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**THE MODIFICATION OF  
BITUMINOUS MATERIALS  
USING TALL OIL PITCH**

A thesis presented in partial fulfilment of the requirements for the  
Degree of Master of Technology in Chemical Technology  
at Massey University, New Zealand

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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  $3024 \pm 8$  hours in an oven at  $60^\circ\text{C}$ . 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  $\mu\text{m}$  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 is 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 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?

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.

<b>Binder Designation</b>	<b>Grade of Bitumen used to Make Blend</b>	<b>Bitumen Content (%)</b>	<b>TOP Content (%)</b>	<b>Penetration Grade of TOP Modified Bitumen</b>
<b>B50-T12</b>	40/50	88	12	80/100
<b>B50-T25</b>	40/50	75	25	180/200
<b>B100-T15</b>	80/100	85	15	180/200
<b>B150-T6</b>	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  $\mu\text{m}$  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  $\text{mJ}/\text{m}^2$  to ~30.6  $\text{mJ}/\text{m}^2$  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  $\text{mJ}/\text{m}^2$  to ~30.0  $\text{mJ}/\text{m}^2$  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.

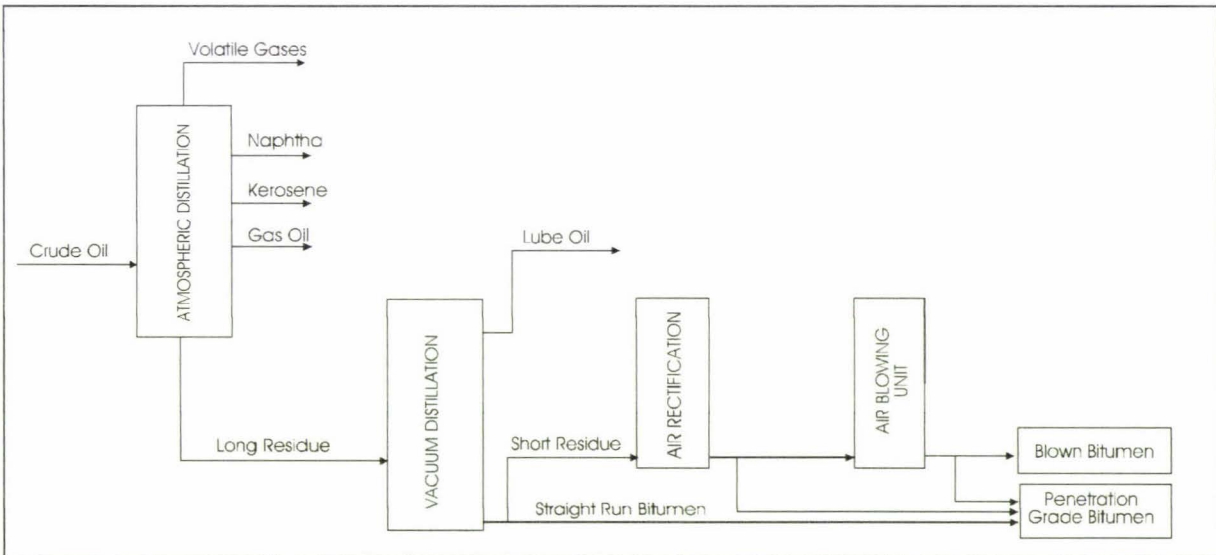
Tall oil pitch (TOP) has been identified as an industrial by-product that can potentially be used as a bitumen extender (Ball *et al*, 1993). The use of TOP in bituminous pavements not only reduces the cost of the bitumen, but also adds value to an industrial by-product and substitutes a renewable resource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