50 min	50 min
Ductility of Residue at 25°C (m)	ASTM D113	0.60 min	0.60 min	0.60 min	0.60 min

9.1.2 Viscosity

An estimate of the error in determining the kinematic viscosity was obtained by conducting 7 replicate determinations of the kinematic viscosity of a sample of bitumen B200-T0. The replicates had a mean and standard deviation of 17643 and 506 mm²/s respectively. From this data the error limits at the 95% significance level were calculated to be ± 468 mm²/s (or ± 2.65%) and the coefficient of variation was 2.9%. This is comparable with the coefficient of variation reported for the test method in ASTM D2170 (1996), which is 3.2%.

If the kinematic viscosity data in Table 10 and Table 11 is compared, it can be seen that the TOP modified bitumens tend to have a slightly higher viscosity relative to that of the unmodified bitumens. Ball *et al* (1993) had also noted this phenomena and suggests that this "may be due as much to the temperature dependence of the viscosity of the bitumen components in the mixture (these bitumens, unlike 180/200, contain air-blown material) as to that of the TOP."

9.1.3 Penetration Index

The penetration index was developed as a means of expressing the temperature susceptibility of a bitumen (Morgan and Mulder, 1995). Penetration index values typically range from –3 for highly susceptible bitumens to +7 for highly blown bitumens with low temperature susceptibility. Roading bitumen tends to have a value near zero.

Table 13 and Figure 15 show the penetration index together with the estimated upper and lower error limits. The error limits were calculated using the error values contained in the precision statement of the penetration (ASTM D5, 1996) and softening point tests (ASTM D36, 1996). The error in the penetration was taken as being 1 dmm for values less than 50 dmm and 3 dmm for values between 50 and 249 dmm and the error in the softening point was taken as being 1.2°C. Using these errors, the maximum and minimum penetration and softening point values were calculated and used to estimate the upper and lower error limits for the penetration index.

Table 13: Calculated penetration index values and their associated error limits.

Bitumen	Grade	Lower Error Limit	Calculated Penetration Index	Upper Error Limit
B50-T0	40/50	-0.34	-0.12	+0.08
B50-T12	80/100	-0.74	-0.48	-0.23
B50-T15	-	-0.72	-0.43	-0.14
B50-T25	180/200	-0.89	-0.41	+0.04
B50-T30	-	-0.90	-0.30	+0.25
B70-T0	60/70	-0.48	-0.30	-0.13
B100-T0	80/100	-0.77	-0.50	-0.26
B100-T15	180/200	-0.91	-0.43	+0.03
B150-T0	130/150	-0.84	-0.46	-0.11
B150-T6	180/200	-1.29	-0.80	-0.34
B200-T0	180/200	-1.00	-0.52	-0.07

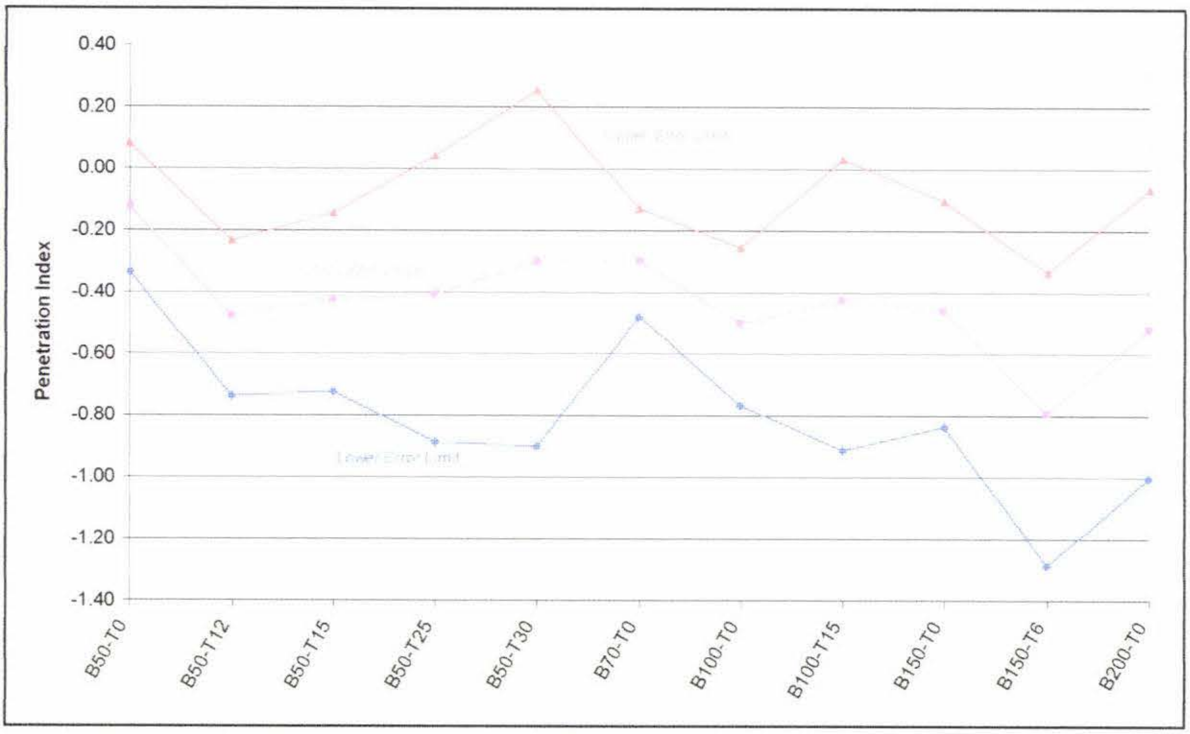


Figure 15: Penetration index of TOP modified bitumen.

No evidence has been found to suggest that TOP affects the temperature susceptibility of the bitumen. Any difference in penetration index can be considered insignificant within the bounds of the errors reported here. This is in contrast to results reported by Peltonen (1989b), Mazuch (1993) and Johnson and Juristovski (1995) who found that the addition of TOP caused the bitumen to become more temperature susceptible. On the other hand, research conducted by Ball (1992) found that the temperature susceptibility of TOP modified bitumen was similar to conventional, unmodified bitumen used in New Zealand. Obviously, the effect of TOP on the bitumen is influenced by the source of the raw materials.

Therefore, it has been shown that the blends B50-T12, B50-T25, B100-T15, and B150-T6 conform to the requirements of TNZ M/1 (1995) with respect to rheological properties.

9.2 The Effect of TOP on Storage Stability

TNZ M/1 (1995) also states that the TOP modified bitumen must exhibit, amongst other things, "compatibility with kerosene and automotive gas oil (AGO) in proportions used in hot sealing work" (TNZ M/1, 1995).

Several researchers have noted that TOP is miscible and compatible with neat bitumen and have demonstrated this by means of a hot storage stability test. The test simply measures changes in a property between the top and bottom portions of a sample of the bitumen that has been stored for a specified duration at a specified temperature. For example, Ball *et al* (1993) found no difference between the ratio of the IR absorption at 1697 and 1376 cm^{-1} of the top and bottom portions of a blend of 85% 80/100 bitumen and 15% TOP that had been stored for 72 hours at 135°C. Similarly, Johnson and Juristovski (1995) found no significant difference in the viscosity, penetration or softening point of the top and bottom portions of a mixture of 100 parts AC-5 and 40 parts TOP that had been stored for 2 months. Peltonen (1989b) mentions that blends of TOP and bitumen "remained homogenous for over 20 days."

However, no research was found that measured the miscibility and compatibility of blends of TOP, bitumen and kerosene or AGO at levels commonly used in chip sealing work in New Zealand. Therefore, kerosene and AGO were blended with TOP modified bitumen and stored for 7 days at 160°C. The compatibility between the TOP, diluent and bitumen was assessed by comparing the viscosity of the top and bottom portions of the sample. The results of the storage stability tests are given in Table 14.

The bitumen sample B200-T0 is known to be stable under hot storage conditions, both as a neat bitumen and also in the presence of diluents such as kerosene and AGO, since it has been used extensively without any instability being observed. It was included in the storage stability investigation so that it could be used as a control sample.

An estimate of the likely systematic error in the testing procedure was obtained using the percentage difference between the top and bottom portion of the four B200-T0 control samples. In theory, if the control samples were storage stable, they would have zero mean percentage difference. In fact the average mean percentage difference in the viscosity between the top and bottom portions was 1.1% with a standard deviation of 5.3%. Consequently it can be concluded that the mean percentage difference in the control samples is 1.1 ± 8.4% at the 95% significance level. Since these error limits envelop zero, it is reasonable to assume that the B200-T0 control samples are stable under hot storage conditions.

Table 14: Compatibility of TOP modified bitumen with kerosene and AGO.

Bitumen	Test Temperature	Viscosity (mm^2/s)			% Difference
		Bottom	Top	Difference	
		No Diluent			
B200-T0	70°C	20209	20484	275	1.4
B50-T12	70°C	69461	73446	3985	5.6
B50-T25	70°C	29205	30183	978	3.3
		5% Kerosene			
B200-T0	60°C	23361	23109	-252	-1.1
B50-T12	60°C	71428	80312	8884	11.7
B50-T25	60°C	23612	24619	1007	4.2
		10% Kerosene			
B200-T0	60°C	10136	11006	870	8.2
B50-T12	60°C	16406	17853	1447	8.5
B50-T25	60°C	8204	7890	-314	-3.9
		5% Automotive Gas Oil			
B200-T0	60°C	30240	29022	-1218	-4.1
B50-T12	60°C	117012	118425	1413	1.2
B50-T25	60°C	22021	22800	779	3.5

Using the same rational, it is reasonable to assume that any of the bitumens tested are storage stable if the percentage difference in viscosity between the top and bottom portions of the sample lie in the bounds of 1.1 ± 8.4% (i.e. –7.3% to +9.5%). Based on this criterion, the only bitumen that displayed evidence of instability was the B50-T12 sample that contained 5% kerosene.

However, an accurate analysis of the results is complicated by the fact that the storage stability test yielded some unexpected observations. Equations have been developed (TNZ T/9, 1998) that can be used to predict the proportion of kerosene and AGO in a bitumen from the kinematic viscosity at 60°C. Using these equations, which are described by Equation 9-1 and Equation 9-2, the proportion of diluent remaining in the TOP modified bitumen can be estimated to an accuracy of ± 2% (TNZ T/9, 1998). The estimated proportions of kerosene and AGO remaining in the bitumen after hot storage are given in Table 15.

Equation 9-1: Equation for estimating the kerosene content of 180/200 bitumen.

$$K = \frac{1}{\log \log V + 0.4250} \cdot (67.44 - 100 \cdot \log \log V)$$

Equation 9-2: Equation for estimating the kerosene content of 80/100 bitumen.

$$K = \frac{1}{\log \log V + 0.4144} \cdot (72.29 - 100 \cdot \log \log V)$$

Where K = Estimated kerosene content (pph v/v)

V = Kinematic viscosity at 60°C (mm^s/s)

Table 15: Estimated proportion of diluent remaining in bitumen after storage testing.

Bitumen	**Grade**	**Diluent Added**	**Estimated Diluent Remaining After Storage (%)**	
			Bottom Portion	**Top Portion**
B200-T0	180/200	5% Kerosene	3.2	3.2
B50-T12	80/100	5% Kerosene	3.3	2.9
B50-T25	180/200	5% Kerosene	3.2	3.0
B200-T0	180/200	10% Kerosene	7.0	6.6
B50-T12	80/100	10% Kerosene	9.4	9.0
B50-T25	180/200	10% Kerosene	8.0	8.2
B200-T0	180/200	5% AGO	2.7	2.9
B50-T12	80/100	5% AGO	2.0	2.0
B50-T25	180/200	5% AGO	4.4	4.2

Upon first glance at the results in Table 15 it is apparent that the diluent may have partially evaporated during storage at 160°C. It is probable that the storage vessels were not airtight although attempts were made to seal them. Consequently, it is also possible that some oxidation may have occurred during storage Oxidation would increase the viscosity and as a result, the estimated diluent content would be lower.

Given this oversight in the test procedure it is not prudent to draw any conclusions regarding the significance of the storage stability results. However, the preliminary results indicate that the TOP modified bitumen is compatible with kerosene and AGO in the proportions commonly used during chipsealing operations in New Zealand. If greater confidence in these results were required it would be necessary to repeat the storage stability test using airtight storage vessels.

10.0 Chemical Properties and Ageing Resistance

10.1 The Ageing Index

The ageing resistance of bitumen has historically been estimated by measuring a physical property of the bitumen, such as penetration, viscosity or modulus, before and after it has been subjected to an ageing procedure. The change in the measured parameter, or more commonly the ratio of the parameter measured before ageing to that measured after ageing, is used as an indicator of the ageing resistance of the bitumen.

As described in Section 4.5.5 a variety of methods and procedures have been used to artificially age bitumen in the laboratory. Of all the methods, those that simulate actual conditions on the road are preferred because the mechanism of ageing is likely to be similar to that which occurs in practise. Consequently, the reaction products and corresponding physical properties of the bitumen will be similar. For this reason, it was decided to age the TOP modified bitumen as a 1 mm thick film in a forced draft convection oven at 60°C for ~ 4 months. Herrington *et al* (1994) suggests that the composition of the aged bitumen varies depending upon the oxidation temperature. Therefore, 60°C was chosen as the lowest practical oxidation temperature, to achieve a similar ageing effect to what is observed in the field.

The equivalent *in-situ* age of the laboratory aged specimens was estimated by plotting the penetration and softening point data for the aged B200-T0 and B100-T0 bitumen on the bitumen rheological properties chart given found in Ball (1992). Using this chart, it is possible to make a rough estimate of the aged binder viscosity at 45°C. The viscosity of the aged B200-T0 and B100-T0 bitumens at 45°C were estimated to be 9,000 and 30,000 Pa.s respectively. Using the plots of bitumen viscosity and age found in Ball (1999), it is possible to estimate that the aged bitumens have a viscosity corresponding to that of a 4 – 5 year old chipseal.

In chemistry, there is a general approximation that the rate of a chemical reaction doubles for every 10°C increase in temperature. Data provided by Herrington (2000b) suggests that a typical average pavement temperature that occurs in New Zealand is in the region of

20°C. Knowing that the bitumen was aged at 60°C indicates that the bitumen was aged 16 times faster than would have occurred in the field. Consequently, it is estimated that ageing for 4 months gives an equivalent age of 5.3 years.

Four TOP modified bitumens, two unmodified bitumens and a sample of TOP were aged as described. The ageing index of the bitumen was estimated by calculating the ratio of the penetration of the binders before and after ageing. The results are given in Table 16. Due to the softer nature of TOP compared to bitumen, it was necessary to measure the kinematic viscosity of the TOP at 60°C instead of the penetration at 25°C. The ageing index for TOP was calculated by taking the ratio of the viscosity before and after ageing. The softening point and penetration index of each of the aged binders was also measured.

Table 16: Ageing index of TOP modified bitumen.

Bitumen	**Penetration (dmm)**		**Ageing Index**	**Softening Point (°C)**		**Penetration Index**	
	Before Ageing	**After Ageing**		**Before Ageing**	**After Ageing**	**Before Ageing**	**After Ageing**
B100-T0	90	27	**3.3**	47.0	62.9	-0.50	+0.19
B200-T0	189	53	**3.6**	39.5	53.2	-0.52	-0.30
B50-T12	89	21	**4.2**	47.2	65.8	-0.48	+0.21
B50-T25	190	30	**6.3**	39.7	58.4	-0.41	-0.43
B100-T15	193	37	**5.2**	39.5	55.3	-0.43	-0.64
B150-T6	185	46	**4.0**	39.1	53.4	-0.80	-0.58
	Viscosity (mm^2/s)						
	Before Ageing	**After Ageing**					
TOP	1390	27057	**19.5**	-	34.1	-	-

Figure 16 shows that the addition of TOP causes an increase in the ageing index of the bitumen. An increase in the ageing index indicates that TOP is expected to have an adverse affect on the durability. If the bitumen ages too quickly it will undergo excessive hardening, as indicated by the low penetration values obtained for the aged TOP modified bitumens, and will be susceptible to cracking. The straight line fitted to the data in Figure 16 has a correlation coefficient of 0.95, which gives some confidence in the trend. The standard error of the slope of the ageing index data given in Figure 16 is 0.0130 and the t-statistic is calculated as being 8.717. Since the t-statistic exceeds the critical t-value for a 95% level of significance with 4 degrees of freedom it can be concluded that the slope is definitely non-zero and the effect seen in Figure 16 is significant.

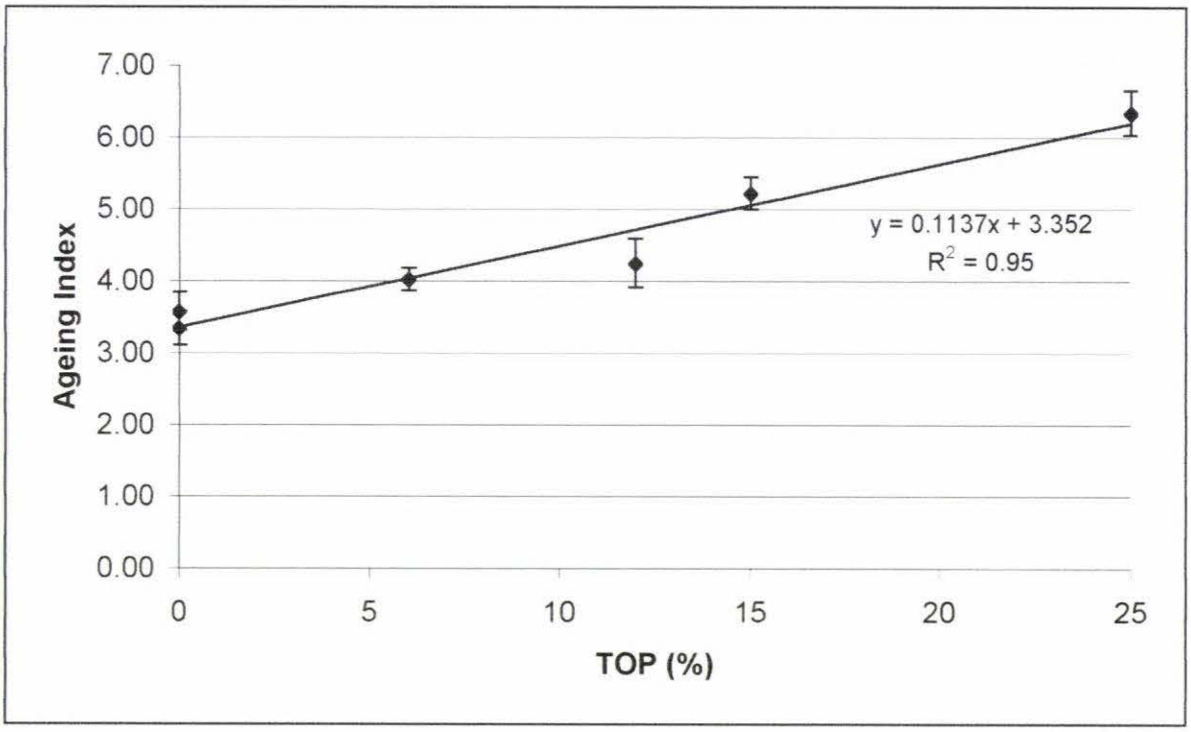


Figure 16: Effect of TOP on ageing index of bitumen.

It is not possible to directly compare the ageing index calculated for the bitumen based binders and the TOP because two different test methods were used to determine the ageing index. However, it would appear that the viscosity of the TOP increases appreciably upon ageing, which may be the cause of the lower penetration values obtained as the proportion of TOP increases.

By comparing the penetration index data in Table 16 it is possible to determine if ageing has any effect on the temperature susceptibility of the bitumen. The average difference between the PI data before and after ageing is +0.26 with a standard deviation of 0.37. The 95% confidence limits for the average difference are calculated as being ± 0.39. Consequently, we are 95% certain that the average difference in PI lies in the range of –0.10 to +0.65. Therefore, since this range includes zero, there is insufficient evidence to suggest that the temperature susceptibility of the TOP modified bitumen changes during ageing.

10.2 Prediction of Durability

The durability is a critical parameter in the expected service life of a bituminous pavement. The durability is akin to the resistance of the binder to oxidative ageing. Although not quantified by TNZ M/1 (1995), it is specified that the bitumen must show "adequate resistance to oxidative hardening at road surface temperatures." Herrington (2000b) has developed a procedure that compares the rate of oxidative ageing of a bitumen to that of the Safaniya bitumen that is used in New Zealand.

The change in oxidative hardening of bitumen as measured by the modulus of the bitumen at 5°C has been modelled by Equation 10-1. Under Herrington's (2000b) criteria, prospective bitumen would be suitable for use in New Zealand if it displayed a rate of oxidative hardening equal to, or less than that displayed by Safaniya bitumen. The constants P and K are fitted to the plot of oxidation time versus modulus at 5°C and if they are equal to, or less than those of Safaniya bitumen, then the bitumen can be accepted as possessing sufficient durability.

Equation 10-1: $$\Delta \log |G^*| = P.(1 - e^{(-K_f.t)}) + K.t$$

Where G^* = modulus of bitumen measured at 5°C (Pa)
P = Constant with value given in Table 18
K_f = Constant with value given in Table 18
K = Constant with value given in Table 18
t = time (hours)

A sample of B50-T12 and B50-T25 were tested for durability using Herrington's (2000b) procedure. The bitumen was aged as 1 mm thick films at 60°C in a pressure oxidation vessel charged with 2069 kPa of oxygen. After various durations the modulus of the bitumen was determined at 5°C as shown in Table 17.

Table 17: Durability test data for B50-T12 and B50-T25 bitumens.

Oxidation Time (hrs)	B50-T12		B50-T25	
	Modulus G* at 5°C (Pa)	Change in log G* (Pa)	Modulus G* at 5°C (Pa)	Change in log G* (Pa)
0.0	31900000	0.0000	15700000	0.0000
25.5	49050000	0.1868	31330000	0.3001
97.7	58240000	0.2614	36000000	0.3604
194.7	61630000	0.2860	42740000	0.4349
310.2	69130000	0.3359	50870000	0.5106
428.8	68360000	0.3310	52630000	0.5253
604.0	68790000	0.3337	53760000	0.5346
861.0	70600000	0.3450	58660000	0.5724

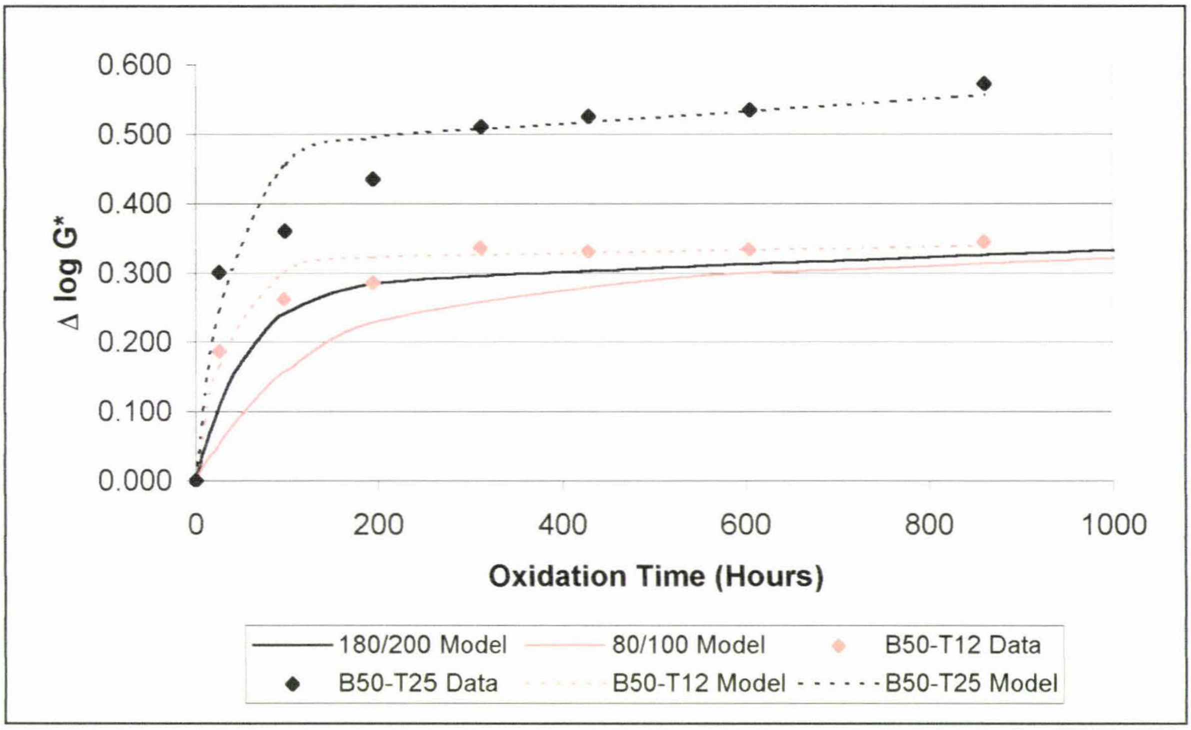


Figure 17: Durability plot for TOP modified bitumen.

Table 18: Fitted coefficients for bitumen aged in the durability test.

Bitumen	P (x 10^{-1})	K_f (x 10^{-3})	K (x 10^{-5})
Safaniya 180/200 [a]	2.81	18.6	5.1
Safaniya 80/100 [a]	2.66	8.62	5.4
B50-T25	4.80	27.6	8.8
B50-T12	3.18	28.7	2.4

[a] Herrington (2000b)

The coefficients of P and K for the plots of bitumen B50-T12 and B50-T25 in Figure 17 were fitted using a method of least squares. The calculated coefficients are given in Table

18. The standard error of the estimate of the fitted models is 0.0283 and 0.0618 for B50-T12 and B50-T25 respectively and was calculated from Equation 10-2.

Equation 10-2: $$s_e^2 = \frac{\Sigma(y - \hat{y})^2}{n - 2}$$

where s_e = the standard error of the estimate
y = the observed value of modulus
$\hat{y}$ = the value of y predicted by the model at a particular oxidation time
n = the number of observations.

Since the value of P exceeds that for the respective Safaniya bitumens, it must be concluded that bitumens B50-T12 and B50-T25 are less durable than Safaniya bitumen. The value of K for B50-T12 also exceeds the K value for the corresponding 80/100 bitumen. Figure 17 clearly shows that the rate of change of modulus of the TOP modified bitumen is greater than that of the Safaniya bitumen. This result is in agreement with that obtained in Figure 16, which showed that the addition of TOP to bitumen causes an increase in the ageing index.

The overall shape of the plot for B50-T12 and B50-T25 in Figure 17 is similar to that the Safaniya bitumen with a large increase in Δ log G* in the first 200 hours followed by a slow, almost linear rate of oxidation. However, it is the magnitude of the change in log G* of the TOP modified bitumens in the first 200 hours that is most interesting when compared to that of the Safaniya bitumen. By increasing the proportion of TOP in the bitumen the rate of oxidation appears to have increased. This suggests that TOP is more reactive towards oxidation than the bitumen and contributes noticeably to the increase in modulus.

The large increase in Δ log G* for Safaniya bitumen in the first 200 hours of oxidation is thought to be due to sulphoxide formation, which is typically a much faster reaction than carbonyl formation. Tall oil pitch is not known to contain any oxidisable sulphur, although it may contain sulphate salts from the pulping process. These salts are likely to be inert under the mild oxidation conditions employed here. Therefore the addition of TOP would be expected to dilute the oxidisable sulphur concentration of the bitumen and it is not unreasonable to assume that the initial Δ log G* would be less than that of the Safaniya bitumen. However, since the opposite is observed it is possible that the TOP is oxidising via some other fast reaction pathway that probably doesn't involve sulphoxide formation. Tall oil pitch is known to contain unsaturated hydrocarbon compounds such as linoleic acid, oleic acid and abietic acid, which may be susceptible to oxidation.

10.3 Heithaus Parameters

The Heithaus parameters were developed by Heithaus (1960) as a means of measuring the compatibility between the asphaltenes and the maltenes phase in a bitumen. The compatibility and dispersion of the asphaltenes in the maltene phase is partially governed by solvent effects. That is, as the solvent power of the maltenes improves the degree of dispersion should improve. The dispersion of the asphaltenes phase has an effect upon physical properties of the bitumen such as viscosity and durability. Heithaus (1960) argues that asphaltenes in a maltene solvent would act in a similar manner to polymer solutions. The rheological properties are partially governed by the compatibility between the polymer and solvent. A good solvent will allow the polymer to occupy a greater hydrodynamic volume whereas a poor solvent will promote polymer aggregation and flocculation. Heithaus (1960) suggests that a similar effect is seen in bitumen, which in this case is viewed as a relatively concentrated dispersion of asphaltenes (polymer) in a maltene solvent.

Heithaus (1960) defined three parameters, P_a, P_o and P that describe the colloidal stability, or compatibility of the bitumen in question. The parameter P_a is defined as the peptisability of the asphaltenes. A higher value of P_a indicates that the asphaltenes are easily dispersed by the system and do not tend to aggregate as readily as asphaltenes that possess a low P_a value. Similarly, bitumens that have a higher P_o value tend to provide better solvency for the asphaltenes. The overall compatibility of the bitumen is defined by the parameter P, and in a similar manner to P_a and P_o, higher values indicate improved compatibility (Pauli and Branthaver, 1998; Branthaver *et al*, 1993; Heithaus, 1960).

Even if a bitumen has a low P_a value, indicating that the asphaltenes are difficult to disperse, colloidal stability can still be achieved if the maltene phase has a high solvent power. Conversely, easily dispersed asphaltenes may still be well dispersed in a medium of poor solvent power as defined by a low P_o value.

The Heithaus parameters that were measured for the TOP modified bitumen samples are given in Table 19. The values are of a similar order of magnitude to those reported by Branthaver *et al* (1993) although the standard deviation of the P_o and P values are slightly higher. This may partially be due to the low number of replicates used since the range of values measured in Table 19 are similar to those reported by Branthaver *et al* (1993). The Heithaus parameters measured for the aged TOP modified bitumen samples are given in Table 20. Due to the limited amount of aged material available no replicates were performed on these samples.

The effect of modifying the bitumen with TOP and of ageing on P_a, P_o and P can be seen in Figure 18, Figure 19 and Figure 20 respectively. Linear regression curves of the form $y = a.x + b$ were fitted to each of the plots for the P_a, P_o and P data and a regression analysis undertaken using Microsoft Excel 97 software. The results of the regression analysis are given in Table 21. At first glance it is apparent that TOP causes a decrease in the P_a value and an increase in the P_o and P values. The regression analysis confirms that the slopes of the plots of the Heithaus parameters against TOP are all non-zero at the 95% level of significance for both the unaged and aged samples.

However, it is also noticeable that there is appreciably more scatter in the data for the unaged bitumens than there is for the aged bitumen as shown by the lower correlation coefficients. A closer examination of the data in Table 19 suggests that the plot of the Heithaus parameters of the unaged bitumens against TOP content shown in Figure 18 – Figure 20 may be misleading. The parameter P_a measures the peptisability of the asphaltene fraction of bitumen. The SARA analysis undertaken in Section 10.5 shows that TOP contains very little in the way of asphaltene like material. Therefore, when TOP is added to the bitumen it is likely to affect the maltene phase more than the asphaltene phase. The averaged P_a values for the unaged B50-T0, B50-T12 and B50-T25 bitumen are all 0.69. These bitumens contain 0, 12 and 25% TOP respectively. If TOP did affect the P_a value, then it is expected that the value reported here would differ for each of the bitumens. It is more likely that the observed decrease in P_a as TOP increases in Figure 18 is due to the fact that as the proportion of TOP increases, the grade of bitumen used to make the blend becomes harder. The harder, more oxidised grades of bitumen tend to have lower P_a values than the softer B200-T0 bitumen.

Table 19: Heithaus parameters for TOP modified bitumen.

Bitumen	Replicate #	P_a, (Asphaltene Peptisability)	P_o, (Maltene Solvent Power)	P, (Compatibility)
B50-T0	1	0.68	1.36	4.28
	2	0.69	1.16	3.78
	3	0.69	1.14	3.68
	Avg., Std. Dev.	**0.69, sd = 0.01**	**1.22, sd = 0.12**	**3.92, sd = 0.32**
B50-T12	1	0.68	1.53	4.81
	2	0.71	1.04	3.55
	3	0.69	1.29	4.16
	Avg., Std. Dev.	**0.69, sd = 0.01**	**1.29, sd = 0.25**	**4.17, sd = 0.63**
B50-T25	1	0.69	1.40	4.45
	2	0.69	1.41	4.49
	Avg., Std. Dev.	**0.69, sd = 0.00**	**1.41, sd = 0.01**	**4.47, sd = 0.24**
B100-T0	1	0.71	0.91	3.13
	Avg.	**0.71**	**0.91**	**3.13**
B100-T15	1	0.70	1.23	4.06
	Avg.	**0.70**	**1.23**	**4.06**
B150-T6	1	0.70	1.22	4.03
	Avg.	**0.70**	**1.22**	**4.03**
B200-T0	1	0.75	0.76	3.02
	2	0.72	1.08	3.79
	3	0.73	0.89	3.28
	4	0.74	0.71	2.73
	Avg., Std. Dev.	**0.73, sd = 0.01**	**0.86, sd = 0.17**	**3.20, sd = 0.45**

Table 20: Heithaus parameters for aged TOP modified bitumen.

Bitumen	P_a, (Asphaltene Peptisability)	P_o, (Maltene Solvent Power)	P, (Compatibility)
B50-T12	0.62	1.33	3.47
B50-T25	0.59	1.58	3.87
B100-T0	0.63	1.11	3.02
B100-T15	0.61	1.40	3.59
B150-T6	0.63	1.20	3.26
B200-T0	0.64	1.16	3.23

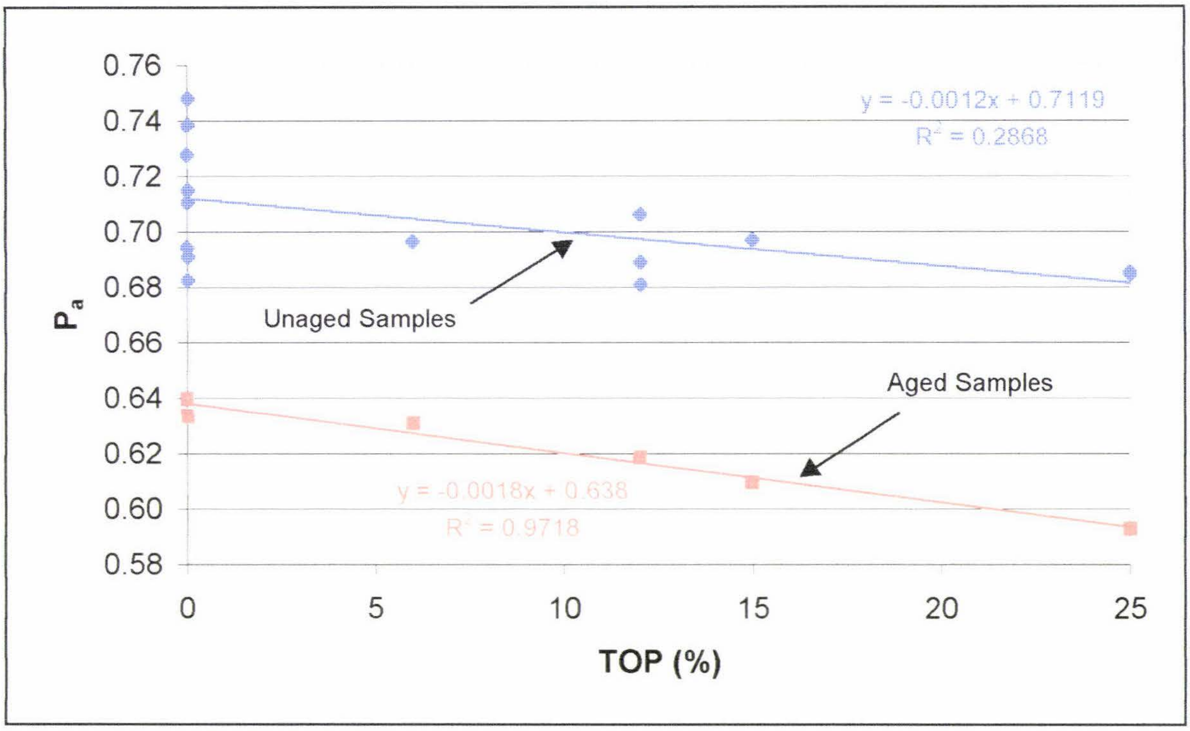


Figure 18: Effect of TOP on peptisability of asphaltenes (P_a).

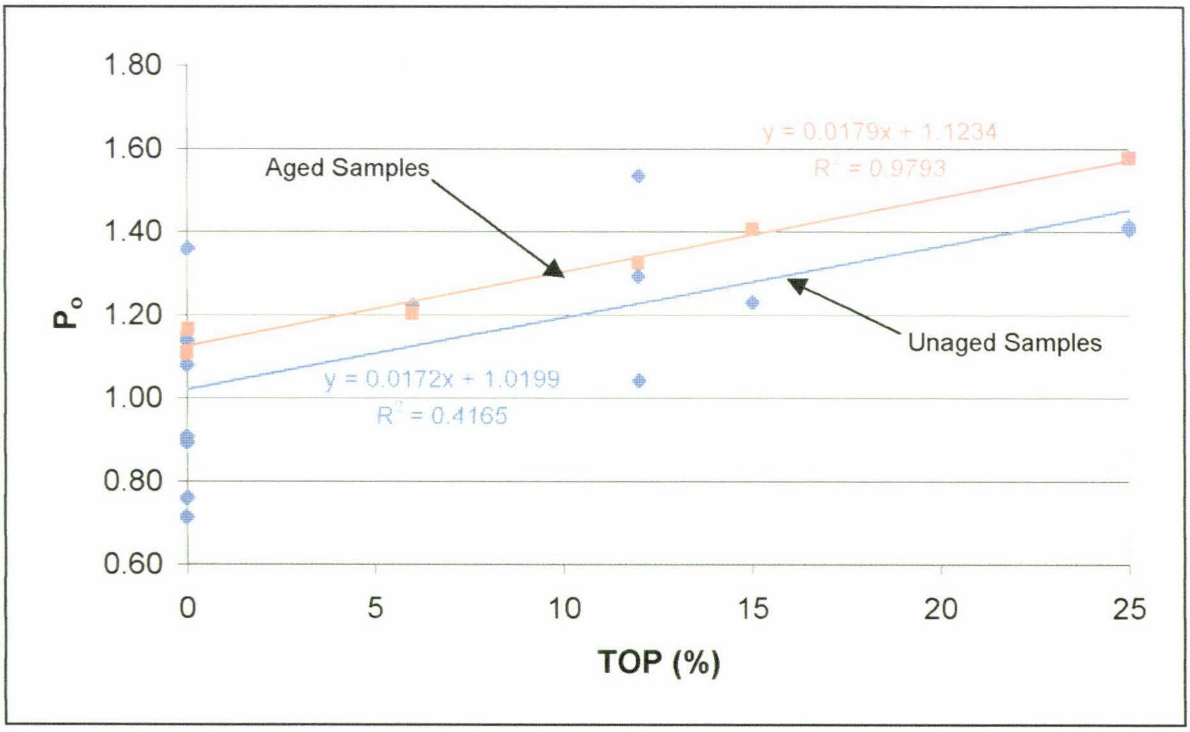


Figure 19: Effect of TOP on solvent power of maltenes (P_o).

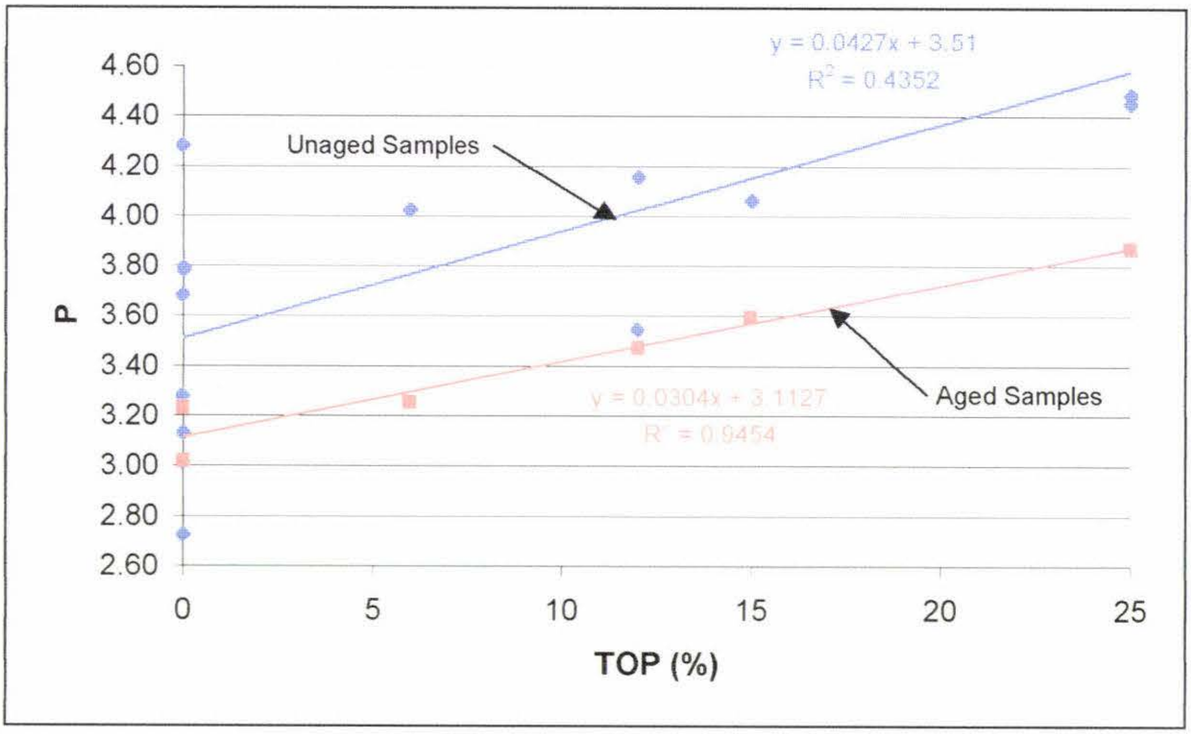


Figure 20: Effect of TOP on compatibility of bitumen (P).

Table 21: Regression analysis of the Heithaus parameter data.

	P_a		**P_o**		**P**	
	Unaged	**Aged**	**Unaged**	**Aged**	**Unaged**	**Aged**
Slope Coefficient Analysis						
Coefficient of Slope	-0.00122	-0.00179	0.0172	0.0179	0.0427	0.0304
Standard Error of Slope	0.000535	0.000152	0.00566	0.00130	0.0135	0.00365
Number of Observations	15	6	15	6	15	6
t-value	-2.29	-11.7	3.05	13.7	3.16	8.32
Critical t-test statistic	2.16	2.78	2.16	2.78	2.16	2.78
Is Slope Non-Zero at 95% level?	**YES**	**YES**	**YES**	**YES**	**YES**	**YES**

If the effect of TOP on the unaged B50-T0 modified bitumen samples is examined in isolation from the rest of the data, the plots given in Figure 21 – Figure 23 are obtained. A regression analysis of the slopes of these plots (a summary of which is given in Table 22) shows that the slopes are not non-zero at the 95% level of significance. Consequently, there is no evidence to suggest that TOP has any significant affect on the Heithaus parameters in unaged samples.

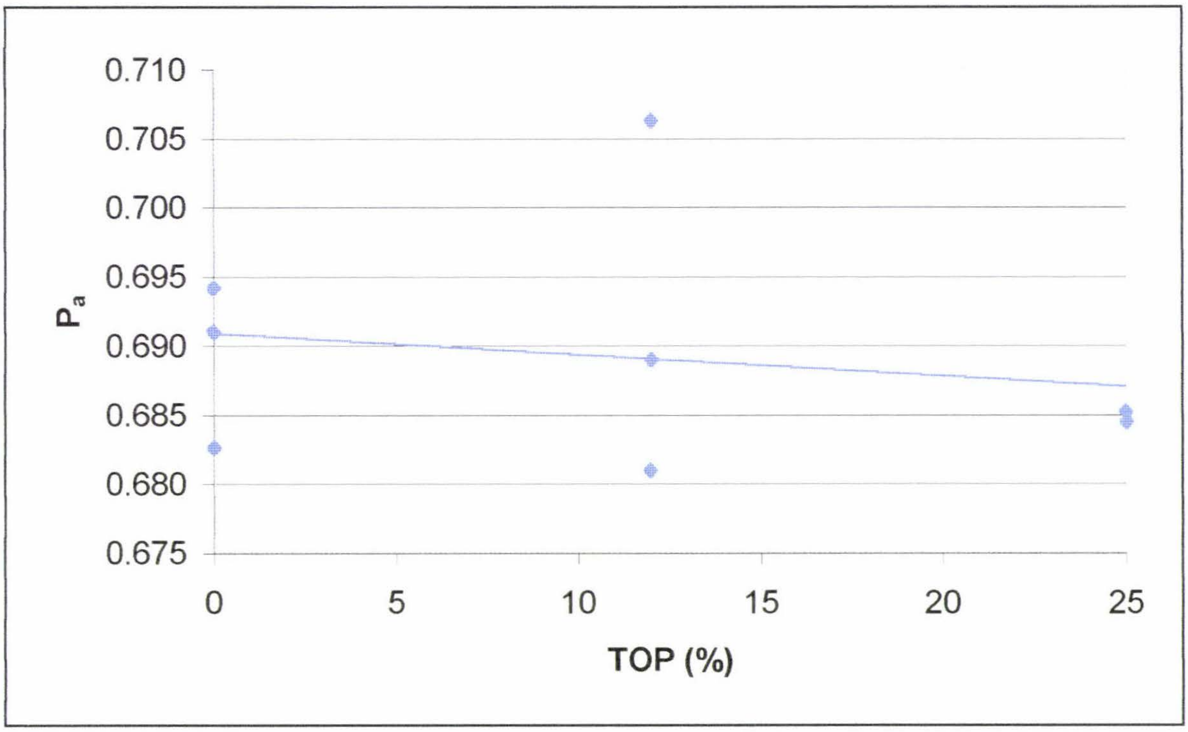


Figure 21: Effect of TOP on P_a of modified B50-T0 bitumen.

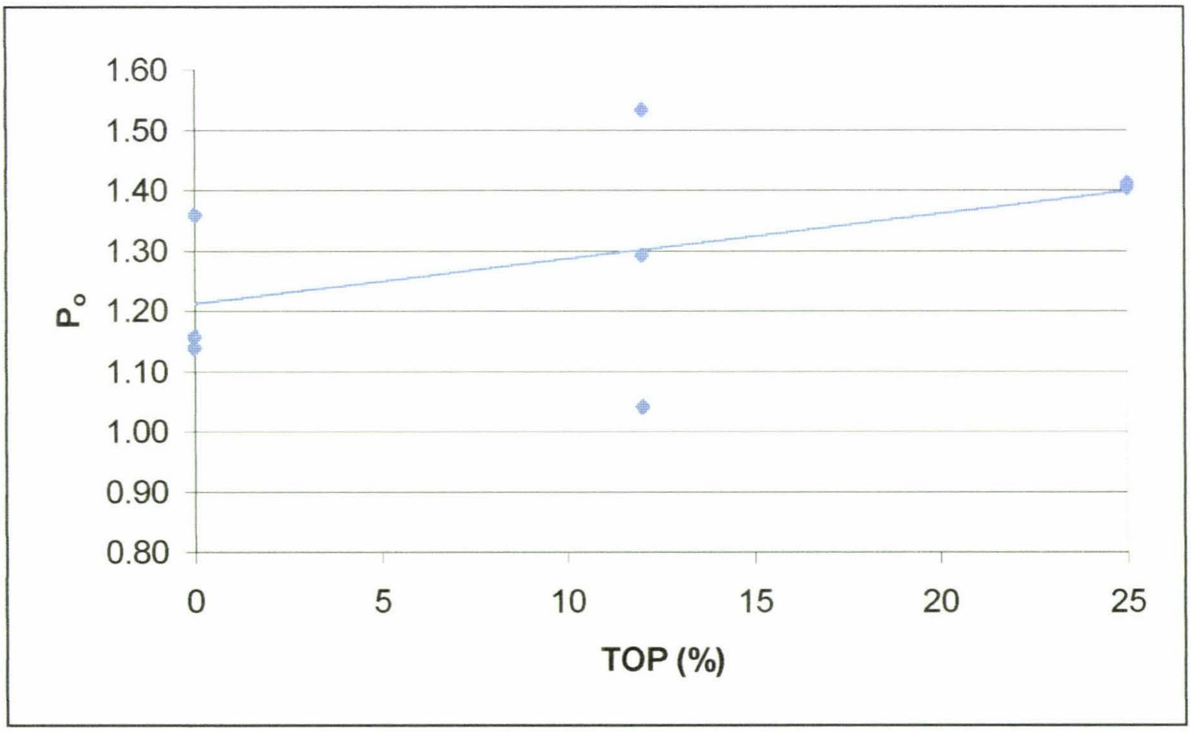


Figure 22: Effect of TOP on P_o of modified B50-T0 bitumen.

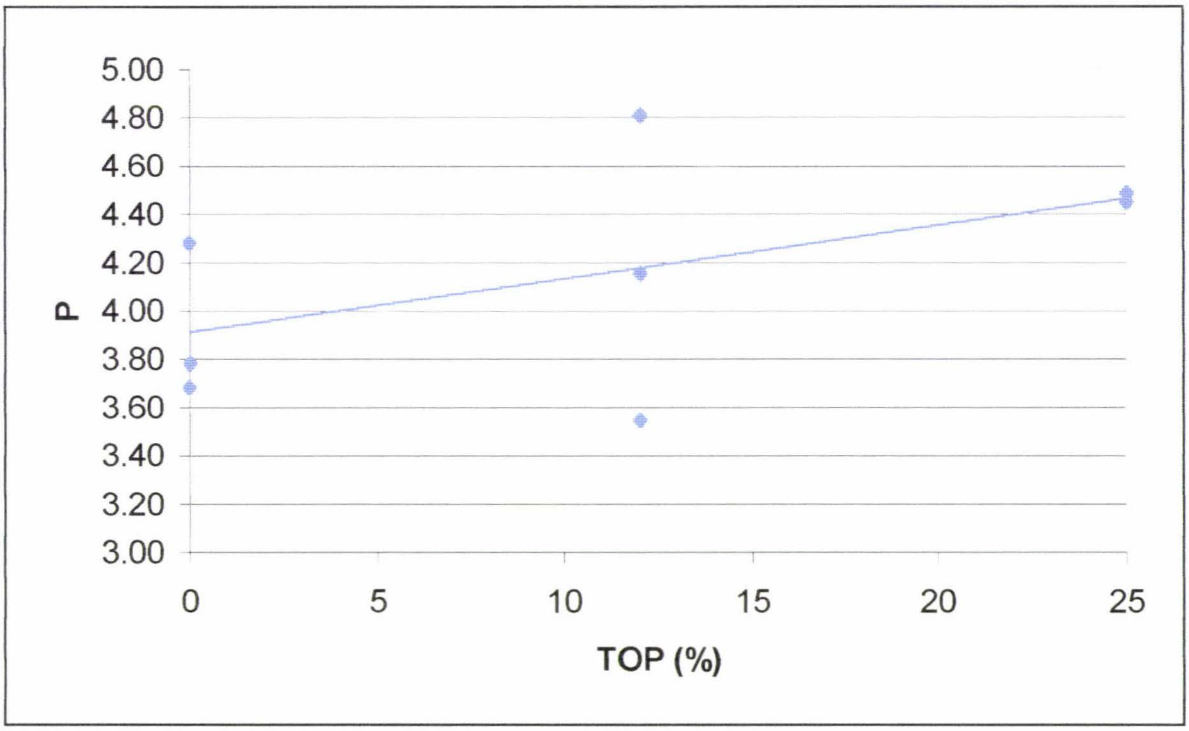


Figure 23: Effect of TOP on P of modified B50-T0 bitumen.

Table 22: Summarised regression analysis of effect of TOP on Heithaus parameters in unaged modified B50-T0 bitumen.

	P_a	P_o	P
Coefficient of Slope	-0.00015	0.00752	0.02206
Standard Error of Slope	0.00032	0.00579	0.01487
Number of Observations	8	8	8
t-value	-0.482	1.30	1.48
Critical t-test statistic	2.45	2.45	2.45
Is Slope Non-Zero at 95% level?	**NO**	**NO**	**NO**

It appears more likely that the grade of bitumen used to make the TOP modified bitumen has a greater effect on the Heithaus parameters in the unaged bitumen. The penetration of the base bitumen used to manufacture the unaged TOP modified bitumen has been plotted against P_a, P_o and P in Figure 24, Figure 25 and Figure 26 respectively. The corresponding regression analysis is summarised in Table 23. Since the t-value of the regression exceeds the critical t-value in Table 23 it must be concluded that there is sufficient evidence to suggest that the penetration of the bitumen used to manufacture the TOP modified bitumen has a significant impact upon the Heithaus parameters.

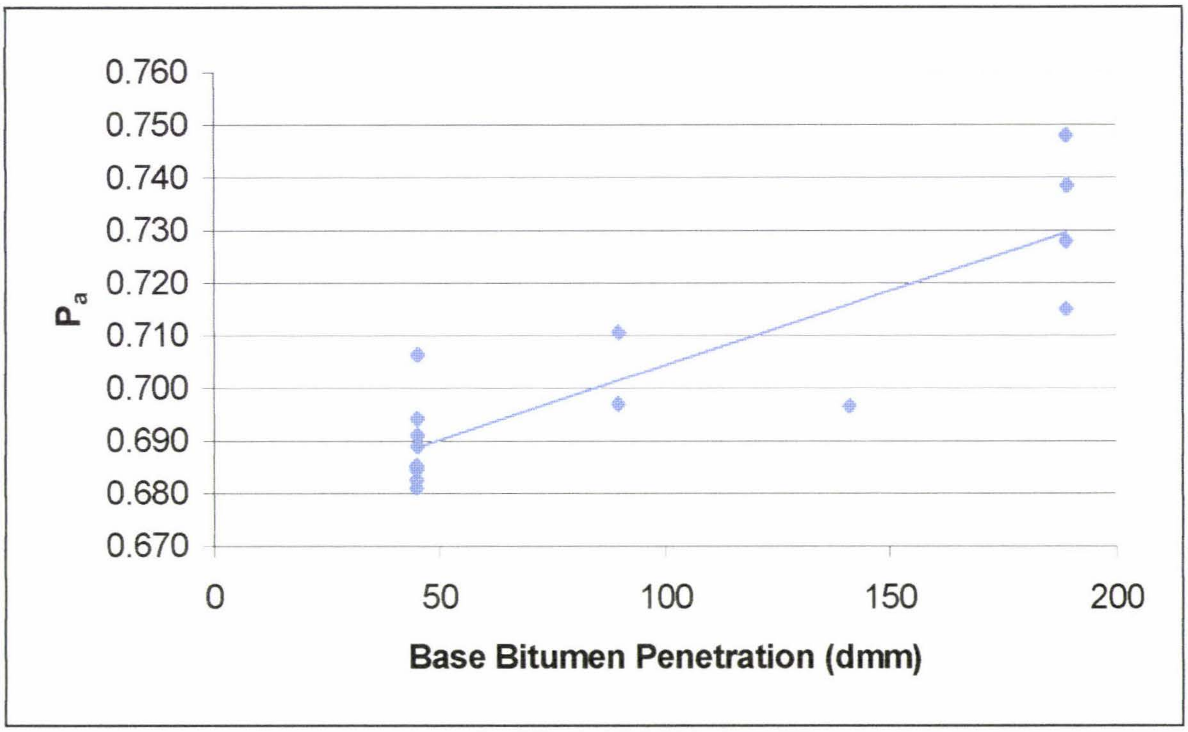


Figure 24: Relationship between the penetration of bitumen used to make TOP modified bitumen and the Heithaus parameter, P_a in unaged bitumen.

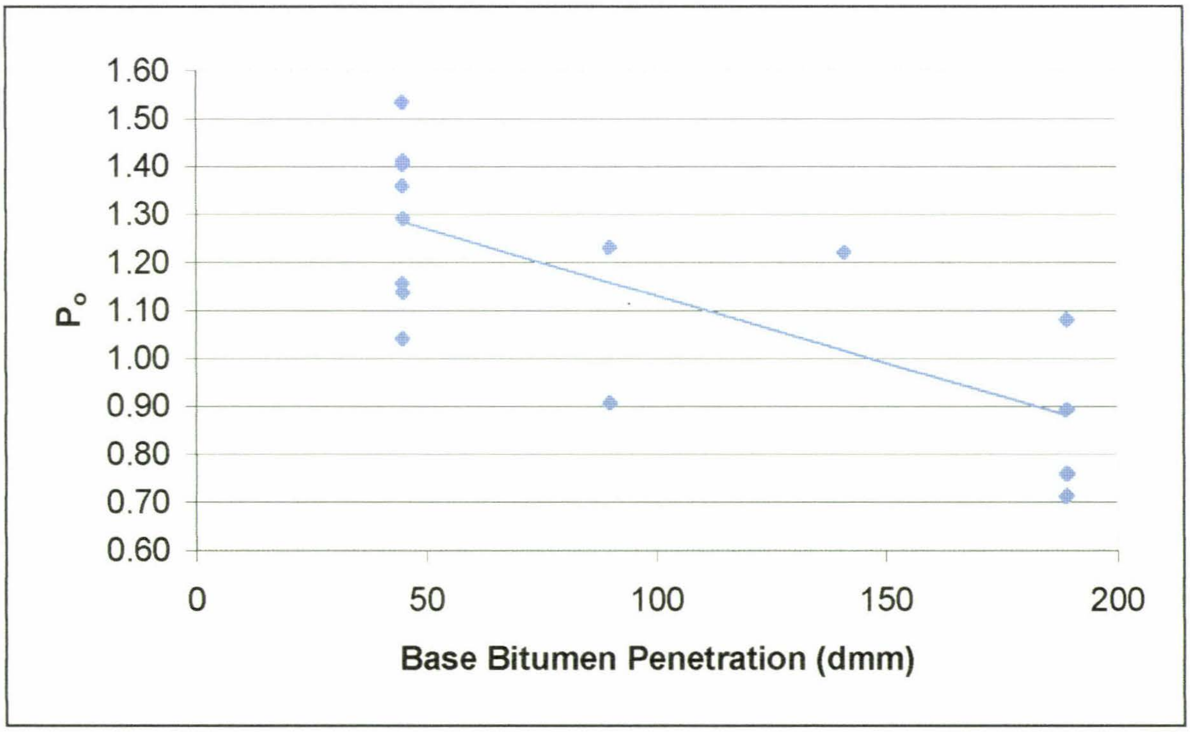


Figure 25: Relationship between the penetration of bitumen used to make TOP modified bitumen and the Heithaus parameter, P_o in unaged bitumen.

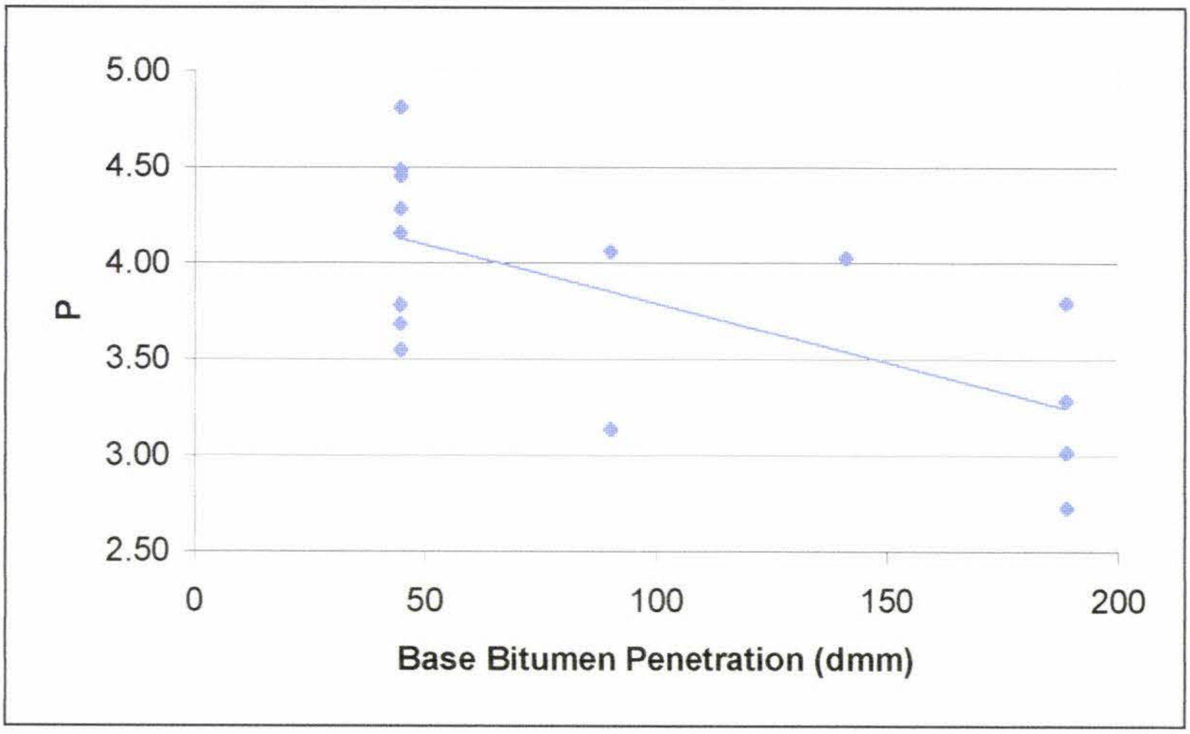


Figure 26: Relationship between the penetration of bitumen used to make TOP modified bitumen and the Heithaus parameter, P in unaged bitumen.

Table 23: Summarised regression analysis of effect of base bitumen penetration on Heithaus parameters in unaged modified B50-T0 bitumen.

	P_a	P_o	P
Coefficient of Slope	0.00028	-0.00280	-0.00612
Standard Error of Slope	0.000046	0.00072	0.00193
Number of Observations	15	15	15
t-value	6.14	-3.89	-3.16
Critical t-test statistic	2.16	2.16	2.16
Is Slope Non-Zero at 95% level?	**YES**	**YES**	**YES**

However, when the aged bitumen samples are analysed in a similar manner, no evidence is found to suggest that the penetration of the bitumen used to manufacture the TOP modified bitumen had any effect on the Heithaus parameters obtained after ageing. If the plots in Figure 18 – Figure 20 and the summarised regression analysis in Table 21 are reviewed, it appears that there is a relationship between the proportion of TOP in the bitumen and the Heithaus parameters after ageing. The slopes of the plots for the aged samples in Figure 18 – Figure 20 are definitely non-zero at the 95% level of significance. It is apparent that TOP causes a reduction in P_a and an increase in P_o and P after ageing.

If it is assumed that the effect of base bitumen penetration on the Heithaus parameter is negligible after ageing and that the TOP proportion is a major determinant of the Heithaus parameters, then it is possible to compare the slopes of the plots of the aged bitumen samples in Figure 18 – Figure 20 to those of the unaged bitumen samples in Figure 21 – Figure 23. A comparison of the slopes between the aged and unaged samples will enable any interaction between TOP content and ageing to become statistically apparent. Although the data in Table 21 shows that TOP has a major effect on the Heithaus parameters in the aged samples the data in Table 22 shows that TOP has no effect on the Heithaus parameters in the unaged bitumen samples. Consequently, it is of interest to know if the effect of TOP on the Heithaus parameters differs statistically between the unaged and aged samples. Table 24 contains a summary of the regression analysis for the comparison of the slopes.

Table 24: Summary of the regression analysis comparing the slopes of the Heithaus parameters of the unaged and aged samples against TOP content.

	Pa		**Po**		**P**	
	Unaged	*Aged*	*Unaged*	*Aged*	*Unaged*	*Aged*
Analysis of Difference Between Slopes						
Coefficient of Slope	-0.00015	-0.00179	0.00752	0.01788	0.02206	0.03039
Number of Observations	8	6	8	6	8	6
Residual Sum of Squares	0.00045	0.000044	0.15214	0.00318	1.004	0.0250
Difference Between Slopes	0.00164		0.01037		-0.00833	
Degrees of Freedom	10		10		10	
Standard Error of Difference in Slopes	0.000414		0.00732		0.0188	
t-value	3.95		-1.42		-0.442	
Critical t-test statistic	2.23		2.23		2.23	
Are Slopes Different at 95% Level?	**YES**		**NO**		**NO**	
Analysis of Difference Between Intercepts						
Common Coefficient of Slope	-		0.01148		0.02525	
Standard Error of Diff. in Intercepts	-		0.0704		0.167	
Difference in Intercepts	-		-0.0166		0.715	
Degrees of Freedom	-		11		11	
t-value	-		-0.236		4.28	
Critical t-test statistic	-		2.201		2.201	
Are Intercepts Different at 95% Level?	-		**NO**		**YES**	

It seems that the slopes of the plots of TOP content against P_a for the unaged and aged bitumen samples are not equal at the 95% level of significance. This implies that there is an interaction between the TOP content and ageing for the P_a parameter. TOP causes a reduction in the dispersability of the asphaltene fraction during ageing, as measured by the P_a value. This may be a change in mass fraction, molecular size or polarity or a combination of all three.

No statistical difference in the slope or intercept of the regression lines for the plot of P_o against TOP content for the unaged and aged samples was detected. This implies that there is no interactive effect between the TOP content and the ageing process that affects the P_o parameter. A difference in the intercepts of the plots of P against TOP for the unaged and aged samples was observed although there is no statistical difference in the slopes. It is apparent that ageing causes a measurable reduction in the P parameter. That is to say, as the bitumen is aged, it becomes less compatible.

It is apparent that the Heithaus parameters in unaged samples are affected by the grade of bitumen, but not by the proportion of TOP in the blend. Conversely, the Heithaus parameters are affected by the TOP content during ageing, whereas the grade of bitumen used in the blend has no effect. An increase in the TOP content causes a decrease in the dispersability of the asphaltenes during ageing as measured by the P_a parameter. Increasing the TOP content also causes the maltene phase to possess improved solvent power (P_o) and the bitumen has improved overall compatibility (P).

10.4 Acid Number

The presence of organic acids in the bitumen has been implicated in affecting viscosity (Petersen, 1984) and adhesion (Plancher *et al*, 1977). As discussed in Section 5.3.1 carboxylic acids are thought to increase the viscosity through molecular interactions and hydrogen bonding. Consequently, bitumen that forms carboxylic acids upon ageing may possess poor age hardening resistance (Petersen, 1984). Being polar, acids can promote molecular structuring by inducing dipole moments in adjacent bitumen molecules. The end result is a bitumen that has a higher viscosity and consequently, may be prone to thermal cracking or poor fatigue resistance.

Similarly, carboxylic acids are strongly attracted to polar surfaces found in mineral aggregates. They also have an affinity for water and as such are easily displaced from the aggregate surface. This leads to loss of adhesion, stripping and moisture damage in asphalt mixtures (Plancher *et al*, 1977). Therefore, it is useful to know the amount of carboxylic acid in the bitumen.

Since previous research has shown that the presence of organic acids may be detrimental to satisfactory bitumen performance, it is useful to gain an understanding of how the acids in TOP will affect the acid number of the bitumen. Bitumen is typically very low in acidic species compared to TOP. The acid number of TOP produced in New Zealand is in the order of 40 mg KOH/g (Ball *et al*, 1993) whereas that of bitumen is typically less than 1 mg KOH/g (West, 1985).

The acid number of each of the TOP modified bitumens before and after ageing is given in Table 25. An analysis of the TOP by the manufacturer showed that it had an acid number of 41.7 mg KOH/g and a rosin acid content of 14.9% w/w. This is comparable with the acid value of 40.6 mg KOH/g obtained during the current analysis. Replicate measurements of three of the binders yielded seven results with a pooled standard deviation of 0.75 mg KOH/g and 4 degrees of freedom. Consequently the estimate of the error in each result is ± 1.0 mg KOH/g at the 95% level of significance.

Table 25: Acid number of unaged and aged TOP modified bitumen.

Bitumen	**TOP (%)**	**Acid Number (mg KOH/g)**	
		Unaged	**Aged**
B50-T0	0	0.6	-
B50-T12	12	4.3	4.5
B50-T25	25	10.2	8.8
B100-T0	0	0.5	0.5
B100-T15	15	5.1	5.4
B150-T6	6	2.9	3.1
B200-T0	0	0.4	0.5
TOP	100	40.6	40.1

From the data displayed in Figure 27 it is clear that the acid number is directly proportional to the amount of TOP in the bitumen. The analysis shows that the acid numbers of the unmodified bitumens are all less than 1.0 mg KOH/g, which is less than the estimate for the error given for the test. The correlation coefficients for the fitted regression lines are both in excess of 0.99. This indicates that the lines are a good fit to the data.

Perhaps what is of more interest is the fact that the acid number for the unaged and aged samples appears to coincide. The implication of this is that ageing does not cause a detectable change in the proportion of acid groups in the bitumen. Similar slopes for the regression lines show that there is no interaction between the ageing process and the proportion of TOP in the bitumen. Obviously the presence of acid functional groups in the TOP does not cause an increase in the formation of acid groups during ageing and the effect seen in Figure 16 is caused by some reaction other than acid induced oxidation.

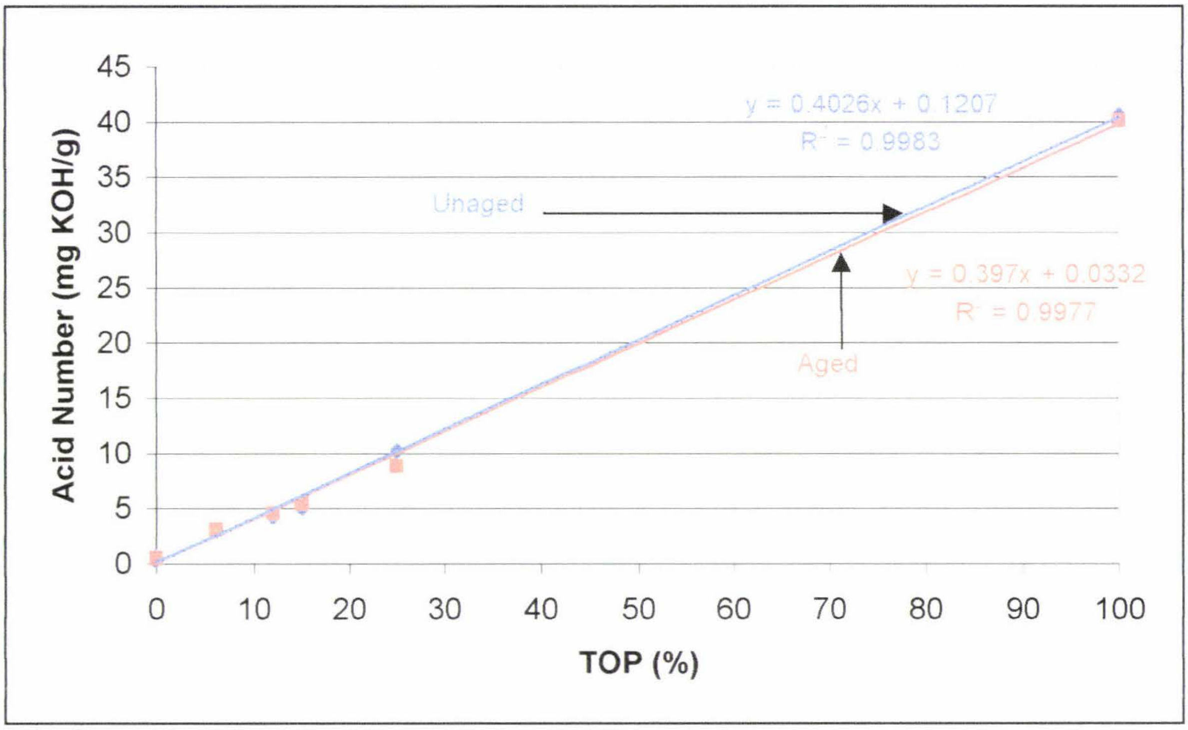


Figure 27: Effect of TOP on acid number of bitumen.

An analysis of the two regression lines can be undertaken to ascertain if in fact there are any significant differences between the unaged and aged acid numbers. Zar (1999) provides a method of analysing the two regression lines using a t-test. The results of this analysis are given in Table 26 where it can be seen that there is no statistical difference in the slope or intercept of the two regression lines. Therefore, the acid number has not changed statistically upon ageing and the effect that TOP has on the acid number before and after ageing can be modelled by Equation 10-3. Zar's (1999) method makes the assumption that the standard deviation of the two data sets is equal. This is validated by the fact that the F-test value is 1.44, which is less than the critical value of 4.39.

Equation 10-3: Acid Number = 0.3999[TOP%] + 0.0782

Table 26: Summarised analysis of acid number regression data.

	Unaged	**Aged**
Slope Coefficient Analysis		
Coefficient of Slope	0.4026	0.3970
Number of Observations	8	7
Residual Sum of Squares	2.2257	2.6630
Pooled Residual Mean Square	0.4444	
Standard Error of Difference Between Slopes	0.0108	
Difference in Slopes	0.0056	
t-test value	0.515	
Critical t-statistic (one-tailed, $\alpha = 0.05$, d.f. = 11)	1.796	
	NO DIFFERENCE IN SLOPE	
Common Coefficient of Slope	0.3999	
	Unaged	**Aged**
Intercept Coefficient Analysis		
Coefficient of Intercept	0.1207	0.0332
Number of Observations	8	7
Residual Sum of Squares for Common Regression	5.0067	
Residual Mean Square for Common Regression	0.4172	
Standard Error of Difference Between Intercepts	0.3346	
Difference in Intercepts of Common Regression	0.2051	
t-test value	0.613	
Critical t-statistic (one-tailed, $\alpha = 0.05$, d.f. = 12)	1.782	
	NO DIFFERENCE IN INTERCEPTS	
Common Coefficient of Intercept	0.0782	

10.5 SARA Analysis

The Corbett fractionation scheme described in Section 4.3.4 has become an industry standard for identifying compositional differences between bitumens. The fractionation scheme has been formally standardised in ASTM D4124 (1996) and will be referred to as the SARA analysis because it separates the bitumen into a Saturate, Aromatic, Resin and Asphaltene fraction. The aromatic and resin fractions are akin to the naphthene aromatic and polar aromatic fractions using the respective Corbett nomenclature.

The results of the SARA analysis of the TOP modified bitumens are given in Table 27. During the analysis it was observed that the percent recovery of the individual fractions did not always sum to 100%. Lower recoveries tended to be obtained with those bitumens that contained higher proportions of TOP and it was also observed that the usually white alumina in the chromatography column was stained yellow-brown after elution of the bitumen. Presumably, a proportion of the bitumen remained adsorbed on the alumina, even after elution with a polar solvent such as methylene chloride. The adsorbed fraction is believed to be resinous in nature since the resin fraction of the bitumen is polar and would be more strongly adsorbed by the polar alumina than the more neutral aromatic fraction. Also, since those bitumens containing high proportions of TOP have the lowest recoveries, it is likely that the absorbed species are acidic resin species from the TOP since the alumina is basic. An attempt was made to desorb the strongly absorbed resins from the alumina by eluting with a solution of 5% acetic acid in methylene chloride. While the percent recoveries did improve, many were still noticeably less than 100%. Therefore, the proportion of resins in the bitumen that are presented in Table 27 were determined from the difference between the whole bitumen and the sum of the other fractions. A notable exception is the composition recorded for the unaged B100-T0 bitumen, which is the average composition of replicate measurements.

Table 27: Fractional composition of TOP modified bitumens.

Bitumen	Asphaltenes	Resins	Aromatics	Saturates	Percent Recovery	Colloidal Index
Unaged						
B200-T0	12.6	27.0	50.3	10.2	99.7	0.29 ± 0.03
B100-T0	15.3	31.4	44.8	8.4	99.7	0.31 ± 0.03
B50-T0	19.4	27.9	43.7	9.0	99.4	0.40 ± 0.04
B150-T6	12.7	26.5	51.3	9.5	100.3	0.29 ± 0.03
B100-T15	14.0	30.7	46.9	8.4	100.3	0.29 ± 0.03
B50-T12	16.6	33.7	41.5	8.2	95.8	0.33 ± 0.03
B50-T25	15.4	44.7	33.0	6.9	93.0	0.29 ± 0.03
TOP	4.8	89.0	5.5	0.7	71.2	0.06 ± 0.02
Aged						
B200-T0	19.2	35.0	36.2	9.7	97.9	0.40 ± 0.04
B100-T0	22.6	33.2	34.2	10.0	96.9	0.48 ± 0.05
B150-T6	19.6	41.1	31.5	7.9	99.5	0.38 ± 0.04
B100-T15	21.6	46.7	22.5	9.2	95.6	0.44 ± 0.04
B50-T12	25.6	42.7	25.2	6.5	99.2	0.47 ± 0.04
B50-T25	24.5	45.7	24.1	5.7	92.2	0.43 ± 0.04
TOP	18.7	77.4	3.4	0.5	90.1	0.24 ± 0.03

An estimate of the precision of the SARA analysis is given in Table 28. A total of four replicates were planned but accidental spillages and contamination of the fractions during the analysis limited the quantity of data available. ASTM C670 (1996) suggests that the acceptable difference between two results at the 95% confidence level can be estimated by multiplying the standard deviation of the replicates by 2.8. The precision of the test method that is reported in ASTM D4124 (1996) is also given as a comparison. Consequently, for a difference between the observed proportions of the fractions to be significant it must exceed 0.8%, 4.5%, 3.4% and 1.7% for the asphaltene, resin, aromatic and saturate fractions respectively.

Table 28: Estimate of the errors associated with the SARA analysis.

	Asphaltenes	**Resins**	**Aromatics**	**Saturates**
B100-T0 Replicate 1	15.2	30.2	45.6	9.0
B100-T0 Replicate 2	15.5	32.5	43.9	7.8
B100-T0 Replicate 3	15.4	-	-	8.4
B100-T0 Replicate 4	14.9	-	-	-
Average	15.3	31.4	44.8	8.4
Standard Deviation	0.3	1.6	1.2	0.6
Factor for determining max. acceptable range of 2 test results *	2.8	2.8	2.8	2.8
Acceptable range of 2 test results	0.8	4.5	3.4	1.7
Acceptable range from ASTM D4124 (1996)	0.9	2.2	2.9	1.2

from ASTM C670 (1996).

The proportion of a particular fraction, whether it be asphaltenes, resins, aromatics or saturates can be estimated to a reasonable degree of accuracy by taking the weighted mean of the proportion of that fraction in the components that make up the blend. For example, bitumen B50-T25 contains 75% B50-T0 and 25% TOP. From the data given in Table 27, the weighted average asphaltene content is calculated as being 15.9%. In fact, it was measured as being 15.4%, which is within range of precision given in Table 28.

Figure 28 shows the measured proportion of the bitumen fractions plotted against the corresponding estimated value. There appears to be a reasonable degree of correlation, as indicated by a correlation coefficient of 0.94, which suggests that the proportion of a particular fraction can be estimated relatively precisely. This implies that the TOP modified bitumen can simply be considered as a physical blend of two components. There is no evidence to suggest that the TOP chemically reacts with the unaged bitumen to produce reaction products that alter the composition of the blend. The noticeable degree of scatter in the data for the resin and aromatic fractions indicates that these fractions can be predicted or measured less accurately than the asphaltene or saturate fractions.

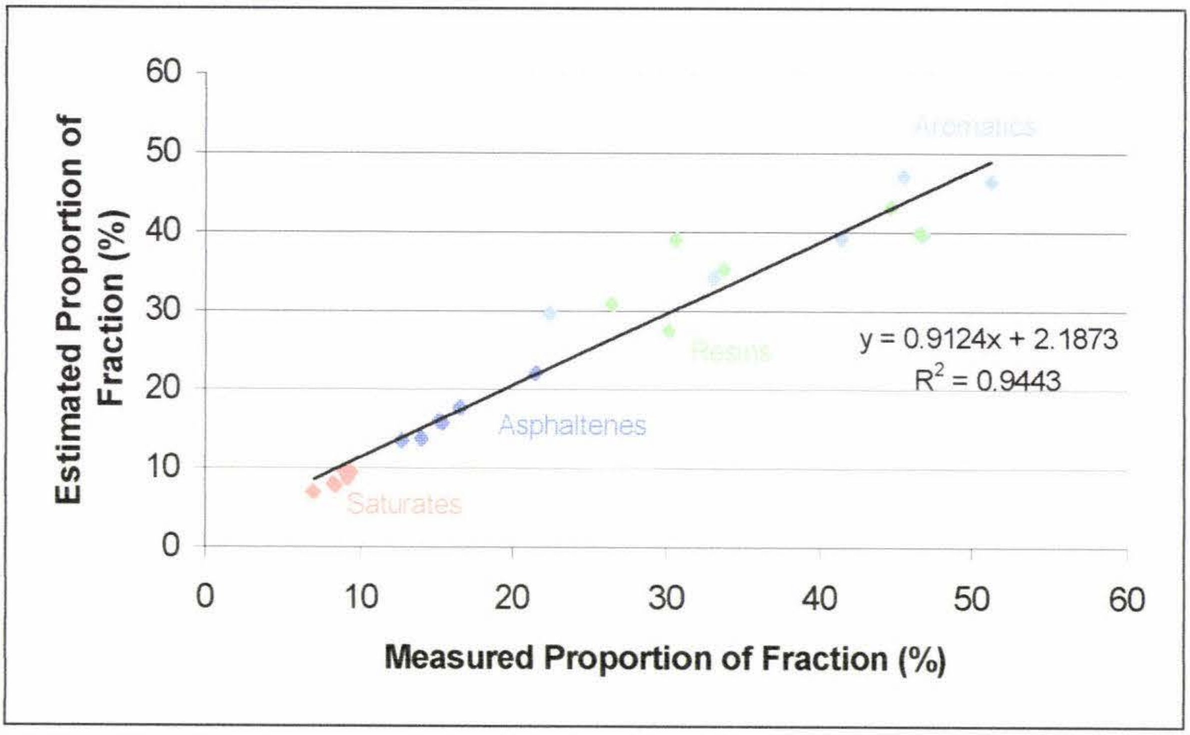


Figure 28: Correlation between measured and predicted values of the bitumen fractions.

10.5.1 Effect of TOP on Bitumen Composition

Figure 29 shows that TOP has a diluting effect on the asphaltene, aromatic and saturate fractions of 40/50 bitumen, while the resin content increases. This is hardly surprising since the data in Table 27 shows that TOP is rich in resins and relatively low in the other fractions. A similar result can be observed in Figure 30, which shows the fractional composition of TOP modified bitumens with a penetration between 180 and 200 dmm. However, in this case the asphaltene content increases instead of decreases. This is likely to be because those blends containing high proportions of TOP are necessarily manufactured using a harder grade of bitumen. The harder grades of bitumen naturally contain higher proportions of asphaltenes.

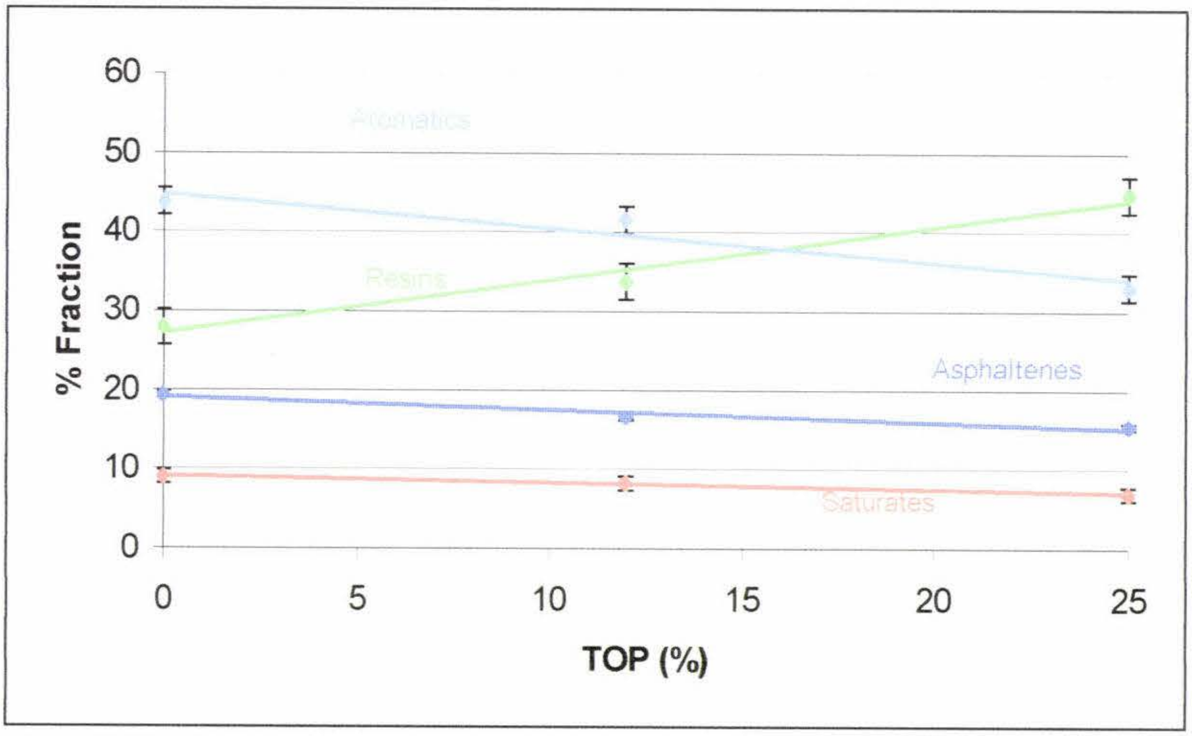


Figure 29: Effect of TOP on composition of blends of B50-T0 bitumen and TOP.

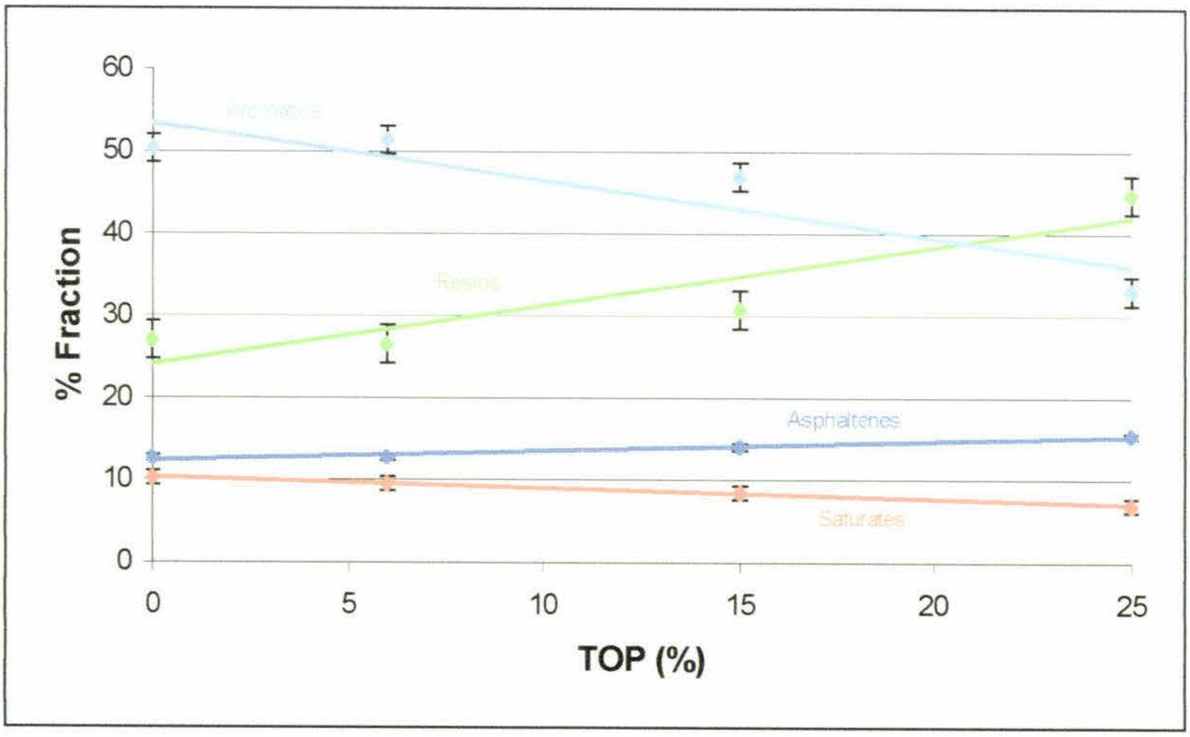


Figure 30: Effect of TOP on the composition of TOP modified bitumens with a penetration of 180 – 200 dmm.

An understanding of the significance of the changes in fractional composition shown in Figure 29 and Figure 30 can be obtained by fitting a linear regression line to the plot of each SARA fraction against TOP content and by performing an analysis of variance. Table 29 gives the slope and standard error of the slope for the plot of each SARA fraction versus TOP content for the 180/200 penetration grade bitumens. There is an appreciable increase in the proportion of asphaltenes in the unaged and aged bitumen samples as the proportion of TOP increases. The slope is both positive and non-zero at the 95% level of significance. A similar result is observed for the saturate fraction in the unaged bitumen sample. However, in this case the slope is negative and non-zero at the 95% level of significance and indicates a reduction in the saturate fraction as the TOP proportion increases. The scatter in the data for the resin and aromatic fractions in both the unaged and aged bitumens, and also the saturate fraction in the aged bitumen samples, is too large to be able to conclusively say that the slopes of the linear regression are non-zero.

Table 29: Effect of TOP on SARA fractions in 180/200 penetration grade bitumens before and after ageing.

	Asphaltenes		**Resins**	
	Unaged	**Aged**	**Unaged**	**Aged**
Coefficient of Slope	0.1186	0.2211	0.7146	0.4266
Number of Observations	4	4	4	4
Standard Error of Slope	0.01608	0.03162	0.2250	0.1712
t-test value to test if slope = 0	7.378	6.991	3.176	2.492
Critical t-statistic (α = 0.05, d.f. = 3)	3.182	3.182	3.182	3.182
Is Slope Non-Zero at 95% Level of Significance	**YES**	**YES**	**NO**	**NO**
	Aromatics		**Saturates**	
	Unaged	**Aged**	**Unaged**	**Aged**
Coefficient of Slope	- 0.7006	- 0.5191	- 0.1326	- 0.1286
Number of Observations	4	4	4	4
Standard Error of Slope	0.2310	0.1950	0.007427	0.07342
t-test value to test if slope = 0	-3.033	-2.663	-17.86	-1.751
Critical t-statistic (α = 0.05, d.f. = 3)	3.182	3.182	3.182	3.182
Is Slope Non-Zero at 95% Level of Significance	**NO**	**NO**	**YES**	**NO**

10.5.2 Change in Composition upon Ageing

The change in the fractional composition of the TOP modified bitumen after ageing is shown in Table 30. Because the saturates are relatively unreactive compared to the other fractions the proportion of saturates does not tend to change. This is illustrated graphically in Figure 31. The scatter in the data for the resins and aromatics prohibits any significant conclusions regarding the relationship between TOP content and change in the fraction of resins and aromatics to be drawn. However, it does appear that the proportion of resins and asphaltenes increases at the expense of the aromatic molecules. A similar result was observed by Petersen (1984) who reported that the proportion of saturates does not change and the aromatics and resins are converted to asphaltenes upon ageing.

Table 30: Change in fractional composition of TOP modified bitumens after ageing.

Bitumen	Asphaltenes	Polar Aromatics	Naphthene Aromatics	Saturates	Change in Colloidal Index
B200-T0	+6.6	+8.0	-14.1	-0.5	+0.11
B100-T0	+7.4	+2.9	-11.4	+1.0	+0.17
B150-T6	+6.8	+14.6	-19.8	-1.6	+0.09
B100-T15	+7.6	+16.0	-24.4	+0.8	+0.16
B50-T12	+9.0	+9.0	-16.3	-1.7	+0.14
B50-T25	+9.1	+1.0	-9.0	-1.2	+0.15
TOP	+13.9	-11.5	-2.2	-0.2	+0.18

If the slopes of the regression analysis for each fraction are compared before and after ageing, it is possible to determine if there is any interaction between the proportion of TOP in the bitumen and the ageing process. If the slopes are significantly different then there is sufficient evidence to conclude that TOP has an effect upon the proportion of the SARA fractions obtained after ageing. Table 31 shows that the slope of the plot of asphaltene fraction against TOP content increases significantly from 0.1186 before ageing to 0.2211 after ageing. In practical terms this implies that the presence of TOP causes an increase in the proportion of asphaltenes obtained after ageing over and above that which would be expected if a conventional, unmodified bitumen was aged. No significant differences were found in the slopes of the regression lines for the resin, aromatic or saturate fractions.

It might be argued that the increase in the slope of the linear regression of asphaltene fraction against TOP content after ageing is a result of the ageing characteristics of the bitumen grade used to make the TOP modified bitumen. However, the observed linear relationship is more likely to be caused by the TOP and not the bitumen. It can be seen in Table 27 that the asphaltene content of TOP increases dramatically from 4.8% before ageing to 18.7% after ageing. It was surmised earlier that the proportion of each fraction in the blended bitumen could be estimated from the weighted mean of the proportion of that particular fraction in each of its constituents. Therefore, there is some anecdotal evidence to suggest that TOP causes an increase in the proportion of asphaltenes over and above what would be expected upon ageing of the unmodified bitumen alone.

Table 31: Analysis of the effect of TOP on the composition of aged TOP modified 180/200 bitumen.

	Asphaltenes		Resins	
	Unaged	**Aged**	**Unaged**	**Aged**
Coefficient of Slope	0.1186	0.2211	0.7146	0.4266
Number of Observations	4	4	4	4
Residual Sum of Squares	0.01845	0.7139	36.15	20.93
Standard Error of Slope	0.01608	0.03162	0.2250	0.1712
Pooled Residual Mean Square	0.2246		14.27	
Standard Error of Difference Between Slopes	0.03547		0.2827	
Difference in Slopes	- 0.1025		0.2880	
t-test value	-2.889		1.019	
Critical t-statistic (one-tail, $\alpha = 0.05$, d.f. = 4)	2.132		2.132	
Are Slopes Different at 95% Level of Significance	**SLOPES ARE DIFFERENT**		**NO DIFFERENCE IN SLOPE**	
	Aromatics		**Saturates**	
	Unaged	**Aged**	**Unaged**	**Aged**
Coefficient of Slope	- 0.7006	- 0.5191	- 0.1326	- 0.1286
Number of Observations	4	4	4	4
Residual Sum of Squares	38.10	27.14	0.03938	3.849
Standard Error of Slope	0.2310	0.1950	0.007427	0.07342
Pooled Residual Mean Square	16.31		0.9721	
Standard Error of Difference Between Slopes	0.3023		0.0738	
Difference in Slopes	- 0.1815		- 0.0041	
t-test value	- 0.600		- 0.055	
Critical t-statistic (one-tail, $\alpha = 0.05$, d.f. = 4)	2.132		2.132	
Are Slopes Different at 95% Level of Significance	**NO DIFFERENCE IN SLOPE**		**NO DIFFERENCE IN SLOPE**	

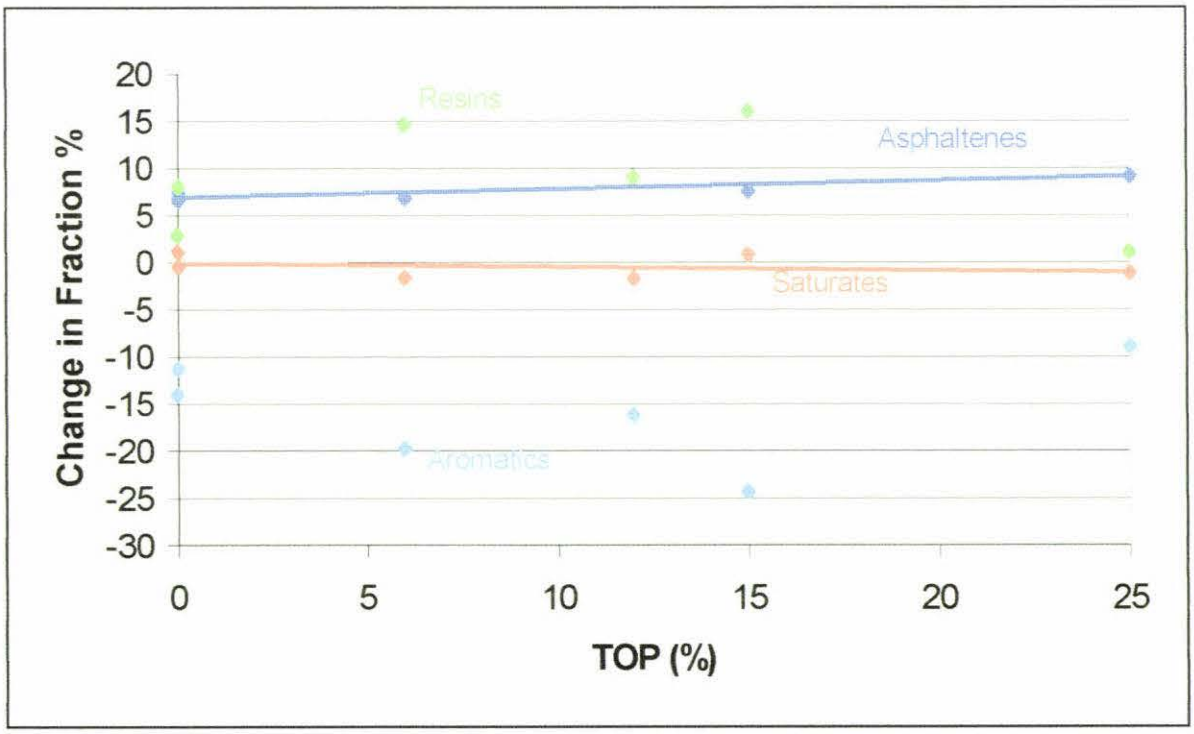


Figure 31: Effect of TOP on change in bitumen composition after ageing.

10.5.3 Anticipated Effect of TOP on Field Performance

How the change in composition may affect the bitumen performance in the field is a matter of conjecture. A reduction in the saturate fraction is desirable since saturates can promote flocculation of the asphaltenes. Flocculation of the asphaltenes may cause excessive stiffness and subsequently might result in cracking (Petersen, 1984). Wax type molecules present in the saturate fraction have been implicated in causing tenderness problems and thermal cracking in asphalt concrete (Crawford, 1986; Petersen *et al*, 1994a). A high proportion of asphaltenes can cause fatigue cracking, ravelling and excessive age hardening in asphalt concrete (Finn *et al*, 1990). Conversely, a low proportion of asphaltenes has been implicated in contributing to rutting and tenderness in asphalt concrete. Although Figure 30 shows that within a particular penetration grade the asphaltene content increases as the TOP content increases, the increase is still within the bounds of what would be termed a typical proportion of asphaltenes (see Section 4.2.1).

A high aromatic content has been associated with thermal cracking, resistance to age hardening and improved ravelling resistance (Finn *et al*, 1990). Since TOP contains very little in the way of aromatic molecules, it has a diluting effect on the proportion of aromatics in the blended bitumen. Resins contribute to the ductility of the bitumen and are more susceptible to ageing than the aromatic and saturate fractions (Petersen, 1984; Roberts *et al*, 1991). They are also thought to be critical for maintaining the colloidal dispersion of the asphaltenes in the aromatic and saturate medium (Morgan and Mulder, 1995). In this sense, the proportion of resins can influence the durability.

It is possible to predict the likely effect on the bitumen performance of modifying Safaniya bitumen with TOP. Firstly, an increase in the proportion of the more reactive asphaltenes and resins, and a lower proportion of the solvating aromatic molecules suggests that the potential for increased age hardening is higher. This is what was observed in Figure 16, which shows that the ageing index increases as the proportion of TOP increases. Secondly, the higher asphaltene content of TOP modified bitumen is expected to provide increased rutting resistance and a low propensity towards producing tender asphalt concrete mixes. Thirdly, the risk of ravelling and fatigue cracking in asphalt concrete manufactured from TOP modified bitumen increases, especially upon ageing, due to the lower aromatic content and increased asphaltene content. And finally, since TOP modified bitumen contains a lower proportion of saturates and aromatics, the potential for thermal cracking in the asphalt concrete is low.

10.5.4 Colloidal Index

The colloidal index is the ratio of the dispersed phase in the bitumen to the solvating or dispersing phase. It has been correlated to aspects of bitumen performance such as durability, rheology and compatibility towards mixing with polymers (Ishai *et al*, 1988; Brûlé *et al*, 1986; Serfass *et al*, 1992). The colloidal index is calculated from Equation 5-4 (pg. 59) where the asphaltenes and saturates constitute the dispersed phase while the aromatics (naphthene aromatics) and resins (polar aromatics) make up the dispersing phase. A lower value of the colloidal index indicates a more compatible and durable bitumen since there is a greater proportion of the solvating phase compared to the highly reactive and associative asphaltene fraction and the less reactive but flocculation promoting saturate fraction.

A comparison of the colloidal index values of B50-T0, B50-T12 and B50-T25 is given in Table 27 and shows that the addition of TOP to a particular bitumen causes a reduction in the colloidal index. This is to be expected since TOP is rich in resins and deficient in saturates and asphaltenes. A similar trend is observed when comparing the colloidal index values of B100-T0 and B100-T15. However, it is perhaps more interesting to compare those bitumens that fall inside a particular penetration grade, i.e. B200-T0, B150-T6, B100-T15, B50-T25. Each has a penetration of between 180 and 200 dmm and a colloidal index of 0.29 despite the fact that they each have different TOP contents and were manufactured using bitumens of different penetration grades. A similar result is observed by comparing B100-T0 and B50-T12, which both have a penetration between 80 and 100 dmm and give colloidal index values of 0.31 and 0.33 respectively.

The estimated errors in determining the colloidal index of each of the bitumens are given in Table 27 and are determined from the errors associated with measuring the proportion of each of the SARA fractions. There does not appear to be any evidence to suggest that TOP has an appreciable affect on the colloidal index of the bitumen after ageing. Regardless of whether the bitumen has been aged or is unaged, the colloidal index of the TOP modified bitumens are similar to that of the unmodified bitumens that are of the same penetration grade and are certainly within the limits of the errors given in Table 27.

Figure 32 shows a plot of the penetration and the colloidal index against the proportion of asphaltenes in the bitumen. The colloidal index is also known as the Gaestel index and is described in Section 5.1.3. The relationship between the colloidal index and the asphaltene content is given in Equation 5-4. The colloidal index also increases as the penetration decreases (or viscosity increases), which is similar to the results obtained by Tuffour *et al* (1989). The penetration is also related to the asphaltene content. Since the asphaltenes can be thought of as the thickening agents in bitumen, it is to be expected that the penetration will decrease (i.e. the bitumen becomes harder) as the proportion of asphaltenes increases.

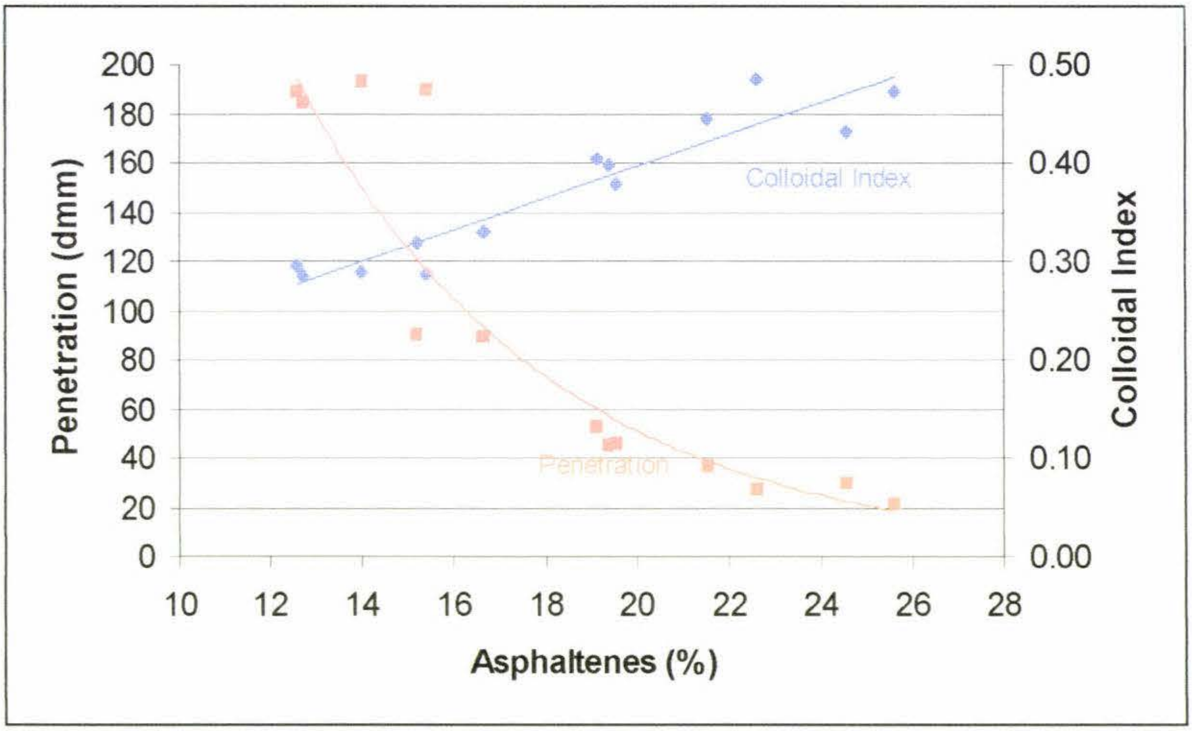


Figure 32: Relationship between colloidal index, penetration and asphaltene content.

11.0 Colloidal Properties

11.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is typically used to fractionate or analyse mixtures based on molecular size. GPC has been combined with high-pressure liquid chromatography (HPLC) equipment for the study of bitumen solutions and the resulting experimental arrangement is termed HP-GPC. Section 4.3.6 describes the effect that the operating conditions have on the quality of the information that can be gleaned from the chromatogram. The conditions under which the HP-GPC apparatus were operated during this investigation are described in Section 8.3.3.1.

The intention was to provide a coarse separation between the associated asphaltene particles and the remainder of the bitumen. By only using a single 1000 Å column, a fast flow rate of 2 mls/min and a relatively high bitumen concentration of 2%, an inefficient separation was deliberately obtained. The philosophy behind operating under these conditions was to prevent the asphaltene aggregates from completely breaking up by minimising the dilution and retention time in the column (Brûlé *et al*, 1986). This allowed an analysis of the effect that TOP has on the micellar nature of the asphaltene fraction in the bitumen. Toluene was chosen as the carrier solvent to minimise any disruption to the polar associations that are thought to be a major cause of the asphaltene aggregations.

Initially, a 10% solution of bitumen was used with the UV detector measuring the absorbance at 340 nm. However, the detector was too sensitive and the readings were off the scale. Subsequent analyses used a bitumen concentration of 2% w/w in toluene and the absorbance detection was shifted to 400 nm to allow more meaningful readings to be obtained.

It must be remembered that UV detection does not give a proportional representation of the mass passing through the column. UV detection at 400 nm is biased towards the asphaltene and resin molecules because they contain a higher proportion of conjugated aromatic components. Consequently, a strong signal is obtained for the asphaltene and resin fractions, which are eluted first due to their higher molecular weight and tendency to associate, while the aromatic and saturate fractions generate a weaker signal. Due to the higher absorbance of the asphaltene fraction, UV detection overestimates the mass proportion of asphaltene molecules in a bitumen sample. The lower absorbance measured for the saturate and aromatic fractions tends to underestimate the mass proportion of these molecules in the bitumen.

A typical chromatogram obtained during the investigation is shown in Figure 33. A common method of analysing the chromatogram is to divide it into three areas of equal elution time corresponding to large-molecular size (LMS), medium-molecular size (MMS) and small-molecular size (SMS) molecules (Yapp *et al*, 1991). The LMS molecules, which correspond to asphaltene aggregates, are eluted first followed by the MMS molecules. However, since the chromatograph was purposely operated so inefficiently, and it was the LMS region that was of interest, the SMS region was ignored and the MMS region that is represented in Figure 33 contains both MMS and SMS molecules.

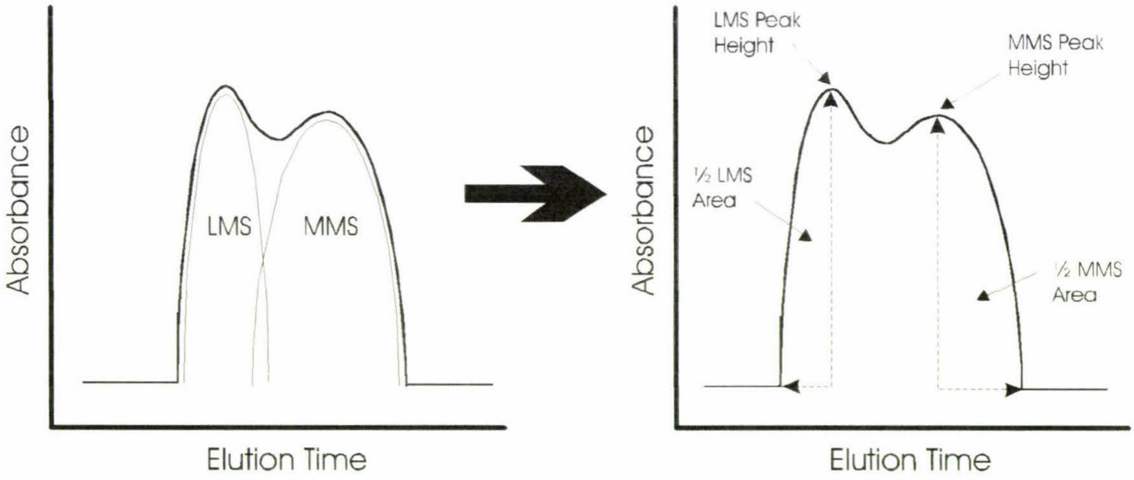


Figure 33: Typical GPC profile of bitumen.

The area under the curve can be integrated to determine the proportion of molecules passing through the column at a particular time. Because the two peaks in the chromatogram tend to overlap and are not distinct it becomes difficult to estimate the area under each curve. The profile in Figure 33 can be modelled as two intersecting parabolic shapes: the first parabola is caused by asphaltene aggregates and the second is due to the remainder of the bitumen species. The area under the LMS curve was estimated by measuring the area under the curve from the start of the chromatogram to the peak of the LMS curve as shown in Figure 33. This corresponded to half the area under the full LMS curve. Integrating the MMS peak in a similar manner gave half the area under the MMS peak. Validity for this method of analysis was given by the fact that the sum of the ½ LMS and ½ MMS areas, multiplied by 2, gave an area of 99 – 101%.

The GPC data for each bitumen is contained in Table 32. It is interesting to note that the elution times (measured at the peak height) for both the LMS and MMS fractions are very similar regardless of the grade of bitumen, the proportion of TOP in the blend, or whether the bitumen is aged or unaged. The elution time is a measure of the molecular mass. This implies that neither ageing nor the proportion of TOP affects the size of the asphaltene aggregates. A similar conclusion was obtained while examining the fluorescence CLSM images in Section 11.2.

Table 32: GPC data obtained for TOP modified bitumen.

Bitumen		**Elution Time**		**LMS Area (%)**	**Ratio of Peak Heights**
		LMS	**MMS**		
B200-T0	Unaged	3.52	4.35	32.43	0.949
B100-T0	Unaged	3.50	4.34	36.97	1.105
B100-T15	Unaged	3.52	4.30	36.07	1.109
B150-T6	Unaged	3.57	4.38	34.19	1.051
B50-T0	Unaged	3.55	4.29	36.95	1.140
B50-T12	Unaged	3.49	4.28	37.81	1.190
B50-T25	Unaged	3.51	4.30	37.77	1.113
B200-T0	Aged	3.58	4.41	35.63	1.133
B100-T0	Aged	3.52	4.37	38.20	1.232
B100-T15	Aged	3.52	4.27	37.89	1.253
B150-T6	Aged	3.56	4.38	36.88	1.211
B50-T12	Aged	3.50	4.25	38.31	1.328
B50-T25	Aged	3.43	4.12	37.79	1.289

A chromatogram of neat TOP and neat aged TOP only had ~10% of the absorbance of the bitumen samples at 400 nm. The low absorbance indicates that TOP contains very little of the aromatic and conjugated aromatic systems thought to be responsible for the absorbance. The neat TOP and neat aged TOP chromatograms consisted of a single broad peak at 4.69 minutes and 4.48 minutes respectively, suggesting that TOP elutes in the MMS fraction of the chromatograph.

Five replicate chromatograms of the B200-T0 bitumen were produced to estimate the error associated with determining the LMS area in the chromatogram. The five replicates gave an average LMS area of 32.4% for the B200-T0, with a standard deviation of 0.369 and an estimated error of ± 0.46 at the 95% level of significance. Consequently, the least significant difference in the LMS that can be detected between two samples is 0.92%.

No relationship between the proportion of TOP in the bitumen and the LMS, or change in LMS, was detected while analysing the data in Table 32. For example, the B50-T0, B50-T12 and B50-T25 bitumens, which contain 0%, 12% and 25% TOP respectively, give LMS areas of 36.95%, 37.81% and 37.77% respectively. The range of these results is less than the least significant difference determined earlier. The B100-T0 and B100-T15 bitumens had TOP contents of 0% and 15% and LMS areas of 36.97 and 36.07% respectively. Similar results can be calculated for the aged samples.

The fact that no relationship between the proportion of TOP in the bitumen and the LMS area was detected is hardly surprising since the UV detector response is much smaller for TOP than it is for bitumen. The GPC profiles are dominated by the absorbance of the bitumen and consequently the presence of TOP is not identified by the UV detector. What is important is that the proportion of TOP in the bitumen does not appear to affect the size of the LMS area. This suggests that TOP does not increase the quantity of molecules that contain aromatic ring systems in the bitumen.

However, a relationship was found between the penetration of the bitumen used in the blend and the change in LMS area that occurred on ageing. This relationship is given in Figure 34. A greater change was detected for the softer 180/200 bitumens than for the harder grades. For example, the LMS area of B200-T0 bitumen (which has a penetration of 189 dmm) increased by 3.21% upon ageing, while the LMS area of the B50-T12 and B50-T25 (which was manufactured from a bitumen with a penetration of 45 dmm) only changed by 0.50 and 0.02% respectively. Based upon the previously derived estimate of the error in the chromatograms these latter changes in LMS are hardly significant.

A plot of the penetration of the bitumen used to make the TOP modified blend versus the LMS area is shown in Figure 35. The LMS area tends to increases as the penetration decreases. A similar relationship is seen the plot of the penetration of the aged samples versus the LMS area shown in Figure 36. This supports the notion that the LMS area is related to the associated, dispersed phase, which is thought to have a significant effect upon the physical properties of the bitumen (Jennings *et al*, 1993).

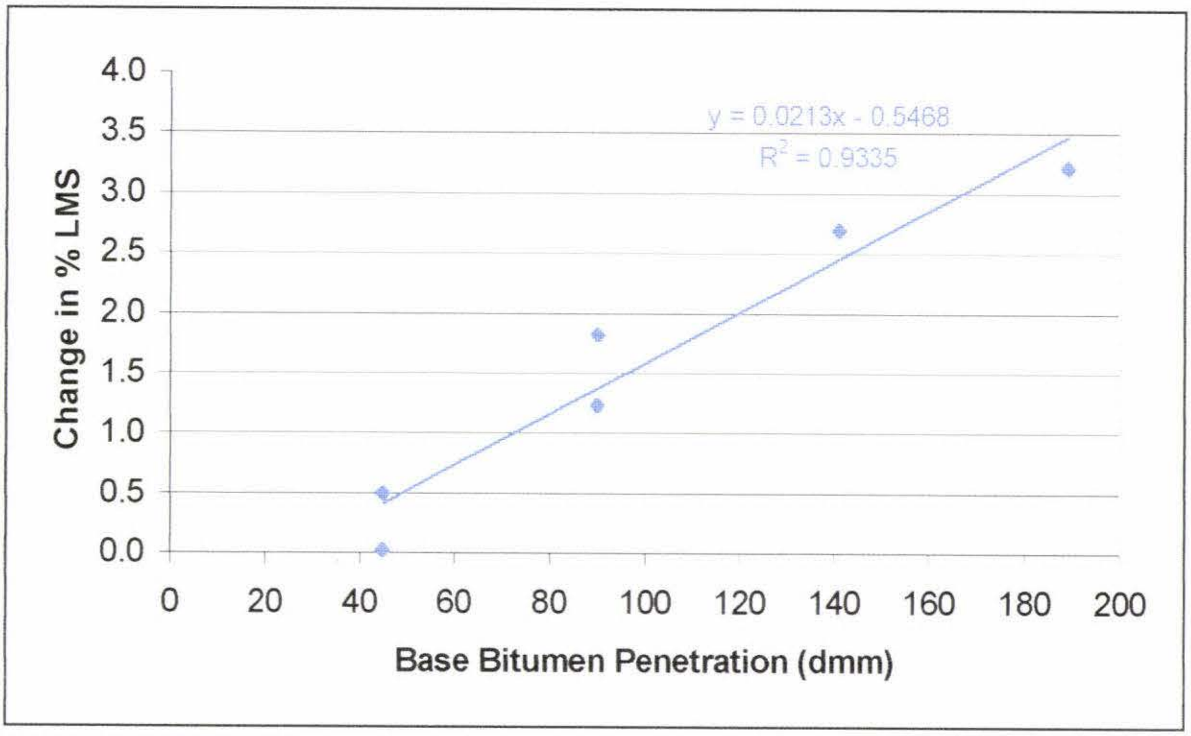


Figure 34: Relationship between base bitumen penetration and the change in LMS area after ageing.

Similar results are shown in Figure 37 for the relationship between the ratio of the LMS to MMS peak heights and the penetration of the bitumen used to make the TOP modified blend. As the penetration of the base bitumen used to make the TOP modified blend decreases the height of the LMS peak increases relative to that of the MMS peak. It is apparent that as the bitumen is oxidised the aromatic nature (as measured by UV absorbance at 400nm) of the MMS molecules decreases or the aromatic nature of the LMS molecules increases or both. Once again, no effect of the TOP content on the shape of the chromatogram is noticed.

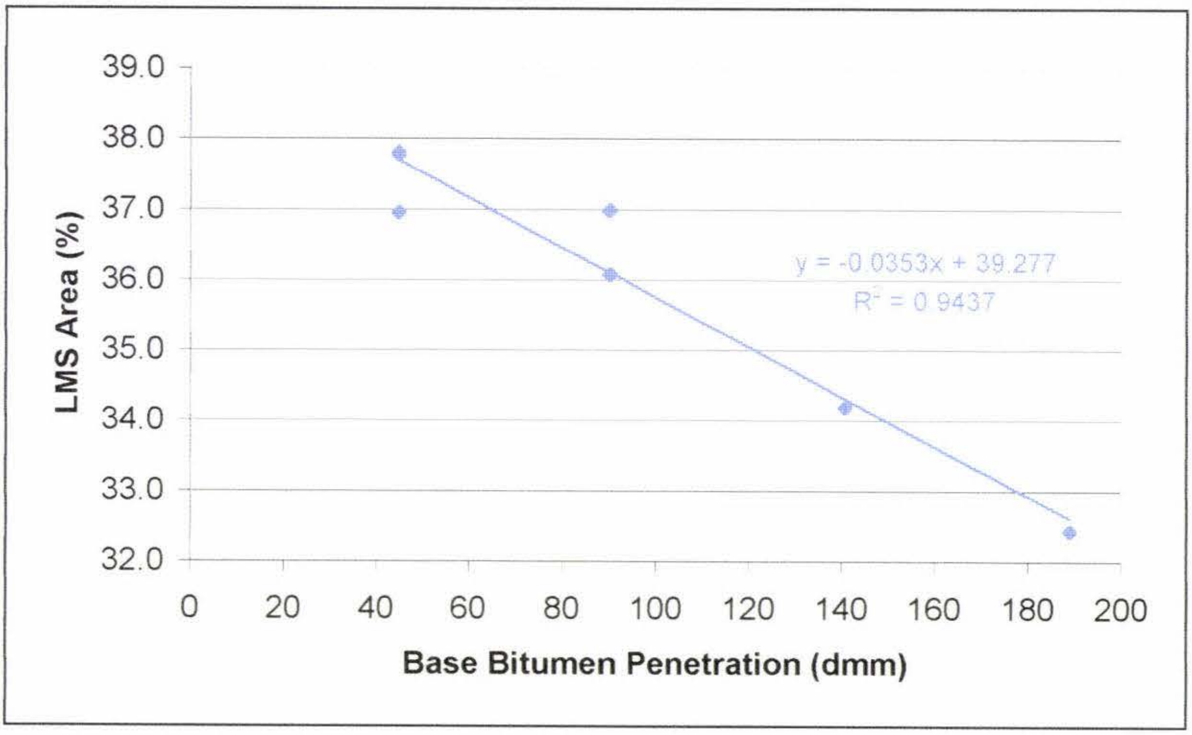


Figure 35: Relationship between base bitumen penetration and LMS area.

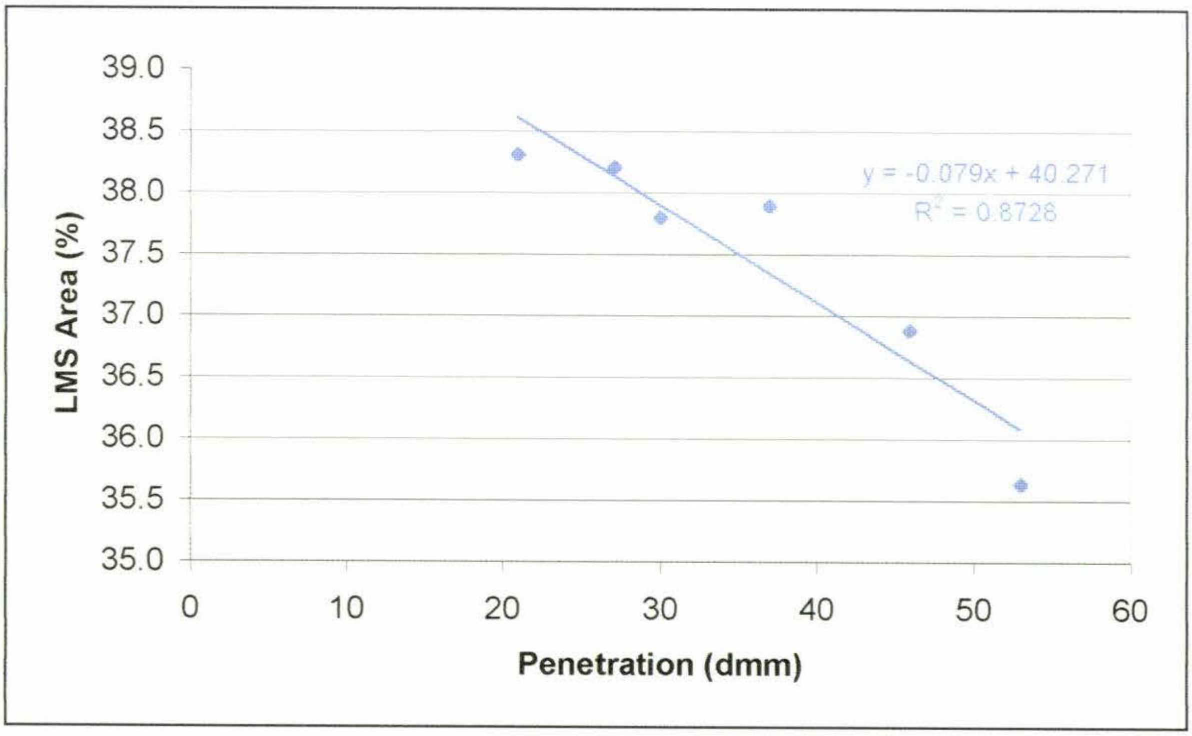


Figure 36: Relationship between penetration and LMS area in aged bitumen samples.

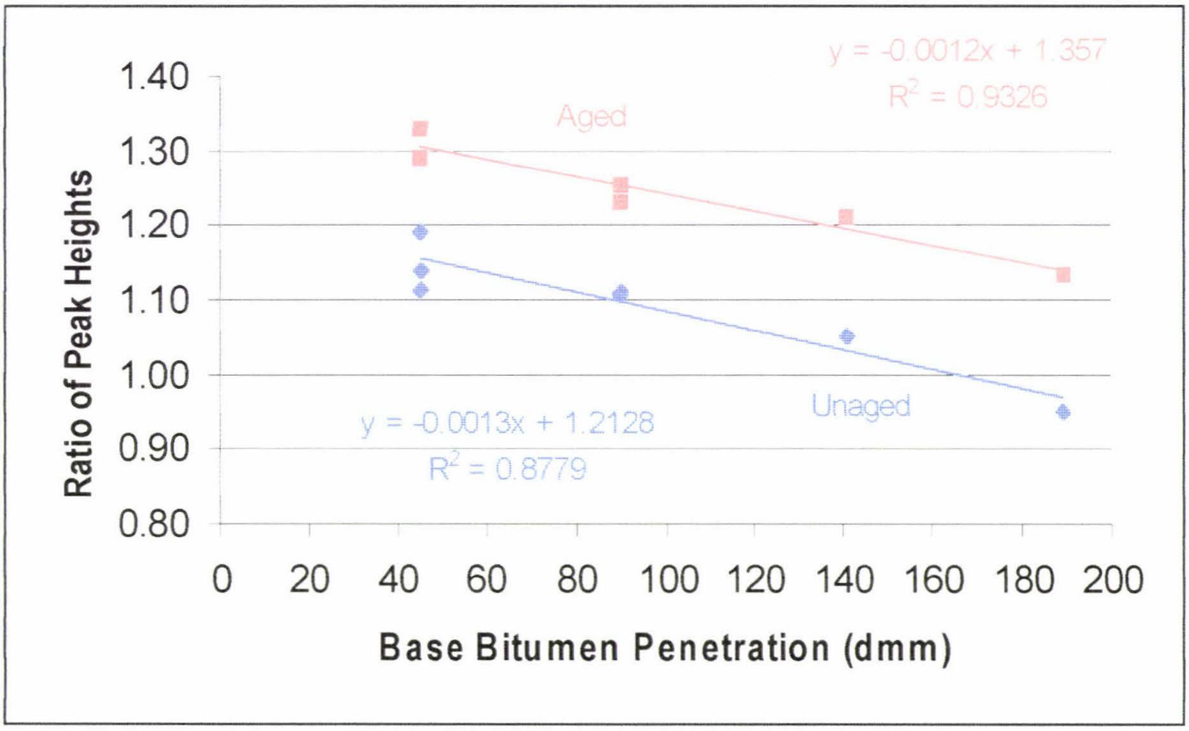


Figure 37: Relationship between base bitumen penetration and the ratio of the LMS to MMS peak heights.

11.2 Microscopical Examination of Bitumen

It has long been recognised that it is not only the amount, but also the nature of the asphaltene phase that has a major effect on the bitumen's rheological properties (Heithaus, 1960; Petersen, 1984; Morgan and Mulder, 1995). The extent to which the highly aromatic, polar asphaltene phase associates with itself has a significant impact upon the physical performance of the bitumen. 'Gel' bitumens are highly associated and contain a greater proportion of asphaltenes than the less associated 'sol' bitumens. As a consequence, gel bitumens exhibit different rheological properties from 'sol' bitumens.

It was of interest to know if the addition of TOP to the bitumen had any effect upon the extent of association between the asphaltene aggregates. TOP is believed to be highly resinous and according to the current models of bitumen structure would be expected to contribute towards the dispersion of the asphaltene phase.

The temperature and the chemical environment are known to affect the structure of the asphaltene phase. A change in the temperature or chemical composition can force associations (or disassociations) that are not present in the original bitumen sample. "It seems important to leave the colloidal structure of the bitumen system intact when structural observation investigations are undertaken" (Loeber *et al*, 1998). This is probably more important for paving grade bitumen, which has a more dispersed, sol structure, than for industrial bitumens, which have a highly associated gel structure. Due to the associated nature of gel bitumens, changes in the chemical environment are less likely to appreciably change the colloidal structure.

Perhaps the technique that shows the most promise for examining the structure of the asphaltene phase *in-situ* is confocal laser scanning microscopy (CLSM). Under ideal conditions CLSM allows structures as small as ~200 nm to be observed (Rowland and Nickless, 2000). The bitumen is imaged at ambient temperature and pressure and requires none of the preparation required by electron microscopy. Furthermore, CLSM allows an internal section of the sample to be imaged rather than just the surface.

The CLSM images of the unaged and aged TOP modified bitumens are shown in Figure 38 – Figure 52. Fluorescing regions can clearly be seen in each of the neat or TOP modified bitumen samples. The fluorescence is attributed to conjugated aromatic ring systems that are characteristic of asphaltene molecules. The asphaltene structure is seen to form a dispersed phase in the continuous maltene matrix, which is representative of the 'sol' structure expected of a paving grade bitumen. The size of the fluorescing particles is in the region of 2 – 7 μm, which is similar to the size of asphaltene aggregates observed by Loeber *et al* (1996).

The structure of the asphaltene phase does not appear to alter radically upon ageing or upon the addition of TOP to the bitumen. Unfortunately, this makes a quantitative assessment of any observed changes difficult. Probably the most promising aspect is that modification of bitumen with TOP does not cause the structure of the bitumen to change appreciably, even after ageing.

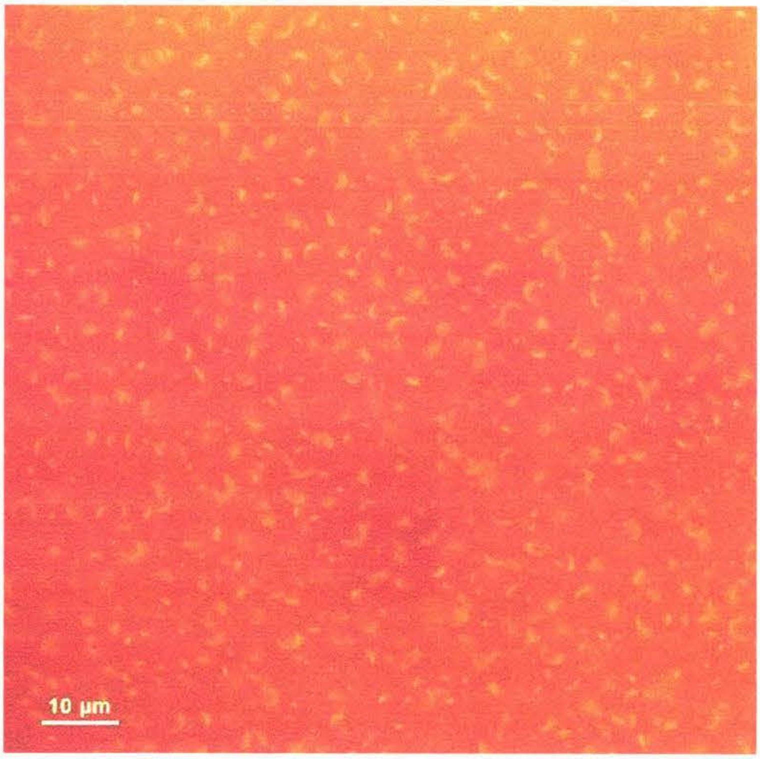


Figure 38: CLSM image of B200-T0 magnified 1000 times.

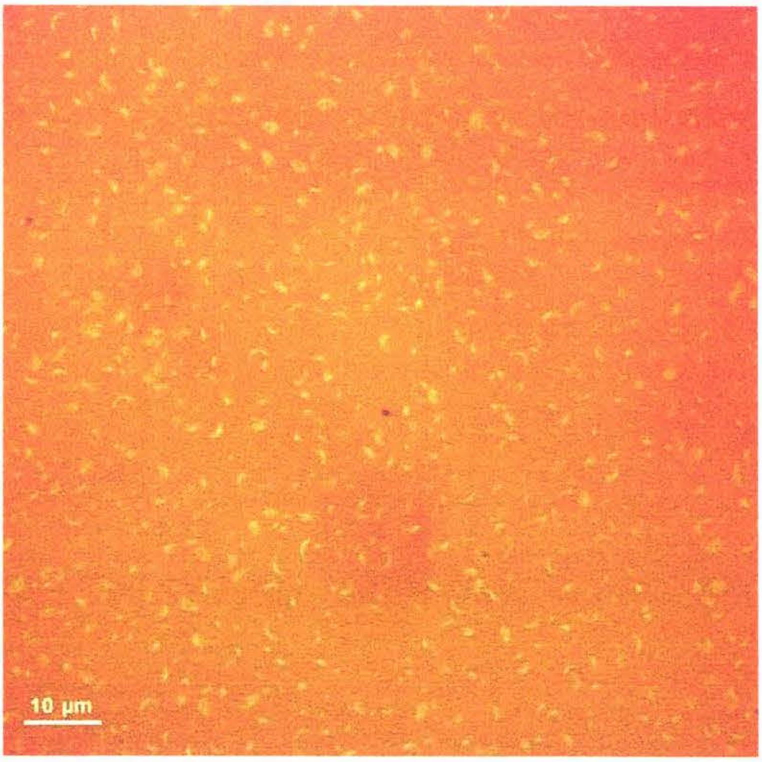


Figure 39: CLSM image of B150-T6 magnified 1000 times.

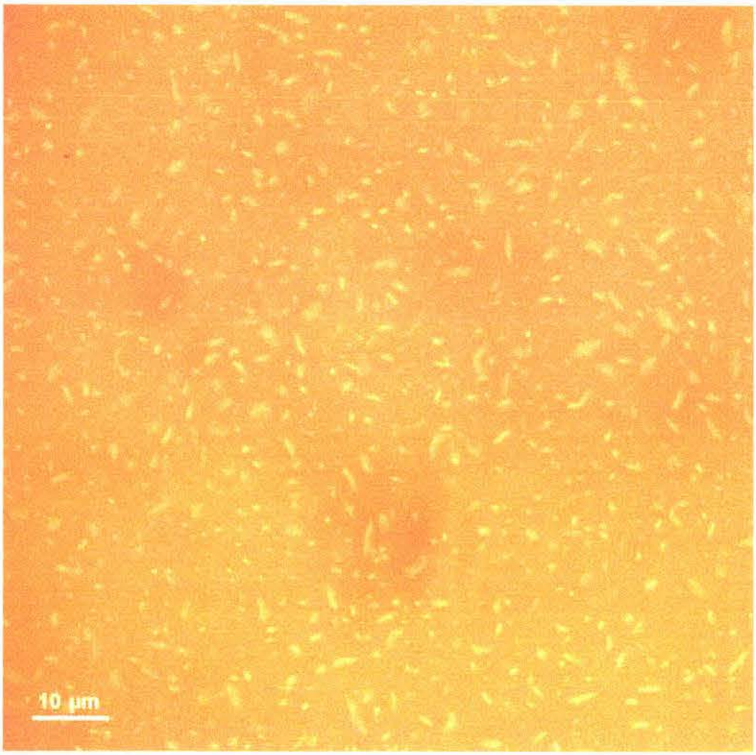


Figure 40: CLSM image of B100-T0 magnified 1000 times.

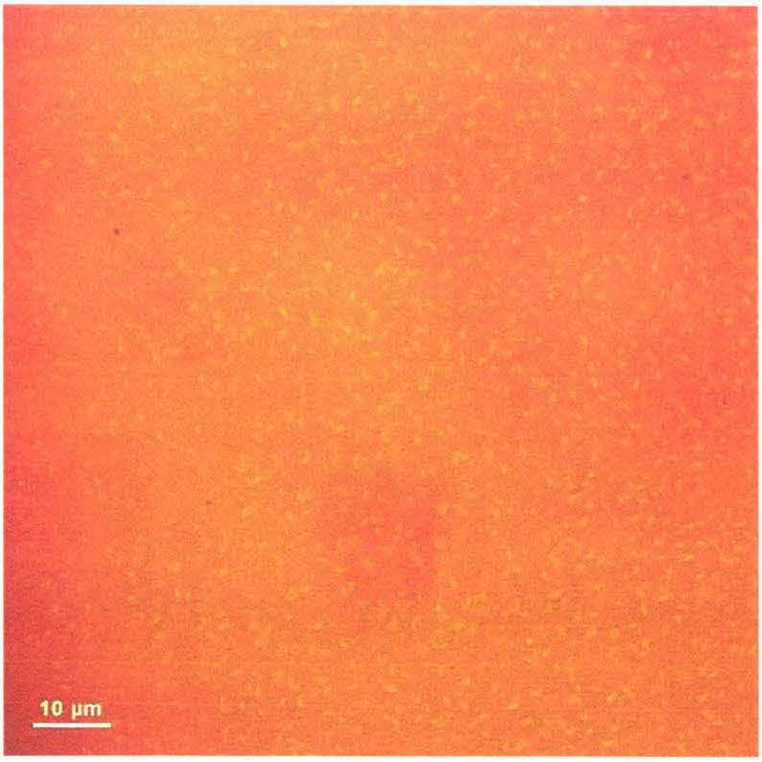


Figure 41: CLSM image of B100-T15 magnified 1000 times.

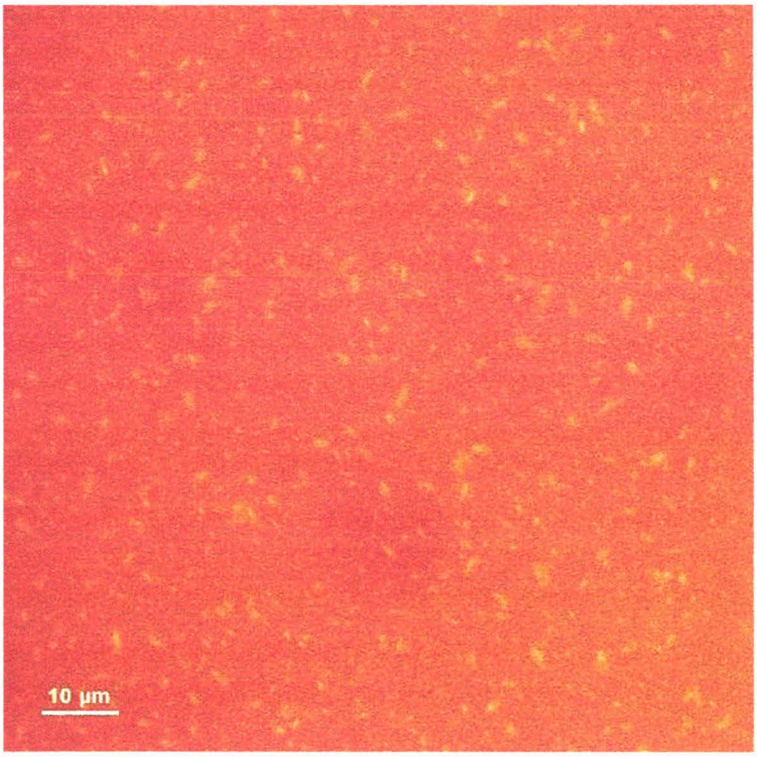


Figure 42: CLSM image of B50-T0 magnified 1000 times.

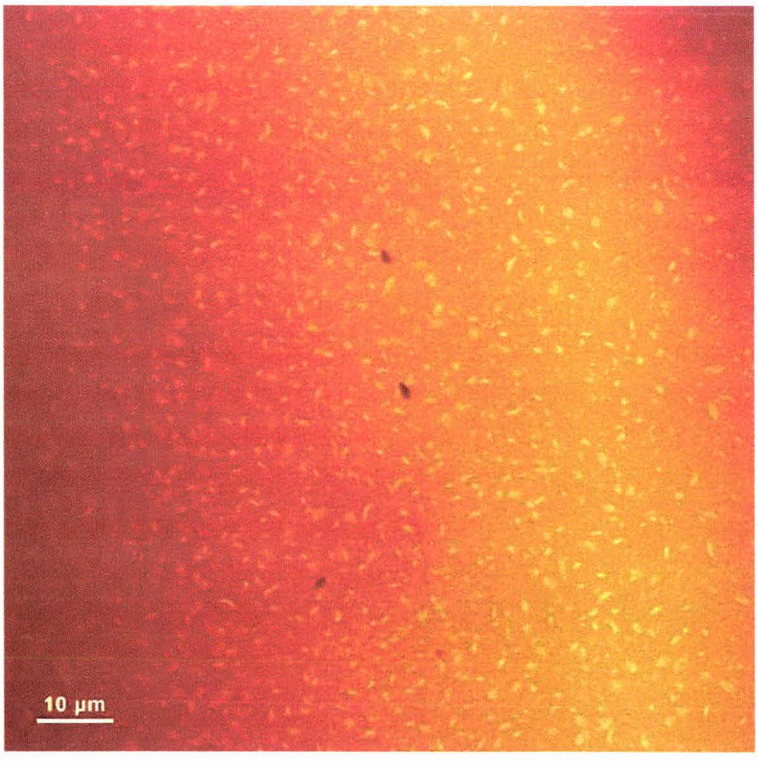


Figure 43: CLSM image of B50-T12 magnified 1000 times.

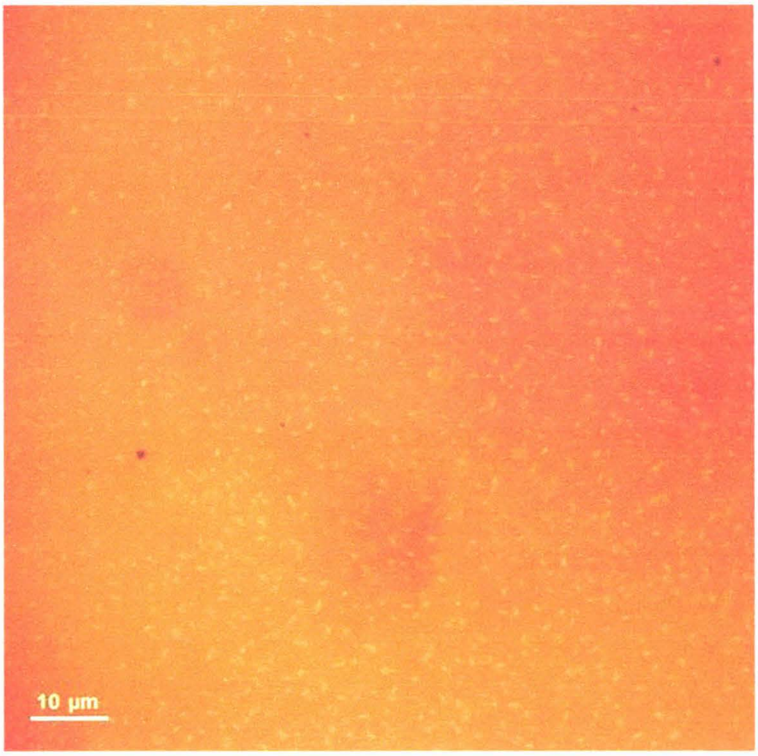


Figure 44: CLSM image of B50-T25 magnified 1000 times.

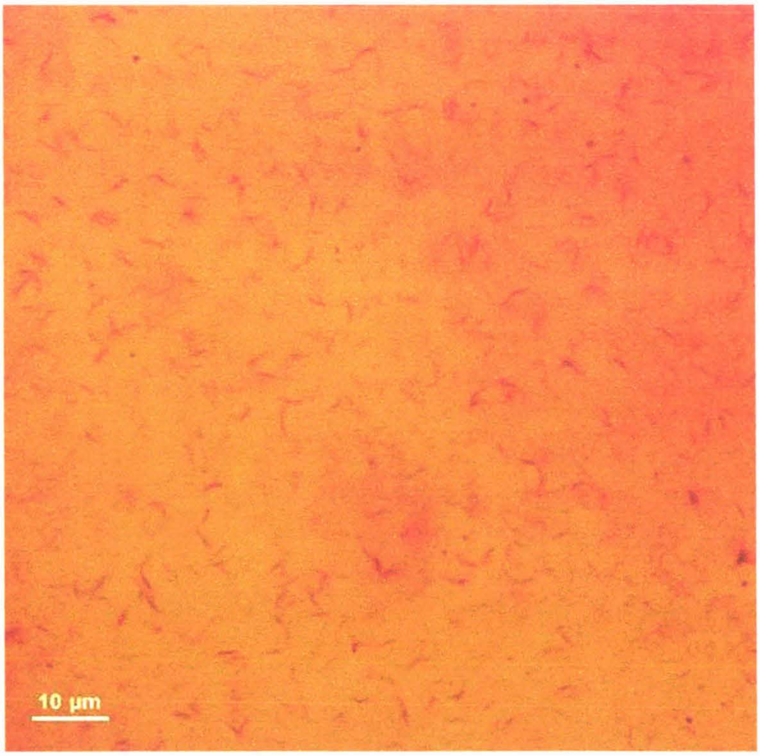


Figure 45: CLSM image of TOP magnified 1000 times.

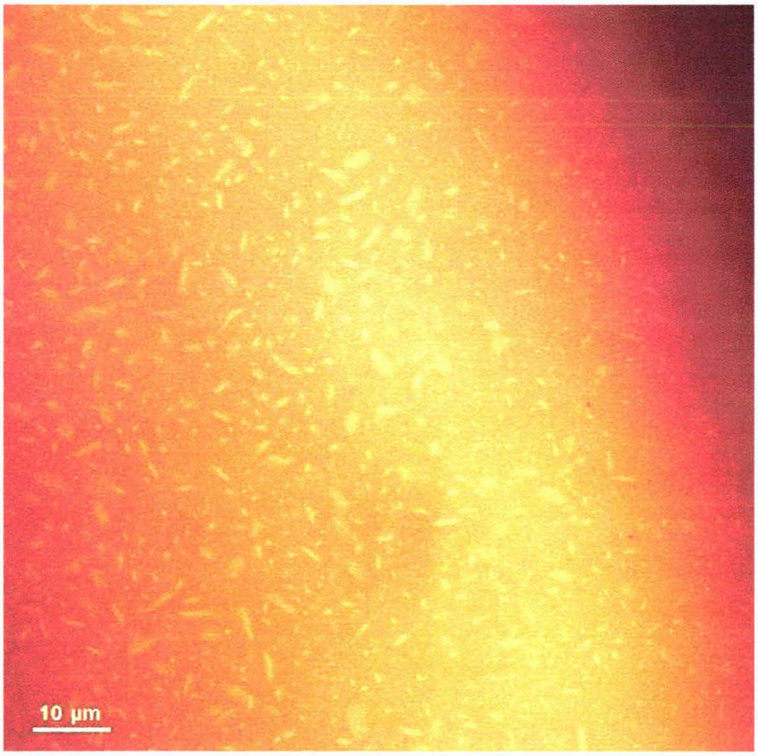


Figure 46: CLSM image of aged B200-T0 magnified 1000 times.

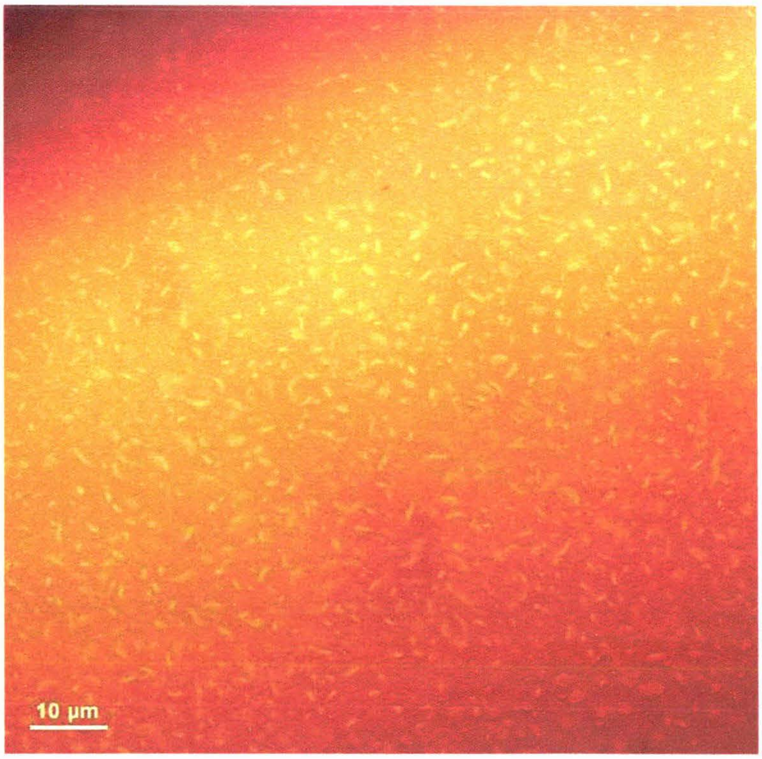


Figure 47: CLSM image of aged B150-T6 magnified 1000 times.

Figure 48: CLSM image of aged B100-T0 magnified 1000 times.

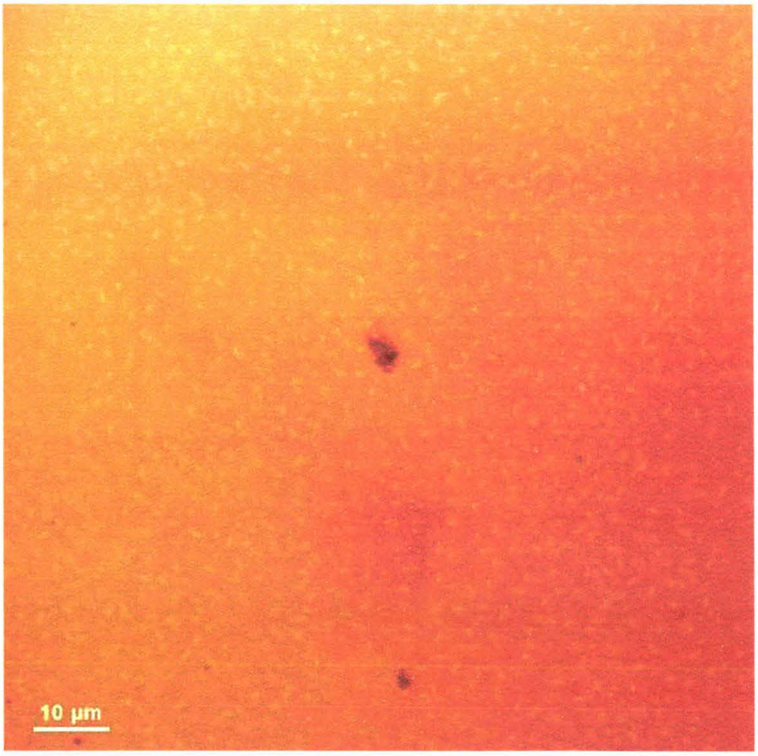


Figure 49: CLSM image of aged B100-T15 magnified 1000 times.

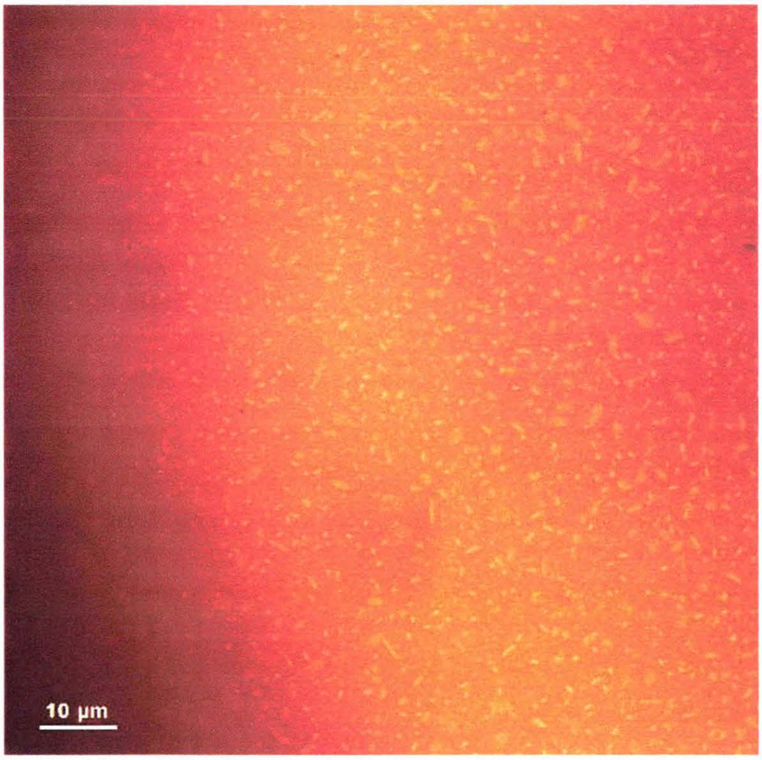


Figure 50: CLSM image of aged B50-T12 magnified 1000 times.

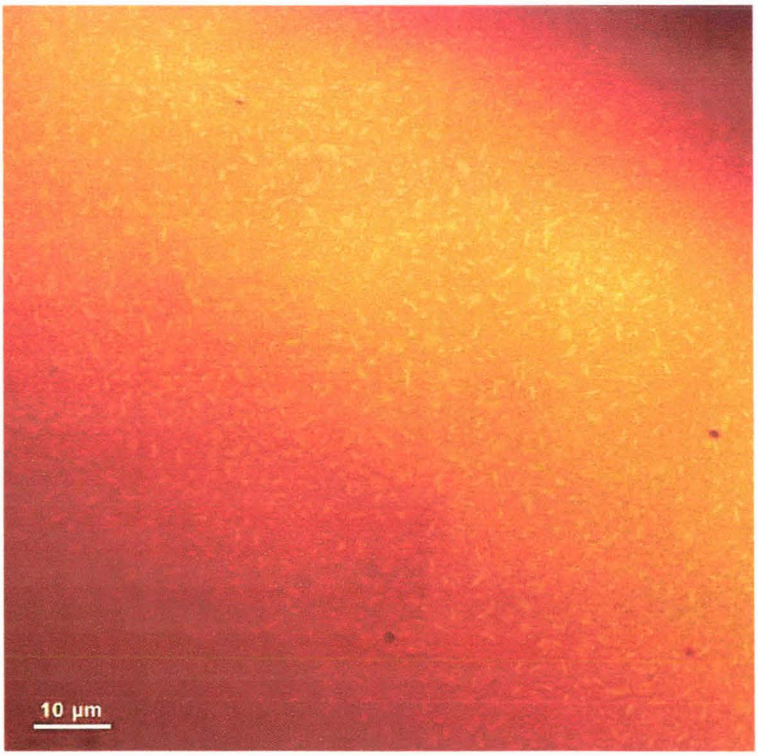


Figure 51: CLSM image of aged B50-T25 magnified 1000 times.

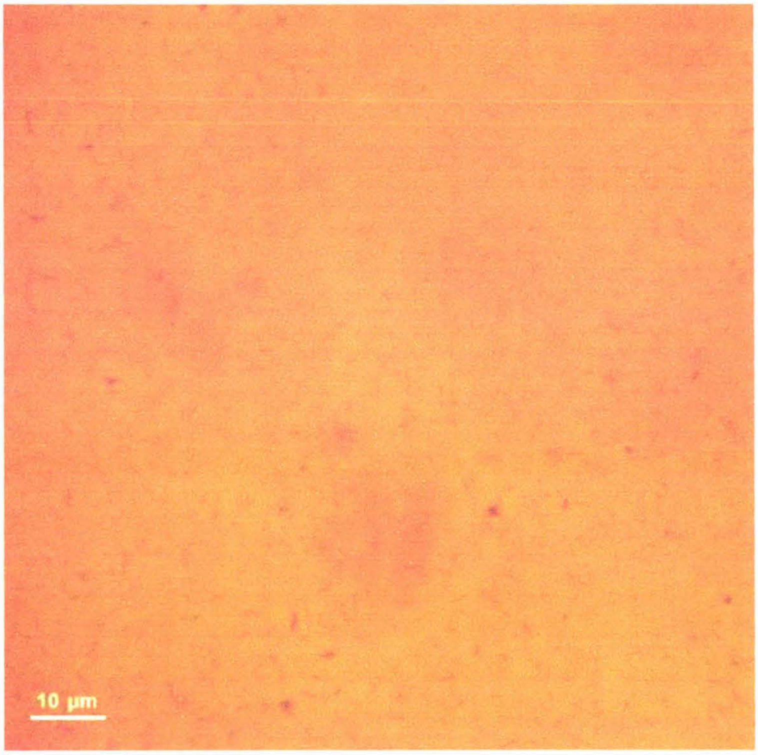


Figure 52: CLSM image of aged TOP magnified 1000 times.

The effect that any chemical reaction between the TOP and asphaltenes has on the strength and wavelength of the fluorescence emission is not known. Similarly, ageing of bitumen will result in oxidation of the asphaltene phase, which is likely to alter the fluorescence emission spectra. Li and Wan (1995) observed that freshly precipitated asphaltenes exhibited strong fluorescence, but after exposure to air for 48 hours the fluorescence emission depleted to almost zero. It is possible that oxidation of the asphaltenes results in a fluorescence quenching mechanism. Solvent effects are also known to affect the fluorescence (Guibault, 1990). In Section 10.3 it was shown that the addition of TOP causes an increase in the solvent power of the maltene phase in aged samples. Consequently, it is probably not prudent to draw conclusions from any minor differences in the CLSM images until the effect of TOP on the fluorescent properties of the asphaltene phase are known.

However, the use of CLSM for observing the asphaltene phase *in-situ* is a relatively new field and it is likely that improvements to the fluorescence observed and to the resolution will allow more meaningful results to be obtained. The images presented in Figure 38 to Figure 52 are only two-dimensional cross-sections of the bitumen samples. It is possible to construct three-dimensional images in CLSM. Three-dimensional images may provide more information on the size, shape, and structure of the asphaltene phase.

12.0 Adhesive Properties

When discussing the adhesive properties of bitumen in relation to road surfaces such as asphalt concrete and chipseal, it is important to realise that the industry has defined two types of adhesion: active adhesion and passive adhesion. Tarrer and Wagh (1991) provide a very basic definition of active and passive adhesion. Essentially, active adhesion is the ability of the bitumen to displace water (and other contaminants) and to wet and adhere to the surface of the aggregate. Passive adhesion is defined as the ability of a bitumen, once it has wet and adhered to the surface of the aggregate, to resist displacement by water and other contaminants. The two types of adhesion are distinctly different, but complimentary and both are crucial for the successful construction and durability of a bituminous pavement.

12.1 Active Adhesion

Adhesion agents are commonly added to the bitumen used for chipsealing in New Zealand. The adhesion agents are usually alkyl amine, alkyl amidoamine or alkyl imidazoline derivatives. The role of the adhesion agent is to promote wetting of the aggregate surface by the bitumen in the presence of moisture. In effect, adhesion agents impart active adhesion properties to the bitumen. Because the New Zealand climate is changeable, it is not unusual for the sealing chip to contain surface moisture when chipsealing.

The effectiveness of the adhesion agent in promoting wetting of the aggregate by the bitumen in the presence of moisture can be evaluated using the Vialit test. A brief description of this test is contained in Section 8.3.4.1. The degree of adhesion is assessed by counting the proportion of chips retained by the bitumen after attempting to dislodge them by applying a standard impact force.

Ball *et al* (1993) expressed concerns that the acids present in TOP could potentially minimise the effectiveness of the amine based adhesion agents by reacting with them to form inactive salts or amides. Therefore, it was thought necessary to evaluate the effect of TOP on the active adhesion of bitumens containing an alkyl amine adhesion agent. The results of the adhesion testing are given in Table 33. Each of the bitumens were dosed with

1.0% Diamine OLB adhesion agent by mass. The aggregate used was a grade 3 sealing chip obtained from Te Matai Road Quarry, near Palmerston North. Each of the TOP modified bitumens were chosen so that the viscosity of each bitumen would be similar at the test temperature as measured by their penetration values. The ability of an adhesive to effectively wet a surface is partially governed by the viscosity of the adhesive (Kinloch, 1987). Therefore, by using bitumens that have similar viscosities, any interference from viscosity effects can be minimised.

Figure 53 clearly shows that TOP has a severe adverse effect on the active adhesion of the bitumen. Current specifications for the use of adhesion agent in chipsealing in New Zealand usually require that a minimum of 80% of chips are retained during the Vialit test (TNZ M/13, 1989). An interpolation of Figure 53 shows that any modification of the bitumen with more than 4% TOP is unlikely to give the bitumen sufficient active adhesion to be used for routine chipsealing operations. Knowing that adhesion agents tend to degrade when stored even for a few hours at the elevated temperatures used in chipsealing, and that they are often used at dosages as low as 0.5%, only exasperates the situation. Consequently, it is apparent that TOP interacts with the adhesion agents in such a way as to render them ineffective.

Table 33: Active adhesion properties of TOP modified bitumen as determined by the Vialit test.

Bitumen	Penetration (dmm)	TOP Content (%)	Chips Retained (%)	
B200-T0	189	0	98 98 92 93	**avg. = 95**
B150-T6	185	6	75 70 76 76	**avg. = 74**
B100-T15	193	15	33 37 46 55	**avg. = 43**
B50-T25	190	25	4 6 7 10	**avg. = 7**

The proportion of chips retained by B200-T0 and B50-T25 bitumen that contained no Diamine OLB was zero in both cases. It appears that in the absence of adhesion agent, both conventional and TOP modified bitumen have no measurable active adhesion properties.

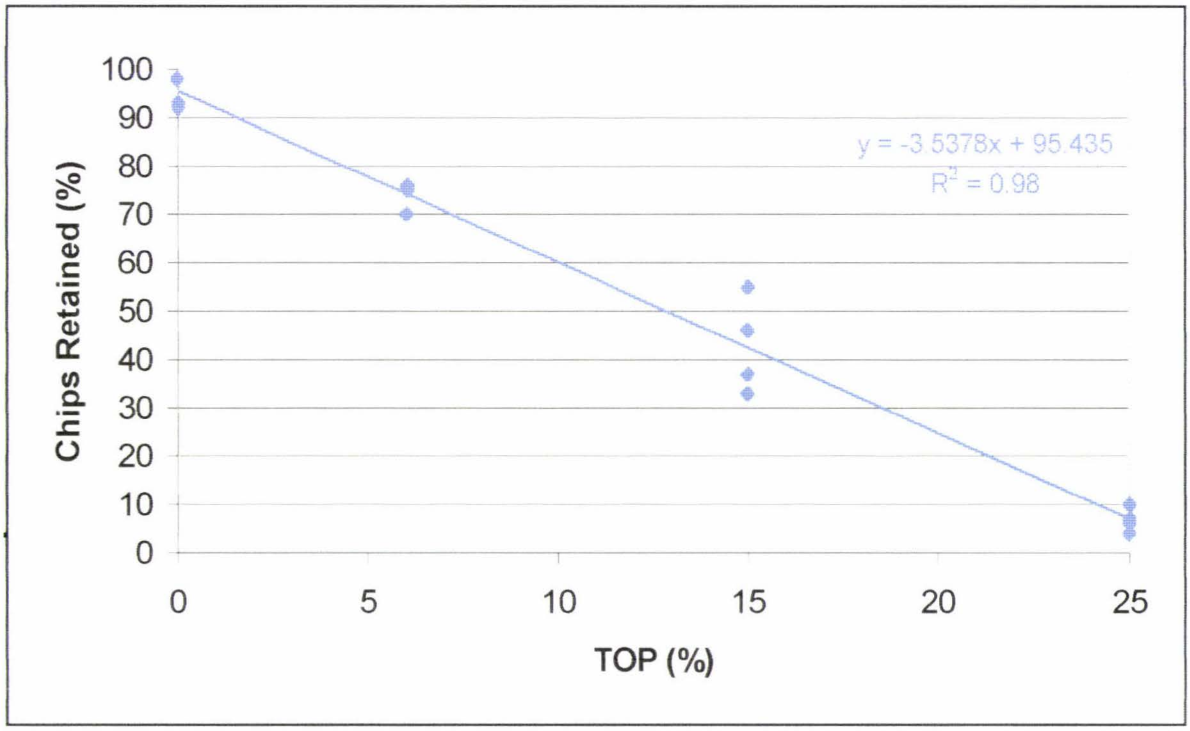


Figure 53: Effect of TOP on active adhesion properties of bitumen.

12.2 Passive Adhesion

While active adhesion tends to be more important for the successful construction of chipseals, passive adhesion plays a more significant role in the long-term ability of the bitumen to resist the stripping action of water in chipseals and asphalt concrete. The passive adhesion of bitumen can be assessed using the method described by ASTM D4867 (1996). This method compares the tensile strength of an asphalt concrete before and after soaking in a water bath at 60°C for 24 hours. The results of the tensile strength testing are given in Table 35 and Figure 54.

Sets of Mix 10 asphalt concrete specimens were made using aggregates from three different sources: Fraser Shingle aggregate in the Hawkes Bay, Te Matai Road Quarry aggregate in the Manawatu and Brookby Quarry aggregate in Auckland. The characteristics of each of the asphalt concrete samples are given in Table 34. Specimens were compacted in 100 mm diameter moulds to a height of 65 mm using a Servopac gyratory compactor. Two sets of six asphalt concrete specimens were manufactured from each source of aggregate using conventional unmodified B100-T0 bitumen and TOP modified B50-T12 bitumen to give a total of 12 asphalt concrete specimens. Three specimens from each subset were soaked in water at 60°C for 24 hours. The other three specimens were used as control specimens. Asphalt concrete is usually made in New Zealand using B100-T0 bitumen. TOP modified B50-T12 bitumen was chosen as a comparison because it had a similar penetration value to the B100-T0 bitumen and consequently would be graded as being in the same class.

Table 34: Characteristics of Mix 10 asphalt concrete samples used for moisture susceptibility testing.

Aggregate Source	**Hawkes Bay**	**Manawatu**	**Auckland**
Aggregate Grading			
% Passing 9.50 mm	99	100	100
4.75 mm	84	81	84
2.36 mm	67	68	66
1.18 mm	48	45	48
0.600 mm	34	31	34
0.300 mm	22	21	21
0.150 mm	14	14	12
0.075 mm	9	10	7
Bitumen Content (%)	6.0	6.7	6.8
Maximum Theoretical Density (t/m^3)	2.413	2.406	2.443

In each case the tensile strength ratio of those asphalt mixtures manufactured using TOP modified bitumen was greater than those asphalt mixtures manufactured from unmodified bitumen. This implies that the presence of TOP in the bitumen reduces the stripping effect of water on asphalt concrete. Therefore, it must be concluded that the passive adhesion of TOP modified bitumen is greater than that of conventional bitumen. The tensile strength ratio is the ratio of the strength of the moisture damaged asphalt concrete to that of the undamaged control asphalt concrete. Similar results were obtained by Mazuch (1993).

Table 35: Passive adhesion properties of TOP modified bitumen.

Aggregate Source	**Hawkes Bay**		**Manawatu**		**Auckland**	
Bitumen	B100-T0	B50-T12	B100-T0	B50-T12	B100-T0	B50-T12
TOP (%)	0	12	0	12	0	12
Bitumen Penetration	90 dmm	89 dmm	90 dmm	89 dmm	90 dmm	89 dmm
Number of Specimens	3	3	3	3	3	3
Voids (Control Set)	5.4 %	5.1 %	5.4 %	5.4 %	5.3 %	5.1 %
Voids (Moisture Conditioned Set)	5.3 %	5.2 %	5.5 %	5.3 %	5.2 %	5.0 %
Average Saturation after Partial Saturation	61 %	60 %	58 %	58 %	57 %	59%
Average Saturation after Moisture Conditioning	91 %	79 %	73 %	73 %	77 %	71%
Average Swell after Partial Saturation	-0.15 %	-0.30 %	-0.15 %	0.05 %	-0.07 %	-0.03 %
Average Swell after Moisture Conditioning	0.72 %	0.03 %	0.30 %	0.29 %	0.71 %	0.23 %
Tensile Strength of Control Set	823 kPa	1030 kPa	836 kPa	964 kPa	749 kPa	803 kPa
Tensile Strength of Moisture Conditioned Set	479 kPa	851 kPa	704 kPa	883 kPa	542 kPa	708 kPa
Tensile Strength Ratio	**58 %**	**83 %**	**84 %**	**92%**	**72 %**	**88 %**

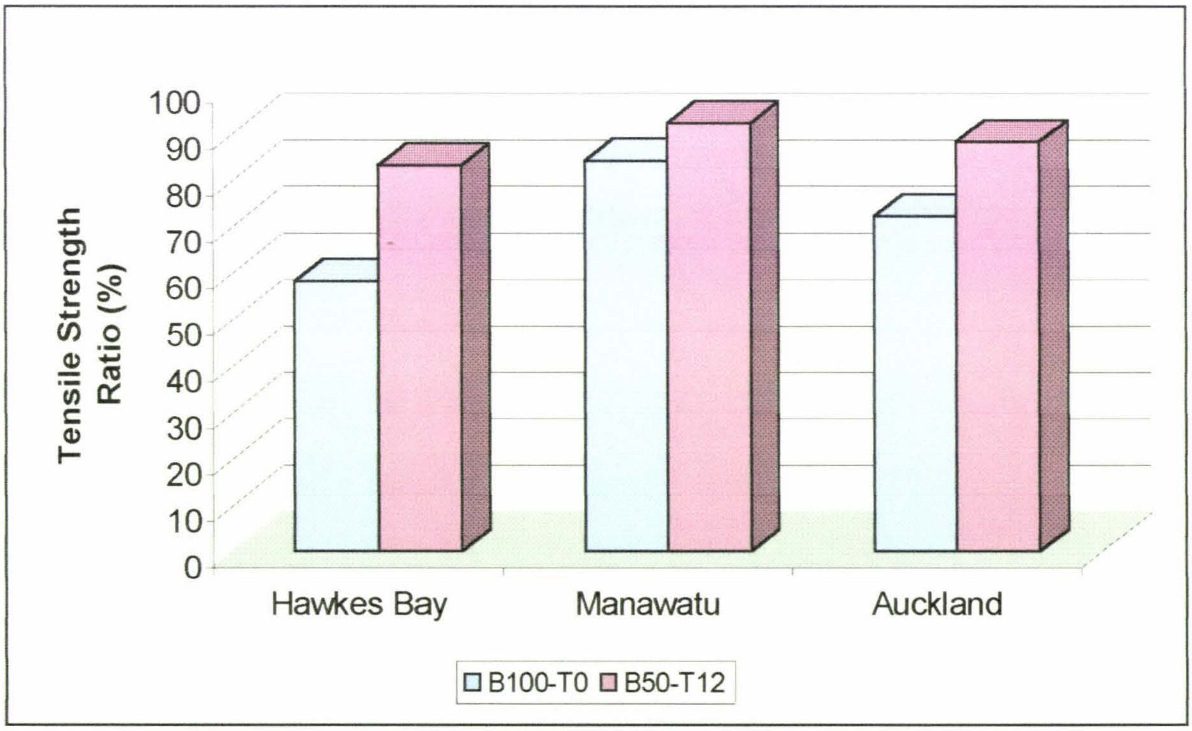


Figure 54: Effect of TOP on passive adhesion properties of bitumen.

The Asphalt Institute (1997) suggests that the tensile strength ratio be at least 75% before an asphalt concrete is considered to be resistant to moisture damage. Table 35 shows that both the Hawkes Bay and Auckland asphalt mixtures that are made using conventional B100-T0 bitumen could be considered moisture susceptible. However, when TOP modified bitumen is used in place of B100-T0 bitumen, the tensile strength ratio exceeds 75% in each case.

It is interesting to note that the tensile strength of the control set for the B50-T12 asphalt concrete specimens exceeds that of the control set for the corresponding asphalt concrete manufactured using conventional B100-T0 bitumen. In fact, the tensile strength of the moisture damaged B50-T12 asphalt concrete specimens exceeds that of the undamaged B100-T0 asphalt concrete specimens for the Hawkes Bay and Manawatu mixes. It appears that TOP modified bitumen produces asphalt concrete that has higher strength than that of asphalt mixtures made from conventional bitumen.

The improvement in the passive adhesion of the bitumen by the addition of TOP appears to be contrary to the findings of Plancher *et al* (1977). TOP contains a significant proportion of carboxylic acid species. Because of Plancher *et al's* (1977) study, it has long been contended that the presence of carboxylic acid species was detrimental to the adhesive properties of bitumen. The reason for this is that although carboxylic acids are readily absorbed onto mineral aggregate surfaces they are also easily displaced by water. One explanation for the observed improvement in passive adhesion is that the carboxylic acids in TOP improve the wetting of the aggregate surface. The improved wetting allows more tenacious bituminous species to come into contact with the aggregate and adhere to the surface. It is possible that the carboxylic acids in the TOP may still be displaced by water, but the improved wetting has allowed other species that are resistant to displacement by water to adhere to the surface.

12.3 Interfacial Tension of Bitumen

The adhesive characteristics of TOP modified bitumen can be further explained by taking a fundamental, thermodynamic approach. Before bitumen can adhere to a substrate it must first displace any other substance, whether it be air, water or another contaminant, from the surface of the substrate. This process is called wetting (Shaw, 1992). The ability for bitumen to wet a substrate is partially governed by the interfacial tensions between the substrate, bitumen and the displaced phase (Kinloch, 1987). Knowledge of the interfacial tension of the bitumen can help predict whether the bitumen will effectively wet the substrate.

The measurement of the interfacial tension (IFT) of bitumen at ambient temperatures poses a unique challenge. Popular methods such as the capillary rise method, Wilhemy plate method, du Noüy ring method, measurement of drop weights (or volume) and the sessile drop profile method all require the bitumen to be in a liquid state (Shaw, 1992). The high viscosity of bitumen at ambient temperatures prohibits the use of these methods. Vargha-Butler *et al* (1988) reports the use of the Wilhemy plate technique to measure the IFT of bitumen at temperatures above 40°C and Simaillaud *et al* (2001) used a sessile drop tensiometer to measure the IFT of bitumen at 90°C. In a separate experiment, Simaillaud *et al* (2001) also used a du Noüy tensiometer to measure the IFT of a solution of 2.5g bitumen in 25g toluene.

The preferred method for measuring the IFT of bitumen at ambient temperatures is to treat the bitumen as a solid surface and measure the contact angle that various probing liquids make with the surface. Rulison (1999) reviews several methods for determining the IFT of solid surfaces. While the Zisman method can be used, it is inadequate for even slightly polar surfaces because it fails to take into account polar interactions between the liquid and the solid surface. Consequently, since bitumen contains polar functionalities, the Zisman method is not suitable.

When the solid surface is polar, other methods such as the Owens/Wendt method, Fowkes method and the van Oss method can be used to more accurately determine the IFT. These methods separate the surface energy into a dispersive and a polar component. Unfortunately, the Fowkes and van Oss methods rely on the use of a non-polar solvent as a probing liquid. Since bitumen is at least partially soluble in such solvents, these two methods are unsuitable for determining the IFT of bitumen. The Owens/Wendt method could theoretically be used to calculate the IFT of bitumen. A draw back of this method is that it relies on knowledge of the value of the dispersive and polar components of the probing liquid's surface tension. It would also be necessary to choose probing liquids that did not dissolve the bitumen, which limits the applicability of the method since most organic solvents at least partially dissolve bitumen. Two solvents that could be used are water and glycerol, but building a plot around only two points limits the confidence that the IFT would be accurately determined.

Perhaps the method of choice for determining the IFT of bitumen is that of Neumann *et al* (1974). Vargha-Butler *et al* (1988) used this method for determining the IFT of bitumen extracted from oil sands using various solvents. Neumann *et al* (1974) developed an equation of state approach that "allows the surface tension of a low-energy solid to be determined from a single contact angle formed by a liquid which is chemically inert with respect to the solid and whose liquid surface tension is known." The contact angle (θ) is related to the IFT of the solid and liquid through Equation 12-1. The IFT between the solid and the liquid can then be determined using Equation 12-2.

Equation 12-1:

$$\cos\theta = \frac{(0.015\,\gamma_{SV} - 2.00)\,(\gamma_{SV}\gamma_{LV})^{1/2} + \gamma_{LV}}{\gamma_{LV}[0.015\,(\gamma_{SV}\gamma_{LV})^{1/2} - 1]}$$

Equation 12-2:

$$\gamma_{SL} = \frac{[(\gamma_{SV})^{1/2} - (\gamma_{LV})^{1/2}]^2}{1 - 0.015\,(\gamma_{SV}\gamma_{LV})^{1/2}}$$

Where θ = contact angle between solid and liquid (°).

γ_{SV} = interfacial tension between the solid and vapour phase ($mJ.m^{-2}$).

γ_{LV} = interfacial tension between the liquid and vapour phase ($mJ.m^{-2}$).

γ_{SL} = interfacial tension between the solid and liquid phase ($mJ.m^{-2}$).

Equation 12-1 is a third order equation with respect to γ_{SV}. If γ_{LV} is known and θ can be measured, then γ_{SV} can be determined by finding the roots of Equation 12-1. In practice, γ_{SV} was determined by finding the solution to Equation 12-1 by iteration rather than finding the roots analytically. In this case, γ_{SV} is the IFT between bitumen and air, γ_{SL} is the IFT between bitumen and water and γ_{LV} is the IFT between water and air. The contact angle that water made with films of TOP modified bitumen are given in Table 36 along with the values of γ_{SV} calculated using Equation 12-1 and the values of γ_{SL} calculated using Young's equation (Equation 12-3). Although γ_{SL} can be calculated using Equation 12-2 it was calculated using Equation 12-3 instead because the calculation was simpler and consequently the estimated error in the calculation was smaller. For the purposes of these calculations, the IFT of water (γ_{LV}) at 23°C was taken as being 72.3 mJ.m^{-2} (Cooper and Le Fevre, 1969).

Equation 12-3: $$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

Table 36: Interfacial tension of TOP modified bitumen at 23°C.

Bitumen	Number of Replicates	Contact Angle (θ)	Interfacial Tension (mJ.m^{-2})	
			In contact with air (γ_{SV})	In contact with water (γ_{SL})
B200-T0	12	91.4 ± 0.7°	29.2 ± 0.6	31.0 ± 0.9
B150-T6	24	92.4 ± 0.8°	28.4 ± 0.6	31.5 ± 0.9
B100-T0	21	92.0 ± 0.8°	28.7 ± 0.6	31.3 ± 1.0
B100-T15	16	90.6 ± 1.0°	29.8 ± 0.7	30.5 ± 1.1
B50-T0	10	93.1 ± 1.3°	27.9 ± 1.0	31.8 ± 1.6
B50-T12	22	90.2 ± 0.5°	30.1 ± 0.3	30.3 ± 0.5
B50-T25	23	89.5 ± 1.0°	30.6 ± 0.8	30.0 ± 1.2
TOP	18	68.6 ± 1.9°	48.2 ± 2.0	21.7 ± 1.5

The values of γ_{SV} obtained here are similar to those obtained by Vargha-Butler *et al* (1988) who reported the IFT of the bitumen in air as ranging from 24.4 – 30.5 mJ.m^{-2} at 23°C. Peltonen (1992) measured the IFT of a B120 bitumen from an Arabian heavy crude oil as being 27 mJ.m^{-2} at room temperature.

Figure 55 shows the effect that TOP has on the measured IFT of bitumen. An increase in TOP content causes an increase in the IFT between air and bitumen (γ_{SV}). This is not surprising since TOP introduces polar groups into the bitumen and it is known that polar substances have higher interfacial tension with air than non-polar substances. The same argument can be used to explain why Figure 56 shows that the IFT between bitumen and water decreases when the TOP content increases. The polar groups in the TOP interact with the polar water phase to lower the interfacial tension between the two phases.

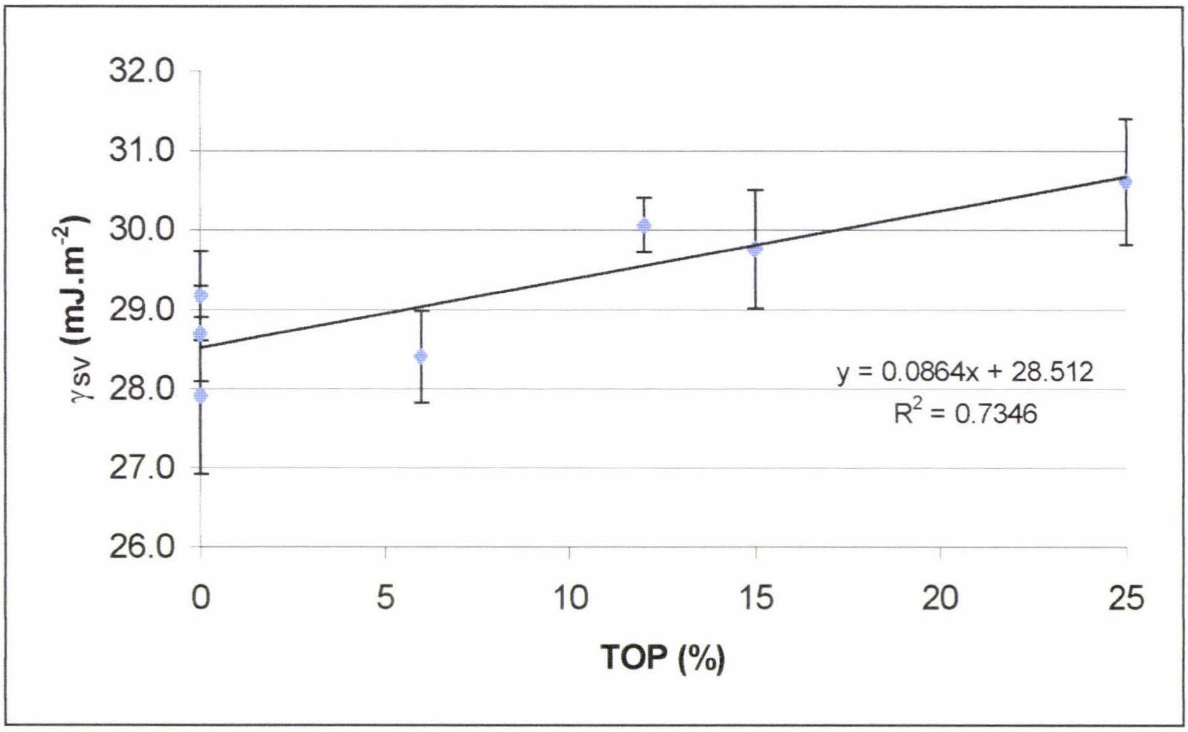


Figure 55: Interfacial Tension of TOP modified bitumen in contact with air (γ_{SV}).

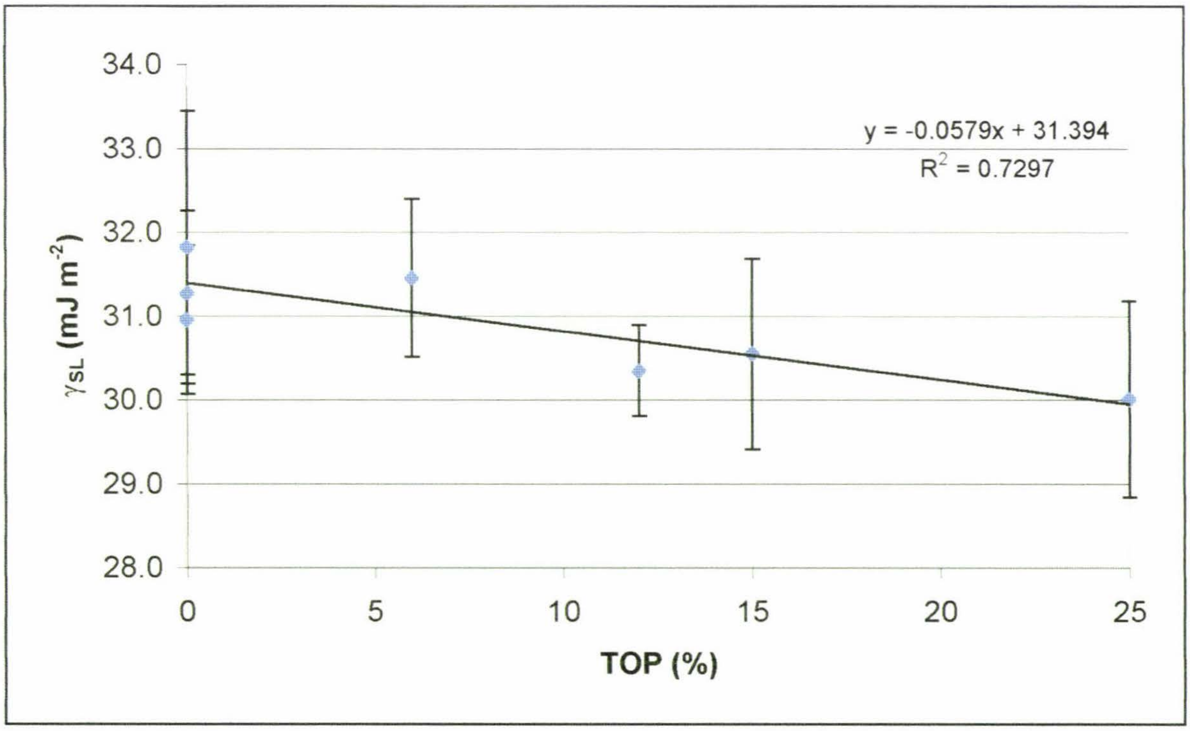


Figure 56: Interfacial tension of TOP modified bitumen in contact with water (γ_{SL}).

Equation 12-4 can be used to define the work of adhesion, W_A (Shaw, 1992). The work of adhesion is the energy released when a liquid wets the substrate. It can be thought of as the energy required to un-wet the surface. It is possible to use Equation 12-4 to help in the understanding of how TOP improves the adhesive properties of bitumen. For example, to increase W_A, (i.e. to increase the energy required to remove the liquid from the surface) it is necessary to either increase γ_{SV}, increase γ_{LV} or decrease γ_{SL}. Figure 55 and Figure 56 show that as the TOP content increases, γ_{LV} increases and γ_{SL} decrease, which would cause W_A to increase. It is reasonable to assume that γ_{SV} does not change. Therefore, by examining the interfacial tension of the bitumen it is possible to explain why TOP improves the passive adhesion.

Equation 12-4: $$W_A = \gamma_{SL} + \gamma_{LV} - \gamma_{SL}$$

Where W_A = Work of adhesion (or energy required to un-wet the system) (mJ).

As a final illustration of how TOP affects the adhesion between bitumen and aggregate surfaces, TOP modified bitumen was heated until fluid and drops of the bitumen were applied to cleaned microscope slides. Microscope slides were chosen as being representative of a smooth (and reproducible) siliceous aggregate surface. The slides were heated at 60°C until the bitumen spread and the contact angle became less than 90°. Each slide was covered with distilled water and stored in an oven at 60°C for three days to ensure that there was sufficient time for the equilibrium contact angle to be established. The contact angle that the bitumen made with the slide in the presence of water was measured from photographs, two examples of which are given in Figure 57. The effect that TOP has on the contact angle of bitumen on the slide is shown in Figure 58.

Each bitumen drop initially had a contact angle less than 90° before the slides were immersed in distilled water. A contact angle less than 90° indicates that bitumen wets the slide in preference to air. Since the final contact angles of the unmodified B200-T0, B100-T0 and B50-T0 all exceeded 90°, it appears that water preferentially wets the slide rather than bitumen. The addition of TOP reduces the receding contact angle, which shows that the passive adhesion of the TOP modified bitumen exceeds that of the unmodified bitumen. Consequently, it is further shown that TOP modified bitumen can resist the stripping action of water to a greater degree than conventional bitumen.

Table 37 contains a summary of the measured contact angles. Although there is a substantial amount of scatter in the measurements, a regression analysis of the data in Figure 58 shows that the slope of the plot is definitely non-zero. It can be concluded that TOP has a significant effect upon the contact angle between bitumen and water on a microscope slide. The standard error of the slope is 0.0043 and the t-statistic is 6.596, which indicates that the slope is significantly non-zero. The scatter in the contact angle measurements is most likely due to heterogeneity existing on the surface of the slide, either from the way the slide is made, or from contaminants on the surface. Differences in the slide's surface characteristics will affect the contact angle of the bitumen on the surface.

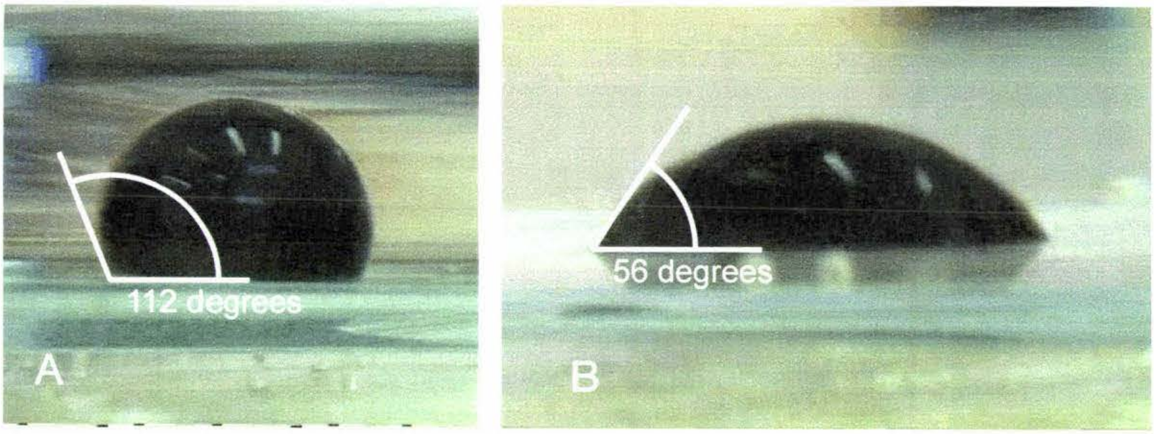


Figure 57: Photographs of contact angle measurements of (A) B200-T0 bitumen and (B) B50-T25 bitumen in water on microscope slides at 60°C.

Table 37: Contact angle measurements of TOP modified bitumen in contact with water on microscope slides at 60°C.

Bitumen	B200-T0	B100-T0	B50-T0	B150-T6	B100-T15	B50-T12	B50-T25	TOP
Average Contact Angle	110°	116°	115°	104°	97°	69°	73°	56°
Standard Deviation	6.2°	8.7°	5.8°	14.2°	13.7°	15.3°	15.9°	6.1°
Number of Measurements	6	6	6	6	6	6	6	6
t-value	2.571	2.571	2.571	2.571	2.571	2.571	2.571	2.571
95% Error	± 6.5°	± 9.1°	± 6.0°	± 14.9°	± 14.4°	± 16.1°	± 16.7°	± 6.4°

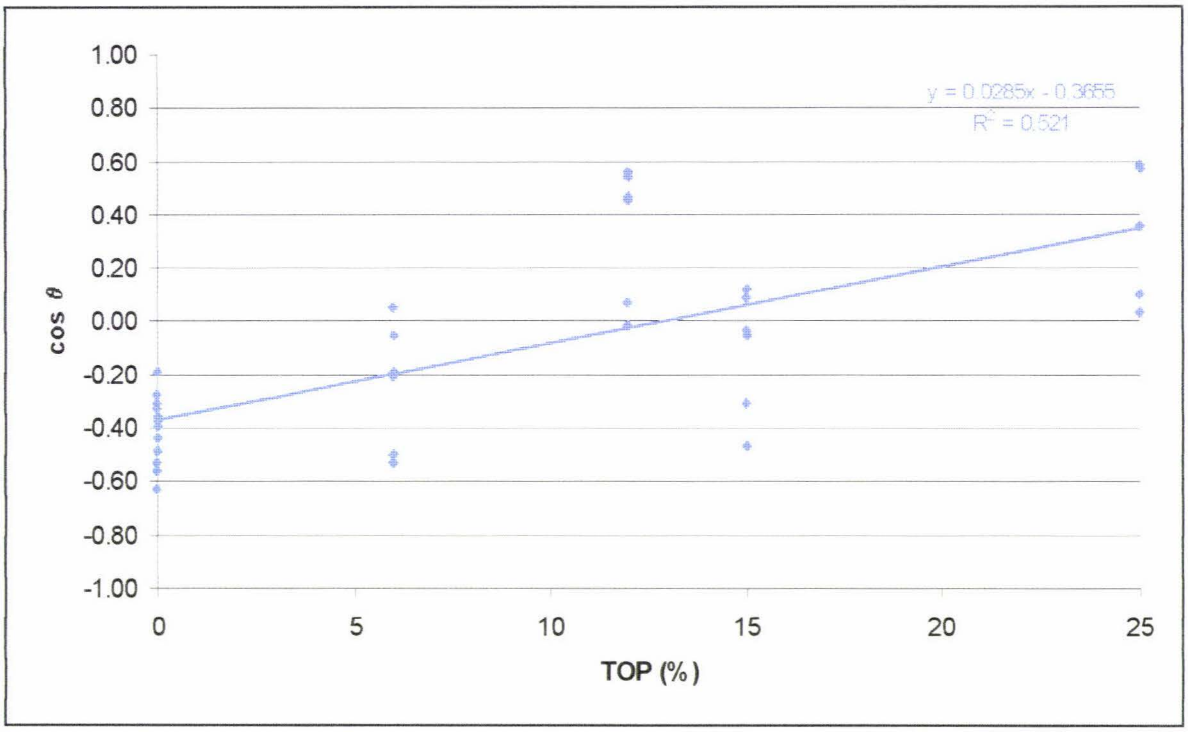


Figure 58: Effect of TOP on contact angle of bitumen in water on a microscope slide.

13.0 Conclusions

The primary aim of the investigation was to determine if TOP could be used as a bitumen modifier in New Zealand. Apart from providing environmental and economic benefits, a body of research exists that suggests that TOP modified bitumen could be used in a similar manner to conventional bitumen. Field trials conducted in Finland and Canada have successfully shown that pavements constructed using TOP modified bitumen performed as well as pavements constructed with conventional bitumen. Although the field trials only reported on the first few years' performance after construction, the initial results were very promising.

Before TOP can be used as a bitumen modifier in New Zealand, it must be shown that the modified bitumen conforms to the requirements of the Transit New Zealand specification for bitumen. This specification sets down requirements not only for the rheological properties of the bitumen, but also its compatibility with materials and products used in the roading industry in New Zealand such as kerosene, AGO, adhesion agents, polymers and emulsions. While this investigation has not addressed the use of TOP in the manufacture of polymer modified bitumen or emulsion it has examined its potential use in chipsealing and hot mix asphalt production.

The findings of other researchers have been confirmed in that the addition of TOP has a softening effect on the bitumen. TOP caused the penetration to increase and the viscosity and softening point of the bitumen to decrease. By blending hard grades of bitumen such as 40/50 penetration grade bitumen with TOP, it was possible to produce binders that had similar rheological properties to that of the softer 80/100 and 180/200 bitumen. For example, the addition of 12% TOP to 40/50 bitumen produced an 80/100 grade binder. Similarly, the addition of 15% and 25% TOP to 80/100 and 40/50 bitumen respectively produced a binder with a penetration between 180 and 200 dmm. While the penetration and softening point of the TOP modified bitumens were similar to those of the same grade of conventional bitumen, it was noticed that the kinematic viscosity measured at 60°C was significantly higher for the modified bitumen than it was for the conventional bitumen. This is thought to be attributable to the rheological properties of the more oxidised bitumen that was used to produce the TOP modified blends, whereas the conventional bitumens have a lesser degree of oxidation or are unoxidised.

The proportion of TOP added to the Safaniya bitumen used in New Zealand during this current study differed from that used in previous research by Ball *et al* (1993). For example, Ball *et al* (1993) blended 31.5% TOP with 40/50 bitumen to produce 180/200 penetration grade bitumen. In this study only 25% TOP was blended with the 40/50 bitumen to produce 180/200 bitumen. Both the bitumen and TOP used by Ball *et al* (1993) and that used in this study were from the same respective sources. This indicates that the composition and rheological properties of the bitumen and TOP have changed over the past 10 years. The implication is that the modification of bitumen with TOP will require careful monitoring of the raw materials to ensure that a modified binder with the appropriate rheological properties is produced.

The modification of bitumen with TOP had no noticeable effect on the penetration index. Therefore, the temperature susceptibility of the TOP modified bitumen, as indicated by the penetration index, was found to be similar to that of the conventional bitumen. An extension of this line of thought is that the TOP modified bitumen can be expected to possess similar engineering properties to that of conventional bitumen over its service temperature range.

While several other researchers (Peltonen, 1989b; Ball *et al*, 1993; Johnson and Juristovski, 1995) have previously reported that TOP was completely miscible with bitumen, no data was found that showed that TOP was miscible with bitumen when blended with kerosene and AGO. Since kerosene and AGO are routinely added to bitumen during chipsealing, an attempt was made to determine if blends of these diluents with TOP modified bitumen remained homogenous during storage. Unfortunately, an accurate assessment of the compatibility could not be made since the test apparatus was not airtight and some of the diluents evaporated during testing. It is also likely that oxidation occurred during storage, which would have interfered with the results. Any further assessment of this kind should be undertaken using airtight storage vessels. However, the data that was obtained indicated that the blends of TOP modified bitumen and kerosene or AGO were likely to be completely miscible and homogenous under hot storage conditions.

TOP was found to conform to the requirements of the New Zealand specification for bitumen with respect to its rheological properties and compatibility with diluents. In this regard it is expected to perform in a similar manner to conventional bitumen during construction of a bituminous pavement surfacing. However, for bitumen to be suitable for use in pavement construction it must also be durable and possess desirable rheological and engineering properties throughout its service life. After assessing its ageing characteristics, it was found that TOP modified bitumen was not as resistant to the effects of oxidation as conventional bitumen. This has serious implications for the durability of pavements constructed with TOP modified bitumen.

Bitumen that has been modified with TOP possessed a higher ageing index, as measured by penetration at 25°C, compared to that of conventional bitumen. A linear relationship was found between the ageing index and the proportion of TOP in the bitumen. The increase in the ageing index was independently confirmed using the durability test. Samples of bitumen aged at 60°C over 1000 hours displayed a greater rate of increase in modulus at 5°C than conventional bitumen. It was concluded that TOP modified bitumen was more reactive towards oxygen and consequently hardened more quickly than conventional bitumen. In terms of long-term durability, a pavement constructed with TOP modified bitumen is more likely to develop a higher modulus than a pavement constructed from conventional bitumen and therefore will be more prone to fatigue and thermal cracking.

The increase in ageing index of the bitumen with increasing TOP content was partially explained by examining the Heithaus parameters. Although TOP had no effect on the peptisability of the asphaltenes (P_a), the solvent power of the maltenes (P_o) or the overall compatibility of the bitumen (P) in unaged bitumens, it did have an effect on these parameters after ageing. In unaged samples the value of the Heithaus parameters were determined by the grade of bitumen used to make the TOP modified bitumen. As the penetration of the unaged bitumen decreased, P_a decreased and P_o and P increased.

TOP caused a reduction in the peptisability of the asphaltenes (P_a) during ageing. A reduction in the P_a value suggested that the asphaltenes were more likely to aggregate together during ageing. This manifested itself as a reduction in the penetration value. The mechanism by which TOP causes a reduction in P_a is not known at this stage, but it is likely to be caused by an increase in polarity, an increase in molecular size or an increase in the proportion of asphaltenes in the bitumen. The solvent power of the bitumen increased as the proportion of TOP increased in the aged bitumen, presumably due to the increase in the polarity of the maltene phase caused by the introduction of the polar TOP molecules into the maltenes. The increase in P_o after ageing resulted in a general increase in the compatibility of the bitumen as measured by the parameter P.

It is known that TOP contains carboxylic acid molecules in the form of linear, saturated and unsaturated molecules and cyclic resin acids such as abietic acid and its derivatives. Although these acids did not appear to influence the rheology of the unaged bitumen significantly, they may have had a more dramatic effect after ageing. It is possible that the unsaturated acids polymerised with the bitumen to either convert maltene molecules to asphaltenes, or to increase the polarity and molecular weight of the existing asphaltenes. This would cause the observed reduction in P_a. Alternatively, the unsaturated acids in the TOP may have polymerised together in a reaction similar to that observed during the cure of alkyd resins. The resulting oligomer would act as an asphaltene molecule with respect to polarity, association potential and molecular weight. An analysis of the bitumen before and after ageing found no appreciable change in the acid value. This indicated that acid groups do not appear to be formed or consumed upon ageing. It was also noted that the acid value of the bitumen increased in a linear, proportional manner with the TOP content.

A Corbett analysis has shown that within a particular penetration grade, unaged TOP modified bitumen tends to have a greater proportion of asphaltenes and a lower proportion of saturates. This was likely to be because TOP modified bitumen was produced from an oxidised bitumen grade that naturally contains more asphaltenes. Also, since TOP was found to be low in saturates, the addition of TOP to the bitumen had a diluting effect on the saturate fraction. No conclusions were drawn regarding the effect of TOP on the resins and aromatic content of the bitumen because of the scatter in the data. It was noted that TOP caused a significant increase in the mass proportion of asphaltenes in the bitumen after ageing. This increase was over and above what was expected for conventional bitumen and is consistent with the data obtained for the ageing index and Heithaus parameters. A higher proportion of asphaltenes will reduce the P_a parameter and reduce the bitumen penetration. A lower penetration after ageing would increase the ageing index.

There was no significant change in the saturate content of the bitumen samples during ageing, but it was observed that the asphaltene and resin fractions increased at the expense of the aromatic fraction. It was also noticed that TOP had no effect on the colloidal index within a particular penetration range, i.e. 80 –100 dmm or 180 – 200 dmm. The colloidal index remained unaffected by the TOP even after ageing.

An analysis of the TOP modified bitumen using GPC showed that the average molecular size of the asphaltene aggregates was not affected by the TOP content or the ageing process. Similar retention times were obtained for each of the bitumens regardless of its TOP content or whether it was aged or unaged. The change in the proportion of asphaltene aggregates detected by GPC after ageing tended to be influenced more by the grade of bitumen used to produce the TOP modified blend rather than by the proportion of TOP in the bitumen.

The independence between asphaltene aggregate size and TOP content was confirmed using CLSM. Although the microphotographs obtained yielded qualitative rather than quantitative data, it appeared that the size of the asphaltene aggregates were all in the range of 2 – 7 μm regardless of the TOP content of the bitumen or whether the bitumen had been aged.

While previous researchers had shown that TOP reduced the moisture susceptibility of hot mix asphalt no research into the adhesive characteristics of the bitumen, TOP or aggregates used in New Zealand had been undertaken. As a matter of course, three Mix 10 asphalt concrete samples were produced using Auckland, Manawatu and Hawkes Bay aggregates respectively. The resistance of each of these three asphalt mixtures to moisture damage improved when TOP modified bitumen was used in place of conventional bitumen. Furthermore, it was observed that the tensile strength of the asphalt concrete produced using TOP modified bitumen exceeded that of the asphalt concrete produced using conventional bitumen. This indicated that although the TOP modified bitumen had similar rheological properties to conventional bitumen, it produced a stiffer asphalt mix.

No prior research had been found that studied the compatibility between adhesion agents and TOP. Alkyl amine based adhesion agents are routinely added to the bitumen to improve the ability of the bitumen to wet and adhere to damp chip during chipsealing operations. After testing the adhesive characteristics of the TOP modified bitumen using the Vialit test, it must be concluded that TOP has a severe adverse effect on the effectiveness of adhesion agents. The adhesion between the bitumen and damp chip in the presence of adhesion agent was found to be inversely proportional to the TOP content of the bitumen. It was estimated that modification of the bitumen with more than 4% TOP would cause the bitumen to fail the Vialit test. Being acidic in nature, it is thought that the TOP neutralises the alkyl amine based adhesion agents in an acid-base reaction, thereby rendering the adhesion agent ineffective.

Measurements of the interfacial tension of the TOP modified bitumen showed that TOP caused an increase in the interfacial tension of bitumen in contact with air at 23°C from ~28.5 mJ/m^2 for bitumen containing no TOP, to ~30.6 mJ/m^2 for bitumen containing 25% TOP. Because TOP contains polar acid species, it is likely that the increase in the interfacial tension with air is caused by an increase in polarity of the bitumen surface due to the introduction of TOP. It could then be argued that the increased polarity of the bitumen resulted in a reduction in the interfacial tension of the bitumen with water from ~31.4 mJ/m^2 in the absence of TOP to ~30.0 mJ/m^2 when the bitumen contains 25% TOP.

In a final experiment designed to illustrate the improved resistance of TOP modified bitumen to displacement by water, the contact angle that drops of bitumen on a microscope slide made with water at 60°C was measured. Increasing the proportion of TOP reduced the change in contact angle that the bitumen made with water. TOP was found to minimise the displacement of bitumen from the slide by the water. The average contact angle that conventional 180/200 bitumen made with water at 60°C was 110°, while the contact angle of bitumen containing 25% TOP was 73° on average.

It is possible to use the results obtained during this investigation to predict the performance of bitumen that has been modified with TOP. Measurements of the rheological properties such as penetration, softening point, viscosity and penetration index indicate that TOP modified bitumen can be used in place of conventional bitumen. Furthermore, there is some evidence that TOP modified bitumen remains homogenous when blended with kerosene and AGO. However, it is plainly obvious that TOP modified bitumen possesses a greater reactivity towards oxidation than conventional bitumen. TOP modified bitumen is expected to undergo age hardening at a faster rate and is likely to be less durable than conventional bitumen.

The observed reduction in the Heithaus parameter, P_a and the increase in the asphaltene content indicates that the asphaltenes are becoming more polar as the proportion of TOP increases and the bitumen is progressively aged. An increase in polarity will result in reduced solubility in n-heptane, which will increase the proportion of asphaltenes during the Corbett analysis. The increased polarity does not appear to translate itself into increased size of asphaltene aggregates as determined using GPC and CLSM. However, the increased polarity of the asphaltene phase is expected to cause an increase in the viscosity and modulus of the bitumen after ageing.

The implication of this in practise is that the TOP modified bitumen is unlikely to produce tender asphalt mixes or mixes that are prone to rutting. However, since the asphaltene content has increased and the aromatic content decreased in the aged TOP modified bitumen, there is an increased risk of ravelling or fatigue cracking occurring. Asphalt concrete produced using TOP modified bitumen is also less likely to be susceptible to moisture damage than asphalt concrete produced using conventional bitumen.

While initial results achieved with TOP modified bitumen for chipsealing may prove promising, it is likely that the chipseal will be more prone to fatigue cracking than conventional chipseals. On the positive side, the higher viscosity after ageing is likely to reduce the occurrence of flushing. The use of adhesion agents with TOP modified bitumen is not recommended since the acid species in the TOP renders the amine based adhesion agents ineffective.

Therefore, while some results have been encouraging it is obvious that further development is required before TOP can be used as a modifier for bitumen. Future research should concentrate on minimising the susceptibility of TOP modified bitumen to age hardening and to improve its compatibility with adhesion agents. Perhaps an appropriate starting point would be to remove or neutralise the acidic species in the TOP. A reduction in the polar nature of the TOP might possibly reduce the age hardening potential of TOP modified bitumen while improving its compatibility with alkyl amine adhesion agents. It is also likely to alter the rheological properties of the blend and consequently, further determination of the appropriate proportion of TOP to add to the bitumen to achieve a particular penetration grade will be required. Neutralisation of the acid content may also have an effect upon the ability of the TOP modified bitumen to resist moisture damage and stripping.

Interestingly, Herrington *et al* (1996) found that the rate of age hardening of a 10% TOP modified 180/200 was similar to that of a control 180/200 bitumen when they were both aged for 3.3 years as 3 mm thick films in an oven at 43°C. Several explanations for this can be put forward. Firstly, the ageing reaction mechanism for TOP is different at 60°C than it is at 43°C. Alternatively, the rate of oxidation of TOP is negligible at 43°C but significant at 60°C. Thirdly, the use of 3 mm thick films instead of 1 mm thick films prevented diffusion of oxygen into the bulk of the sample. Or finally, the composition of the TOP has changed and the sample obtained by Herrington *et al* (1996) differs from that used in the current study. Consequently, the oxidation potential of the TOP used by Herrington *et al* (1996) may differ from that used during this study. Nonetheless, since the current ageing results differ from those obtained by Herrington *et al* (1996) it is apparent that further research is required into the rate and mechanism of oxidation and ageing of TOP modified bitumen.

The investigation into the suitability of using TOP as a bitumen modifier in New Zealand will not be complete until research is conducted that assesses the suitability of using TOP modified bitumen in the manufacture of bituminous emulsions and polymer modified bitumens.

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15.0 Glossary of Terms

15.1 Definitions

Active Adhesion is the ability of a bitumen to wet and adhere to an aggregate surface by displacing water and other contaminants that were initially in contact with the aggregate surface. *See also Passive Adhesion*

Adhesion, *see Active Adhesion and Passive Adhesion*

Adhesion Agents are any of a range of chemicals used to improve the adhesive bond that occurs between asphalt and mineral aggregate, thereby making it more resistant to displacement by water. Adhesion agents are commonly alkyl amines, but may also include hydrated lime or other chemicals. *See also Active Adhesion and Passive Adhesion.*

Age Hardening is the process that naturally occurs in bituminous materials over time that results in an increase in the viscosity and modulus of the bitumen. *See also Oxidation.*

Aromatic refers to bituminous molecules that are characterised by the presence and predominance of cyclic unsaturated structures typified by benzene. *See also Naphthenic and Paraffinic.*

Aromatics are a group of molecules in bitumen that are obtained by fractionation. The aromatics fraction is characterised by the presence of unsaturated cyclic structures and is predominately non-polar. They are thought to act as solvents for the resins and asphaltenes.

Asphalt is the term used in the USA for bitumen. In Europe, Australia and New Zealand, the term asphalt refers to the mixture of aggregates and bitumen. It is generally recognised that the terms asphalt and bitumen may be used interchangeably.

Asphalt Cement is a term used in North America for bitumen.

Asphalt Concrete is the mixture of asphalt and mineral aggregates. It is manufactured at elevated temperatures and is laid and compacted while hot to form a smooth, uniform pavement surface. The term asphalt concrete is predominately used in North America. Asphalt concrete is sometimes called asphalt or hot mix asphalt (HMA).

Asphaltenes are the most polar fraction of bitumen. They are highly aromatic and associate into three dimensional structures that are thought to be responsible for contributing the most to the rheological properties of the bitumen.

Bitumen is the residue from distillation of crude oil and is the black, or dark coloured hydrocarbon material that is used in the manufacture of bituminous pavements. Bitumen may also occur as natural deposits.

Bituminous Emulsion is a finely divided dispersion of bitumen in water that is stabilised by surface active agents and is used in pavement construction.

Bleeding is the spontaneous exudation of bituminous binder from a bituminous pavement, usually during periods of high pavement temperatures. It can occur in the absence of vehicular traffic. *See also Flushing.*

Butane Precipitated Asphalt is the precipitate derived from the treatment of bitumen with liquid butane. *See also Propane Precipitated Asphalt.*

Chipseal is a bituminous pavement surfacing product that consists of a single layer of uniformly graded mineral aggregates that are predominately a single size, spread on top of a sprayed layer of bitumen that is used to cement the aggregates to the existing pavement surface.

Cracking, Fatigue, *see Fatigue Cracking.*

Cracking, Thermal, *see Thermal Cracking.*

Crude Tall Oil is a resinous by-product from the Kraft pulping of pine or spruce wood. It is composed of degraded lignin products and contains a significant proportion of resin and fatty acids.

Cutback Bitumen is bitumen that has had kerosene, AGO, or another solvent added to it to reduce the application viscosity.

Diluents are a range of substances that are added to the bitumen during pavement construction. The term diluent usually refers to the use of kerosene, AGO, mineral turpentine or other solvents for producing cutback bitumen. In some cases, adhesion agents are referred to as diluents.

Emulsion, *see Bituminous Emulsion.*

Fatigue Cracking is a load-associated failure mode in bituminous pavements that is caused by vehicular traffic repeatedly applying a loading stress to the pavement, which eventually causes the pavement to crack.

First Acidaffins are a fraction of the bitumen obtained from the Rostler and Sternberg method of fractionation. The first acidaffins contain some of the aromatics and some of the resins fraction.

Flushing is the exudation of bituminous binder from a bituminous pavement under the action of vehicular traffic. *See also Bleeding.*

Heteroatoms are those atoms present in hydrocarbon molecules that are not carbon or hydrogen. The term heteroatom usually refers to the elements nitrogen, oxygen and sulphur.

Hot Mix Asphalt, *see Asphalt Concrete.*

Lime is a term commonly used to describe either limestone ($CaCO_3$), burnt lime (CaO) or slaked or hydrated lime ($Ca(OH)_2$). Burnt lime and hydrated lime are often used in asphalt concrete to reduce its susceptibility to stripping.

Maltenes are the fraction of the bitumen that remains after the removal of the asphaltenes, usually by precipitation. Maltenes are sometimes referred to as the 'oils' or 'petrolenes'.

Moisture Damage is a failure mode in asphalt concrete and refers to loss of strength of an asphalt concrete surface caused by the ingress of water into the asphalt concrete. Moisture damage can be caused by displacement of the bitumen film from the aggregate surface (stripping) or by the inclusion of water in the bitumen film, which has a softening effect. *See also Stripping.*

Moisture Susceptibility refers to the effect that water has on the mechanical properties of hot mix asphalt or the effect that water has on the strength of the adhesive bond that occurs between bitumen and mineral aggregate. *See also Moisture Damage.*

Naphthene Aromatics are a fraction of the bitumen obtained from the Corbett method of fractionation. *See Aromatics.*

Naphthenic refers to the bituminous molecules that are characterised by the presence and predominance of cyclic aliphatic structures typified by cyclohexane. *See also Aromatic and Paraffinic.*

Oxidation usually refers to the reaction of bitumen with atmospheric oxygen and results in age hardening.

Paraffinic refers to the bituminous molecules that are characterised by the presence and predominance of straight or branched aliphatic structures. *See also Aromatic and Naphthenic.*

Paraffins are a fraction of the bitumen obtained from the Rostler and Sternberg method of fractionation. They are not reactive towards sulphuric acid. *See Saturates.*

Passive Adhesion is the ability of a bitumen, initially in contact with and adhering to an aggregate surface, to resist displacement from the aggregate surface by water or other contaminants. *See also Active Adhesion.*

Penetration is a test used to classify or grade bitumen depending upon how far a needle of defined mass and dimensions penetrates into a sample of bitumen at a defined temperature when the needle is allowed to fall under the influence of gravity for a defined length of time.

Penetration Index is a test used to assess the temperature susceptibility of bitumen.

Permanent Deformation, *see Rutting.*

Pitch refers to the dark, sticky, viscous materials that are the residue from distillation of substances such as crude oil, coal tar or wood tar. That is to say, pitch may refer to either tar or bitumen.

Polar Aromatics is a fraction of the bitumen obtained from the Corbett method of fractionation. *See Resins.*

Polymer Modified Bitumen is a dispersion of synthetic or natural polymer in bitumen. Polymers are added to enhance the bitumen's rheological properties.

Propane Precipitated Asphalt is the precipitate derived from the treatment of bitumen with liquid propane. *See Butane Precipitated Asphalt.*

Ravelling is a failure mode in asphalt concrete. Ravelling refers to the loss of surface aggregate from an asphalt concrete mix and is due to cohesive failure of the bitumen film. It usually occurs when the bitumen develops excessive stiffness and becomes brittle through age hardening or excessive oxidation. *See also Stripping.*

Resins are a polar, aromatic fraction of bitumen that is thought to be responsible for acting as dispersing agents for the asphaltene fraction.

Rutting is the permanent deformation of an asphalt concrete layer caused by vehicular traffic. Rutting can be a result of either plastic flow or consolidation within the asphalt concrete or other pavement layers.

Saturates are a non-polar fraction of bitumen and are predominately composed of aliphatic and naphthenic molecules. The saturate fraction has a plasticising effect on the bitumen. The saturates are not adsorbed on alumina, clay, silica or ion exchange chromatography columns.

Second Acidaffins are a fraction of the bitumen obtained from the Rostler and Sternberg method of fractionation. They are thought to contain most of the aromatics and possibly some of the resin fraction.

Steric Hardening refers to the physical rearrangement of bitumen molecules at ambient temperatures to form a more thermodynamically stable conformation. Steric hardening is a reversible, slow process that occurs over a period of months or years and results in age hardening.

Stripping is a failure mode in bituminous surfaces such as chipseals and asphalt concrete. It refers to the loss aggregate from the surface of a chipseal or asphalt concrete due to the displacement of the bitumen film from the aggregate surface by water. It is an adhesive failure as opposed to a cohesive failure such as ravelling. *See also Ravelling and Moisture Damage.*

Tall Oil is a distillate product obtained from the distillation of crude tall oil.

Tall Oil Pitch is the residue from the distillation of crude tall oil. *See also Pitch.*

Tar is the residue obtained from the destructive distillation of organic substances such as wood and coal.

Temperature Susceptibility refers to the effect that a change in temperature has on the rheological properties of bitumen.

Tenderness in asphalt concrete refers to either mixes that are difficult to compact because the asphalt concrete shoves and flows under normal compactive efforts, or those mixes that are slow to set and develop strength after cooling to ambient pavement temperatures.

Thermal Cracking is a non-load associated failure mode in bituminous pavements that occurs in low temperature environments and is a result of a thermal gradient being generated throughout the pavement profile. The cooler surface of the pavement contracts at a faster rate than the bulk of the material, which causes stresses to develop that exceed the tensile strength of the pavement.

Visco-elastic is a term used to describe the rheological properties of bitumen, which are partially viscous and partially elastic in nature.

15.2 Abbreviations

AFM	Atomic Force Microscopy
AGO	Automotive Gas Oil (Diesel)
ASTM	American Society for Testing and Materials
BPA	Butane Precipitated Asphalt
CLSM	Confocal Laser Scanning Microscopy
CTO	Crude Tall Oil
ESEM	Environmental Scanning Electron Microscopy
GPC	Gel Permeation Chromatography
HMA	Hot Mix Asphalt
HP-GPC	High Pressure Gel Permeation Chromatography
HPLC	High Pressure Liquid Chromatography
Ic	Index of Colloidal Stability (or alternatively the Colloidal Instability Index)
IEC	Ion Exchange Chromatography
IFT	Interfacial Tension
IR	Infra-red
KOH	Potassium Hydroxide
LMS	Large Molecular Size
MMS	Medium Molecular Size
NMR	Nuclear Magnetic Resonance

PMB	Polymer Modified Bitumen
POV	Pressure Oxidation Vessel
PPA	Propane Precipitated Asphalt
ppm	parts per million
RDR	Rostler Durability Ratio
RTFOT	Rolling Thin Film Oven Test
SARA	Saturates, Aromatics, Resins, Asphaltenes
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SFC	Supercritical Fluid Chromatography
SHRP	Strategic Highways Research Program
SMS	Small Molecular Size
TBAH	Tetrabutylammonium Hydroxide
TEM	Transmission Electron Microscopy.
TFOT	Thin Film Oven Test
TNZ	Transit New Zealand
TOFA	Tall Oil Fatty Acids
TOP	Tall Oil Pitch
TOR	Tall Oil Rosin
UV	Ultra Violet