ABSTRACT

Bitumen is one of the most complex materials used in the construction industry. The purpose of this dissertation is to give a basic understanding of its origin, production and the chemistry related to its composition.

The study then examines the performance of bitumen as a road making material by comparing it with a conceptual ideal material. From this comparison the shortcomings of bitumen are discussed along with a historical background on early attempts to improve its performance. Modern modification techniques are then examined with an explanation of the theory behind the techniques and an indication of the benefits they impart.

Finally the problem of lack of an appropriate standard or specification, with complementary compliance tests, is examined. Two possible approaches to producing specifications are explored, the first is a compositional approach, the second an end result method based upon physical performance criteria. The latter is the preferred approach due to the complexity of the compliance testing required for compositional specification. Outline frameworks for specifications and complementary tests are then discussed.

CONTENTS

Chapter Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES.

Acknowledgements

I would like to thank my course tutor professor S.F. Brown for his advice and guidance in preparing this dissertation. I would also like to thank the following for their material support and assistane

The Institution of Civil Engineers, Rees-Jeffreys road fund.
Northampton Borough Council I.T. Services Department.
Mr. K.M.Stevenson, head of the Traffic Engineering Division of Northampton Borough Council.
Mr. D.Watt Director of Environment Services Northampton Borough Council.
Marilyn Dalrymple.

CHAPTER ONE

INTRODUCTION

1.1) Binders in road construction - a brief history

Among road engineers the term binder is usually reserved to describe the dark coloured, viscous hydrocarbon substance which is used as a cementing and waterproofing agent in road construction. In general other materials having a similar function, such as Portland cement, are not included in this loose definition.

There is evidence of the use of naturally occurring bitumen, for waterproofing purposes, in ancient times. In the United Kingdom the widespread use of hydrocarbon or bituminous binders first began at the end of the nineteenth century with the advent of the pneumatic tyre and the motor car. Up to this time roads were constructed using layers of broken angular stones, cemented with wet fine aggregates. Such roads, constructed in the time honoured fashion of Telford and Macadam, proved to have serious shortcomings in the automobile era. Clouds of dust in dry summer weather and serious surface erosion in wet conditions forced road engineers to consider new materials for road construction.

Conveniently large quantities of coal tar were available as a by-product of the then new and expanding gas industry. Initially this tar was poured onto the road surface in order to seal it and prevent erosion. Later sand and then gravel were added in order to prevent the sticky tar creating a nuisance. Experiments were carried out to coat aggregates and create early tarmacadam mixes to replace the wet bound macadams in use at that time. Problems were experienced with early tars because they were fairly fluid, more viscous tars were, therefore, produced by distillation, and a coated macadam industry gradually grew up out of the need for increasing quantities of these materials.

The use of bitumen as a binder developed from the early part of the twentieth century with the growth of the crude oil refining industry. This new petro-chemical industry initially produced bitumen as a residue of the fractional distillation of crude oil. It was soon discovered that this by-product could be usefully employed in the same road making applications as tar.

Tar and bitumen were used in roughly equal quantities, as road binders, in the United Kingdom until the 1960's. The decline in the production of coal gas led to a corresponding reduction in the availability of tar and from the late 1960's bitumen became the predominant material in use as a road binder.

1.2) <u>The nature of binders</u>

In any discussion of the materials used as road binders one immediately encounters some confusion in the nomenclature. The following definitions will be helpful in clarifying the terminology.

a) Tar[1]- Tar is a generic word for the liquid obtained from the destructive distillation of organic material, such as wood or coal, in the absence of air. Usually the word tar is prefixed with a description of the source material, for example coal tar

b) Pitch- Crude tar, obtained from the carbonation of coal for example, requires further treatment before it is considered suitable as a road binder. Pitch is the base tar that remains after lighter fractions have been removed from crude tar. Road tars are produced by appropriate blending of pitch and some of the fractions previously removed.

c) Bitumen- The well known and classical definition of bitumen is that it is "a viscous liquid or solid material, black or brown in colour, having adhesive properties, consisting essentially of hydrocarbons derived from petroleum or occurring in natural asphalt and soluble in carbon disulphide"[2]

Bitumen derived from petroleum by a refinery distillation process contributes by far the greatest proportion of bitumen used in the United Kingdom. Such bitumen is sometimes called residual bitumen in order to distinguish it from naturally occurring bitumen.

d) Asphalt- Both naturally occurring and man made, essentially comprises of a combination of rock or aggregate material and bitumen. In the U.S.A. the term asphalt is applied to bitumen.

e) Emulsions- An emulsion is a two phase system consisting of two immiscible liquids, with one, for example bitumen, being dispersed as finite globules in another, such as water. The discrete globules are referred to as the dispersed phase and the surrounding medium is known as the continuous phase.

Both tar and bitumen are capable of being used as road binders in their own right. When examining the modification of binders it is necessary to point out that either tar or bitumen will form the main body of the road binder, following treatment. It is fair to say, however, that with the major decline in tar usage, and technology, bitumen now forms the major source of road binder material. Tar is still produced in small quantities and binders comprising of tar-bitumen blends are available, to some extent such materials can rightly be considered as bitumen modification by the addition of road tar.

As bitumen, and, to a lesser extent, road tar comprise the main body of a binder it is necessary to consider their origin and structure and in particular to examine how this affects their performance in practice. From such a stand point it is then possible to assess the binder properties which may or may not require improvement by modification. Later it will also be seen that the structure of binders also affects their performance both in terms of their suitability for modification and the subsequent effect of incorporated modifiers.

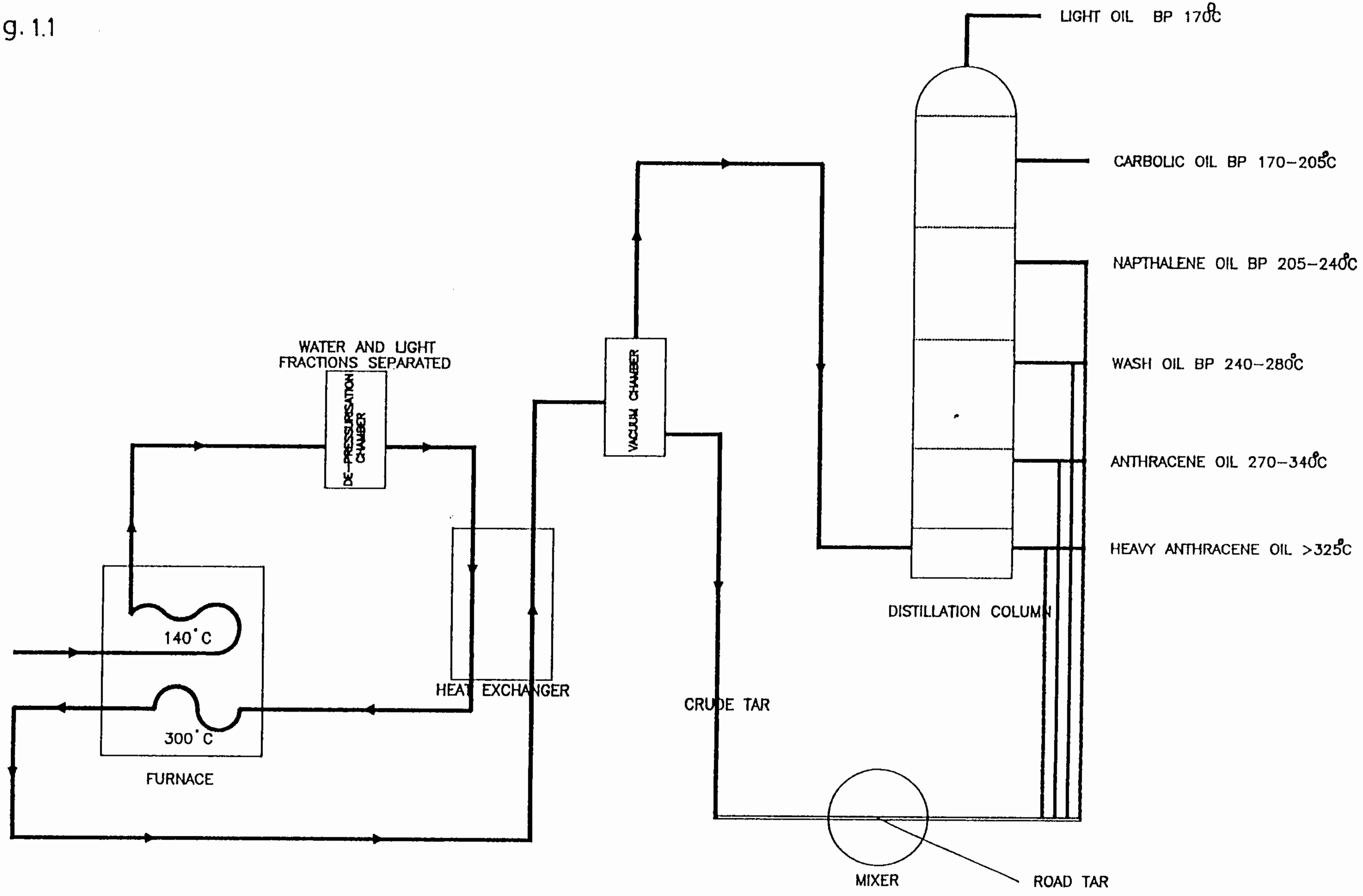
1.3) **The origin and production of road tar binders.**[3]

Road tar binders are produced from the distillation of crude tars which are themselves a by-product of the carbonisation of coal. In the past a range of tars were available from the gas production industry. A coal high in volatile material was preferred for gas production and, depending upon the type of retort used, the tar by-product varied in chemical structure. Crude tars produced from carbonisation in vertical retorts were rich in paraffinic and phenolic compounds and correspondingly lower in aromatic hydrocarbons, tars produced in horizontal retorts, on the other hand, were almost entirely composed of aromatic hydrocarbons.

In the modern context crude tar is available from the production of coke for the steel making industry. This, like the earlier gas production methods, is a relatively high temperature process (1200°C). The crude tars so produced are high in aromatic compounds and are quite distinct from tar produced in a low temperature process (600°C) as a by-product of the smokeless fuel industry. In this latter case the crude tar is unsuitable for refining to produce road tar binders and is excluded by the preparation clause of B.S. 76.

Road tar is produced from crude tar in a continuous distillation process,illustrated in figure 1.1. The crude tar is fed through tubes and heated by a furnace to around 140°C, it is then led under pressure to a vessel where the pressure is suddenly removed. This causes water and light oil to evaporate allowing them

Fig. 1.1



DIAGRAMMATIC REPRESENTATION OF THE ROAD TAR PRODUCTION PROCESS to be separated off. The residue is then returned to the furnace and heated further to around 300°C, it is piped to a low pressure chamber where lighter fractions evaporate-these are led into a fractioning column where they are condensed at different levels to give a range of oils of varying boiling point-from top to bottom of the column. A second residue then remains in the low pressure chamber, this is the base tar or pitch. It is generally fluxed to the desired viscosity of road tar by blending with some of the heavier oils produced in the fractioning column. Prior to blending the 200-270°C boiling point range oil is checked, in accordance with B.S. 76, in order to ensure that the phenol and napthalene content are below certain levels. In practice this is a continuous monitoring process with levels of phenol controlled by washing with sodium hydroxide solution and excess napthalene removed by cooling in order to crystallise it out of the oil. Control of phenol and napthalene levels is necessary because both are deleterious to performance of the binder. Phenol tends to oxidise and produce resinous compounds which can increase the viscosity of the tar and produce rapid ageing, furthermore phenols are poisonous and their slight solubility poses a hazard to the environment in certain circumstances. Napthalene, on the other hand, poses a problem due to its tendency to crystallise out of the tar at low temperatures. This tendency causes an increase in binder viscosity by acting as a filler and also by removing some of the oil component of the tar. The process of removing these deleterious substances is known as washing hence the name wash oil is often applied to the affected fraction.

1.4) The origin and production of bitumen.[4,5,6]

Bitumen may be found occurring in a native form as rock asphalt or lake asphalt. It may also be extracted from some crude oils, usually in the course of petroleum refining. It is thought that similar processes were responsible for the formation of native bitumen deposits and crude oil. The scientific explanations of the origin of these hydrocarbon deposits are vague. Various theories have been advanced, one assumes that the deposits are the result of the decomposition of a large number of animal bodies collected in the same place. Another theory ascribes the origin of hydrocarbon deposits to the deposition of large quantities of small organisms from sea water. A mineral theory assumes interaction between water and hypothetical metal carbides below the earths surface (Berthelot 1866). The whole problem is further complicated by other variables which affect reactions, for example temperature, pressure, catalysts, radioactivity and bacteria.

Crude petroleum is not a uniform substance, its composition varies from oil field to oil field. Not all crude oils are suitable for the production of bitumen, generally speaking it is the heavy oils which are rich in high molecular weight aromatic and napthenic compounds which are most suitable. Naturally occurring bitumen can probably be considered as an extreme form of crude oil, from which the lighter fractions have been removed by geological processes. Its usual to find such native bitumen in close association with rock or mineral aggregates into which it has become impregnated.

Rock asphalt comprises of porous limestone, or occasionally sandstone, impregnated with bitumen. Natural rock asphalt and mastic asphalt were once used in the United Kingdom for very dense expensive road surfacings. B.S. 348 and B.S. 1446 were standards that governed their use and composition. Nowadays their use is limited to all but the most specialised of functions, for example a highly stressed thin surfacing on a metal bridge deck.

Lake asphalt is another naturally occurring bitumen mixture. In this case a finely divided mineral matter is dispersed through bitumen, which comprises the major component of the mix. The material is capable of flow and large surface deposits are, therefore, referred to as asphalt lakes. The Trinidad asphalt lake is probably the best known lake asphalt deposit, and in the United Kingdom it has been the only source of lake asphalt used in road construction. Various theories have been put forward as to the origin of the lake, the most widely accepted (Atwooll and Broome[7]) is that the lake was formed when a surface extrusion of viscous bitumen occurred in the late Miocene era. The area was subsequently inundated by the sea due to local lowering of the earths surface, depositions of silt and clay covered the area and these then became saturated by the bitumen. On subsequent elevation of the land above sea level the lake was subject to lateral pressure which shaped it into a pseudo laccolith. Gradual erosion of soft overlying rock exposed the surface of the asphalt lake.

An analysis of the material of the Trinidad lake is quoted by Abraham[1] as follows in table one below.

Table 1.1 Composition of Trinidad lake asphalt

	Per cent by weight
Bitumen soluble in carbon disulphide	39.0
Bitumen absorbed in mineral matter	0.3
Water and gas (volatilised at 100 C)	29.0
Mineral matter on ignition	27.2
Water of hydration in mineral matter	4.3

Material extracted from the lake is coarsely refined by heating to melting point thus driving off water in the process. The whole mix is then agitated and stirred by blowing steam through the mass, next the molten mixture is screened of foreign matter and barrelled. In this state the lake asphalt is referred to as Trinidad Epure. The material is too hard for use as road binder and requires fluxing with a heavy petroleum oil. Alternatively it may be blended with petroleum bitumen or coal tar of appropriate viscosity.

Both lake asphalt and rock asphalt have some distinct advantages over man made asphalts. These advantages stem from the natural origin of the materials. In effect these natural asphalt blends are millions of years old, they have formed stable combinations with aggregates and have exhibited their long term dur ability. Lake asphalt, when used for producing hot rolled asphalt effectively comprise the filler, bitumen and fine aggregate part of the mix. Rock asphalt is usable, after some initial preparation, in its own right. Another advantage in using these materials was the way that the bitumen binder weathered, this ensured good macro texture in wearing courses, as the binders weathered away to leave chippings proud of the surrounding sand carpet.

Decline in the use of natural asphalt materials was due to improvements in binders produced from refining petroleum and also due to the fact that the way the materials were used tended to be somewhat more time consuming and labour intensive.

1.4.1 Production of bitumen from crude petroleum.[5]

There is a very wide variation in the composition of crude petroleum obtained from various oil fields, indeed there are variations in composition even between adjacent wells. There have been several attempts to classify crude oils on the basis of their composition, one such attempt was to categorise them as asphaltic (bitumen bearing), mixed base and paraffinic. As the classification infers such crude oils contained bitumen, a mixture of bitumen and wax, or paraffin wax only, as their lowest fractions. Asphaltic crudes have been identified with those produced in the Middle East or Central America, paraffinic crude oils with those produced in Pennsylvania and mixed base with Oklahoma. Some crude oils do not fit into any category but the classification system for bituminous crudes has persisted in the absence of anything more appropriate.

Upon extraction the crude petroleum is "topped" at a refinery near the oil field. This process involves heating the oil to 300-350 C and passing it into a fractioning column, operating just above atmospheric pressure. Upon entering the column the crude oil separates into liquids and vapours of various boiling points. The vapours condense on trays set at various levels in the fractioning column, the higher the level in the column the lower the boiling point of the fraction. Usually the range of products varies from light gases at the top of the column through to a residue at the bottom. The residue is the "topped" crude oil which is then taken to a second, vacuum distillation process, illustrated in figure 1.2. Here the "topped" crude, or long residuum, is heated to between 200° and 400° C. Ordinarily these temperatures would be insufficient to drive off heavy oil fractions but the reduced pressure in the fractioning column along with injections of super heated steam assist in the vaporisation. Bitumen is withdrawn from the base of the column whilst the more volatile fractions condense at various levels throughout the column.

The bitumen obtained from this vacuum distillation process generally needs to be blended with other grades of bitumen or high boiling point flux oils before it is at a suitable viscosity for use as a road binder. The vacuum distillation process is necessary, rather than heating the topped crude to high temperatures, for fractional distillation because above 400 C thermally unstable compounds in the oil begin to decompose or "crack".

Fig.1.2

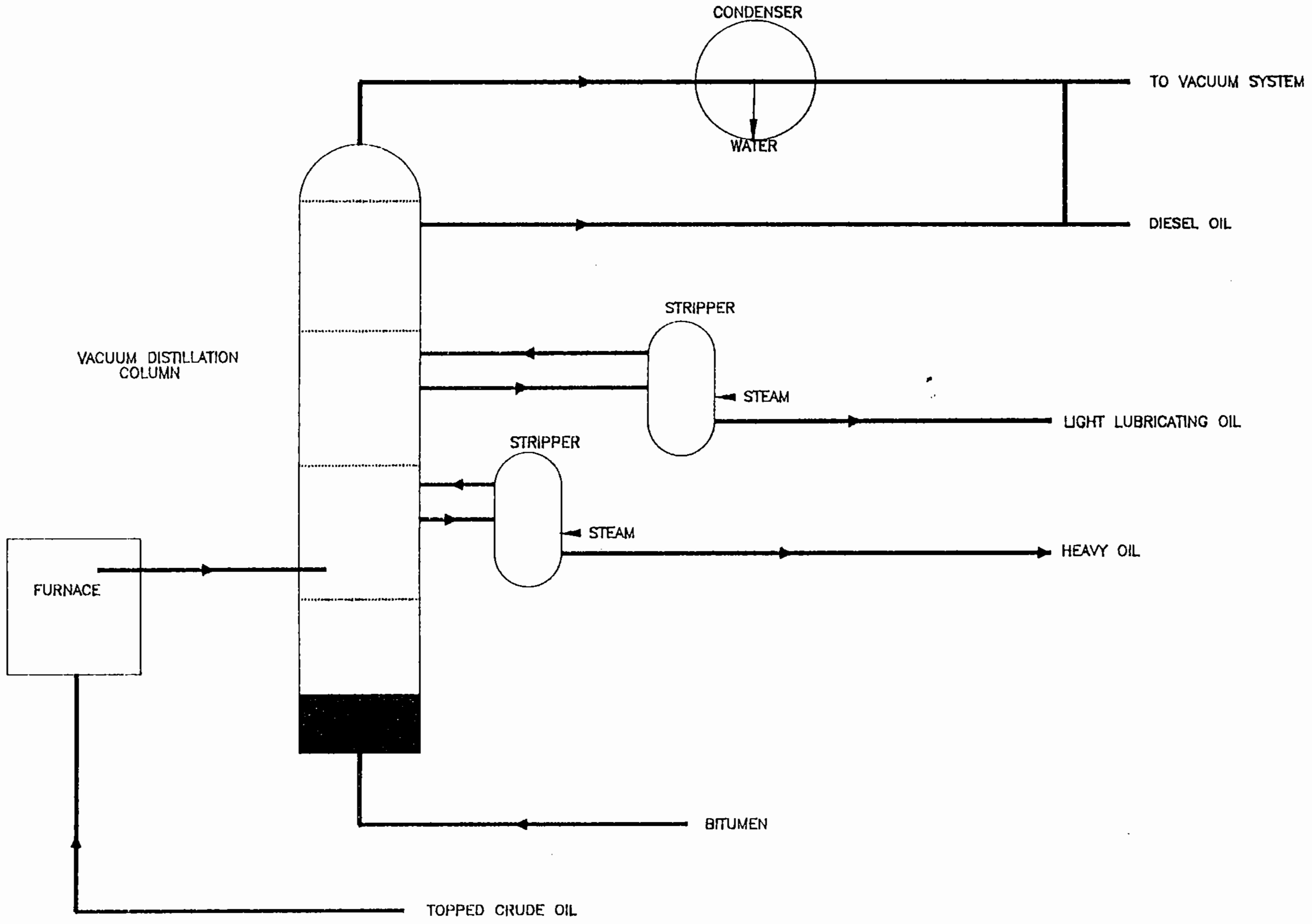


DIAGRAM OF THE PRODUCTION OF BITUMEN FROM TOPPED CRUDE OIL

Products of cracking are objectionable in both bitumen and heavy lubricating oils because they adversely modify the temperature susceptibility of these lower fractions. It has been found that the production of light lubricating oils can be increased, at the expense of the heavier ones, by mild cracking. Objectionable by-products of the cracking are then removed from the oil. Clearly demand for light lubricating oil would be the economic factor that might initiate such a production method at a refinery. The bitumen residue from this process would be unsuitable for use as a road binder, that is not to say that it might not find itself on the market in some form.

By far the greatest proportion of bitumen for road use is obtained from the distillation of crude petroleum. However, small quantities of bitumen are produced as a by-product of the extraction method of refining. This is mainly used for the production of light lubricating oils and involves the fractioning of petroleum with solvents (for example sulphuric acid).

REFERENCES

1. Abraham H. Asphalt and allied substances. New York (Van Nostrand Co. Ltd.) 6th Ed.
2. B.S. 892 1954 now superseded by B.S. 3690 part 1
3. Road Research Laboratory. Department of Scientific and industrial research. Bituminous materials in road construction. London 1962 (H.M.S.O.)
4. Whiteoak D. The Shell Bitumen handbook.1990 (Shell Bitumen U.K.)
5. Speight J.G. The chemistry and technology of petroleum. 1991 (Marcel Dekker inc.) 2nd Ed.
6. Dalrymple N. 1989/90 undergraduate project on modified binders
7. Atwooll and Broome. Trinidad Lake Asphalt. London 1954 (The Banyard Press) 2nd Ed.
8. B.S. 76 Tar for road purposes
9. B.S. 348 Compressed natural rock asphalt
10. B.S. 1446 Mastic asphalt (natural rock asphalt aggregate) for roads and footways.

CHAPTER TWO

THE CHEMICAL STRUCTURE OF BITUMINOUS BINDERS

Both tar and bitumen are of variable composition dependent upon method of production and the origin of the source material. In general terms they comprise of mixtures of hydrocarbons of a wide range of molecular weights. A knowledge of the detailed chemical composition and structure of both tars and bitumens would be of considerable advantage in assessing their suitability for use as road binders. Thus far the complexity and variability of both have made it impossible to obtain such a detailed picture. At present the chemical composition of tar and bitumen has been isolated to several broad fractional groups of organic structures. Relationships have been established which associate the physical properties of the binders with the existence and properties of these functional groups.

2.1. Chemical nomenclature[2]

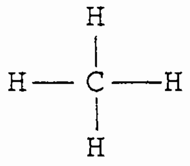
It has been estimated that there are over 10000[1] compounds in tar and even more in bitumen. Most hydrocarbons and derivatives are combinations of basic organic chemical structures. Although the detailed chemistry is complex and not fully researched it is possible to gain an insight into this detail by examining the behaviour of the "typical" functional groups. There is a recurring chemical nomenclature for which an outline explanation will assist in understanding the following discussion.

a) Aliphatic groups- This is a general term used to describe organic compounds with an open chain structure rather than a ring structure. It embraces the three hydrocarbon series of alkanes (paraffins), alkenes and alkynes.

b) Alkanes (paraffins, saturated aliphatic groups)- In the technical jargon these are hydrocarbons with only sp^3 carbon atoms. Sp^3 refers to the configuration of electrons in the outer shell (the second energy level) of the carbon atom. Carbon has four electrons in its outer shell, the s electron is at a slightly lower energy orbit around the carbon nucleus than the three p orbiting electrons. Consequently the orbital paths of the electrons differ in shape. Alkanes are compounds characterised by the formation of single bonds with hydrogen such that one of each of the carbon electrons is co-valent with a hydrogen atom and its electron.

Methane is a typical example

With structure CH_4



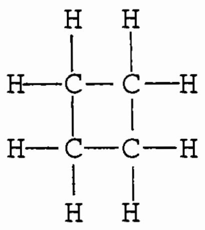
$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - H \\ & | & \\ & H & \end{array}$$

The first five members of the Alkane series are:-

CH_4	Methane
CH_3CH_3	Ethane
$CH_3CH_2CH_3$	Propane
$CH_3(CH_2)_2CH_3$	Butane
$CH_3(CH_2)_3CH_3$	Pentane

Non cyclic alkanes have the general chemical formula C_nH_{2n+2} for the C/H ratio of atoms where n= the number of carbon atoms in the molecule.

c) Cyclo-alkanes (cyclo-paraffins)- Both alkanes and cyclo-alkanes are said to be saturated hydrocarbons because all the available electron bonds are occupied, or saturated, with hydrogen, whereas non-cyclic alkanes have the general formula C_nH_{2n+2}, the presence of one ring (or double bond) reduces the number of hydrogen atoms required for saturation by two. A cyclo-alkane has the general formula C_nH_{2n} for example.

ALKANE	ALKENE	CYCLO-ALKANE
C_4H_{10}	C_4H_8	C_4H_8
$CH_3CH_2CH_3$	$CH_3CH_2CH=CH_2$	

A compound of general form C_nH_{2n-2} may contain a double ring structure. Cyclo-alkanes are suffixed according to the number of carbon atoms in the ring, for example five for cyclopentane, six for cyclohexane and so on.

d) Alkenes and alkynes- Unbranched hydrocarbons having one double bond are termed alkenes. The alkane, ane, ending is changed to ene hence alkene. They have the general structure

C_nH_{2n} though the series begins with two carbon atoms in order to satisfy the valence requirements of the series. Examples of simple members of the series are:

$CH_2{=}CH_2$ ethylene

$CH_2{=}CHCH_3$ propylene

The structures in this series become more complex after polypropylene due to isomerism, butylene (C_4H_8) for example has three alternative structures.

If there are two or more double bonds the ending of the hydrocarbon name is adiene, atriene etc. The molecule chain is numbered to give the lowest numbers to the carbon atoms immediately preceding the double bonds. These numbers are used to further define the structure of the molecule. Two examples are listed below.

$CH^1{}_3CH^2{=}CH^3CH^4{}_2CH^5{}_2$

2-PENTENE

$CH^1{}_2{=}CH^2CH^3{=}CH^4CH^5{}_3$

1,3-PENTADIENE (Two bonds)

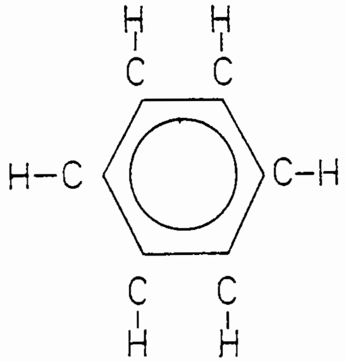
Unbranched hydrocarbons having one triple bond are named by replacing the ending <u>ane</u> of the alkane with <u>yne</u> and two or more triple bonds are ended adiyne, atriyne etc. Examples of the various types of bonding in chemical series are given below.

CH_3CH_3	$CH_2{=}CH_2$	$HC{\equiv}CH$
ethane	ethene	ethyne
an alkane	an alkene	an alkyne
	(ethylene)	(acetylene).

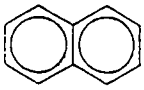
e) Aromatics- Aromatic hydrocarbons have the following structural features:-

1) They are cyclic (ring) structures.
2) They are planar (flat).
3) Each atom of the ring must have a p orbital electron perpendicular to the plane of the ring.
4) They comply with Huckel's rule, i.e. they must have (4_n+2) de-localised pi-electrons, $_n=0,1,2,3...$

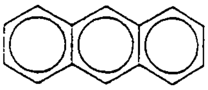
Benzene (C_6H_6) is one member of a large class of aromatic compounds typified by the ring structure.



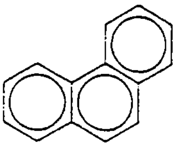
More complex aromatic compounds can be grouped into two classes, heterocyclic and polycyclic aromatics. Polycyclic aromatics are found occurring in oils, tars and bitumens. The following are examples of poly-aromatic structures:-



NAPTHALENE



ANTHRACENE



PHENANTHRENE

2.1. The chemical structure of tar.

With the decline in the use and production of tar there has been a corresponding reduction in scientific research aimed at elucidating its chemical structure. At the time of peak tar consumption in the United Kingdom scientists knew very little about the higher molecular weight pitch fractions. More was known about the heavy distillate oil fractions and the composition of pitch was generally inferred from the oil component.

Different methods of tar production have an influence on the chemical structure of tar. Work by Adam[1] and Dickinson[2] led to the development of the process of solvent fractioning which involved the separation of tar into broad fractions according to their solubility in a series of solvents of increasing dispersing power. Examination of these fractions allowed some insight into the chemical makeup of tar and the effects of the different methods of production.

Table 2.1[3] Variation of the chemical composition of tar.

Source of tar	Vertical retort	Horizontal retort	Coke oven	
	Gas prod.	Gas prod.	Gas prod.	Steel works
G.S. at 16 C	1.090	1.145	1.170	1.185
Crude phenols w/w%	5.6	4.7	3.4	2.5
Napthalene w/w%	2.6	5.7	6.5	7.5
Anthracene w/w%	0.2	2.0	1.1	1.3
Pitch w/w%	42	53.4	60.0	63.0

In general terms tars produced as a by product of coke ovens have an oil fraction that is predominantly aromatic, containing hydrocarbons of the benzene, napthalene, anthracene, phenanthrene series. The same oil fraction from tars produced in vertical retorts, by the now defunct coal gas industry, was relatively low in aromatics and contained significant quantities of phenols and paraffinic compounds.

2.2. Basic organic chemistry related to the composition of bitumen

Bitumen is predominantly hydrocarbon in nature and its chemical composition is dominated by the interaction of carbon with other atoms, particularly hydrogen. The chemistry of carbon is dominated by the particular configuration of its outer electron shell and its central position the electronegativity series. Elements in general comprise of an atomic nucleus surrounded by orbiting electrons which conform to a standard orbital pattern. In simple atoms the electron shell configuration comprises of a first orbital containing up to two electrons, the second and third orbitals may contain up to eight electrons. Each lower orbital must be filled prior to the existence of a subsequent one.

Elements aspire to a condition where the outer electron shell is full which equates to a low activity state akin to the inert gases. For example helium, which is an inert gas has its outer, and only, electron shell full with two electrons. Similarly neon, which possesses ten electrons, has its outer electron shell full with eight. Reactive elements may undergo ionic bonding, where there is an electron transfer between atoms, causing them to combine in order to achieve the stable low activity states described above.

A simple example which illustrates ionic bonding is the reaction between sodium and chlorine. Sodium carries eleven electrons in three orbital shells, two in the first, eight in the second and one in the outermost shell. Chlorine carries seventeen electrons arranged in the same fashion as the sodium atom with the exception of the outermost shell, which contains seven electrons. In a reaction between sodium metal and chlorine gas the sodium atom donates its outermost electron to the chlorine atom, creating a sodium ion which is positively charged, and has a full outer electron shell (the second shell). The chlorine atom accepts the donated electron and thus attains a full outer electron shell, becoming a negative ion in the process. Bonding between the ions results from the attraction between opposite electrostatic charges. In this particular example the resulting compound sodium chloride is a good deal more stable, in terms of reactivity, than either sodium or chlorine.

In different circumstances elements may undergo covalent bonding which occurs as a result of sharing of the outer orbital (or valence) electrons between atoms. The main factor which determines whether elements will undergo ionic or covalent bonding is the electronegativity difference between the respective atoms. If the difference in electronegativity is large , greater than 1.7, then ionic bonding takes place. For lower values of electronegativity difference covalent bonding occurs.

2.2.1. Electronegativity

Electronegativity is a measure of the attraction of an atomic nucleus for its outer bonding electrons. An atomic nucleus containing a large number of protons will have a correspondingly large attraction for its outer electrons, coupled with a small atomic radius. In addition, the attraction between oppositely charged particles increases with decreasing distance, therefore large atoms with many electron shells tend to be less electronegative than atoms in the same periodic group with a smaller atomic radius.

Figure 2.1[2] Electronegativities of key elements

Increasing electronegativity →

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
						Br
						2.8
						I
						2.5

The magnitude of the electronegativity of a given element is measured on the Pauling scale. This is derived from bond energy calculations for various elements joined by covalent bonds.

Within the Pauling scale it may be observed from, figure 2.1 that the element fluorine exhibits a high electronegativity with lithium exhibiting a low value. Carbon has an intermediate value of 2.5, this is very significant because it indicates that carbon is never sufficiently different in electronegativity to other elements for it to form ionic bonds. The key element in bitumen, therefore, is carbon because it determines the nature of chemical bonding and to a great extent the general chemical makeup of bitumen. Hydrogen is also important, but it is carbon which is responsible for the molecular arrangement of hydrogen atoms.

2.3. The electron orbital of the carbon atom and its effect upon the reactivity of bituminous compounds

From the point of view of chemical reactivity it is the outer electron shell of an atom which is significant. Carbon carries four electrons in its outer shell, of these two are at a slightly lower energy level and describe a spherical orbit around the nucleus. The other two electrons are at a slightly higher energy level and have separate double pear shaped orbits around the nucleus. The orbitals described in each case are referred to as **s** and **p** orbitals respectively. A general principle applies to the numbers of electrons in various atomic orbits which is that the lowest energy levels are filled first.

Depending upon the particular atomic interaction, the outer electron orbitals of carbon may take up various hybridised states, referred to as sp^3, sp^2 and sp hybridisation. In essence what occurs is that the electrons at the slightly different energy levels are either raised or lowered from the s or p orbitals to an intermediate, sp, energy level. The number of electrons, in the outer shell, which undergo hybridisation is largely dependent upon the number of available bonding electrons in other elements and the desire of atoms to attain full electron shells resulting in low activity states.

2.3.1. Sp^3 - Hybridisation

This particular bonding arrangement is typified by saturates such as methane. In order to undergo such a reaction the outer orbital electrons of the carbon atom change energy level. One of the s orbital electrons is temporarily raised to a p energy level. The three p energy level electrons and the remaining s electron are then hybridised to an sp state, referred to as sp^3 because the hybridisation involves one s electron three p electrons. Four sp^3 electrons are thus available for sharing with bonding electrons from other elements. In the case of methane, CH_4, the hydrogen atom carries a single s electron which enters a shared orbit with the sp^3 carbon electron, resulting in an sp^3-s covalent, sigma, bond. Also in the series, ethane C_2H_6 has sp^3-s bonds between the carbon and hydrogen atoms with a single sp^3-sp^3 sigma, bond between the two carbon atoms. In all the various electron sharing combinations the desire of atoms to achieve full outer electron shells is met, for carbon and hydrogen this state is achieved with two and eight electrons respectively. Figure 2.2. illustrates the sharing of electrons in the ethane molecule and their disposition, in order to achieve full outer electron shells.

2.3.2. Sp^2 - Hybridisation.

Sp^2 hybridisation of the outer shell electrons of carbon occurs when three are required to bond with adjacent atoms. The sequence of events for sp^2 hybridisation is as follows:

1) One of the s electrons is raised, temporarily, to a p energy level, the other is hybridised to an sp level.

2) Two of the three p energy level electrons are hybridised to an intermediate sp level.

3) The three sp^2 electrons are shared with other atoms for form sp-s or sp-sp sigma bonds.

4) There remains a p electron in a relatively high energy orbit which merges with the orbits of p electrons of adjacent atoms of carbon to form pi (π) bonds. In the case of ethylene it is the pi bonding which forms the second part of the carbon-carbon double bond.

At this stage it is necessary to point out that the sp orbital, formed from the spherical s or double pear shaped p orbital, is skittle shaped as illustrated in figure 2.3. In the case of ethylene the sp^2 orbits are arranged at 120 degrees to each other, in the same plane, due to electrostatic repulsion between electrons. The p electron orbit is at 90 degrees to this plane moving both above and below it. Figure 2.4 illustrates the full bonding arrangement for ethylene.

2.3.3. Sp - Hybridisation

Sp hybridisation is typified by the members of the alkyne series of which acetylene $HC\equiv CH$ is the simplest member. In this instance one of the s orbital electrons is raised to a p orbital energy level. Hybridisation then takes place of a single p orbital and the remaining s orbital electron.

The molecular structure of acetylene comprises of two carbon atoms linked by an sp-sp electron bond. Atoms of hydrogen are bonded, by sp-s electron orbital overlaps, to the carbon atoms. The remaining "surplus" p electron orbitals of each carbon atom merge to form two Pi (π) bonds. In terms of its three dimensional physical structure, acetylene comprises of the sp-s and sp-sp (sigma) bonds displaced at 180 degrees to each other. The two Pi bonding orbitals are at right angles to each other and perpendicular to the plane of the sigma bonding orbitals. Figure 2.5 illustrates the configuration of the bonding orbitals in acetylene.

Fig. 2.2 The Electron orbital overlaps of ethane.[2]

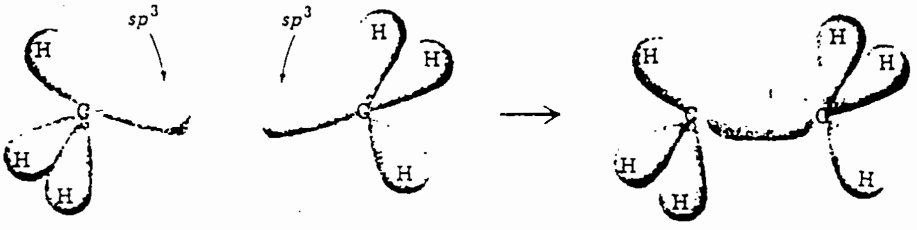
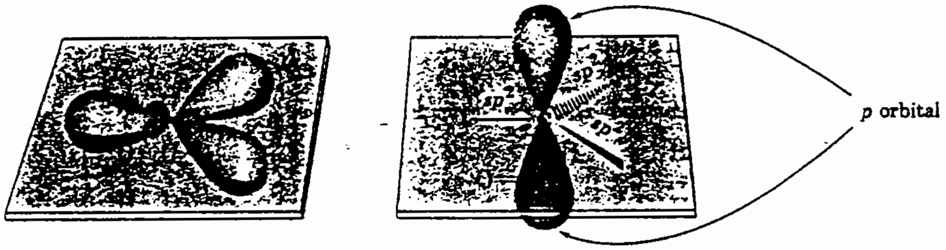


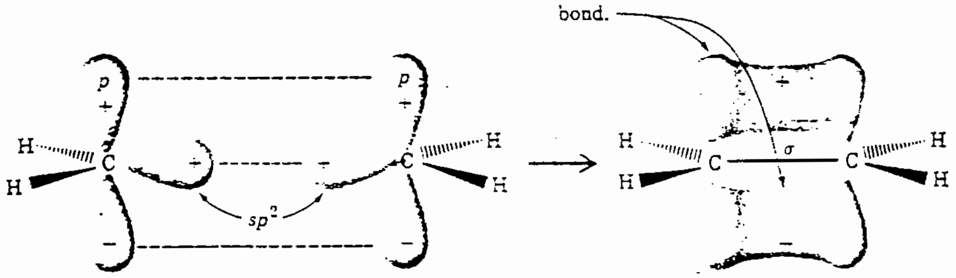
Fig. 2.3 The arrangement of SP^2 and P orbitals.[2]



a trigonal carbon; three sp^2 orbitals in a plane with 120° angles between them

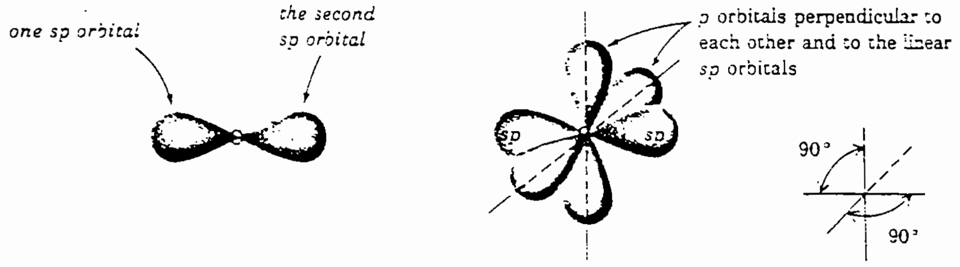
p orbital at a right angle to the plane

Fig. 2.4 The arrangement of SP^2 and P bonding orbitals in ethylene.[2]



The π bond is a two-lobed molecular orbital containing one pair of e^- and having a node at the site of the sigma bond.

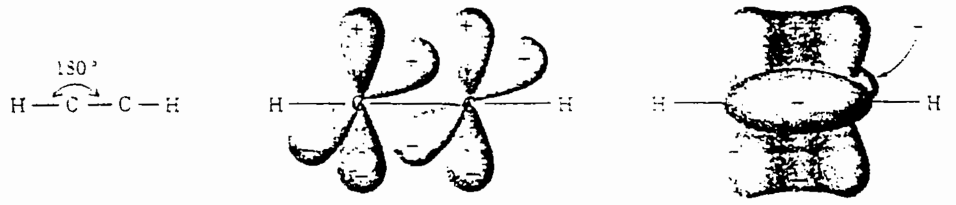
Fig. 2.5 The configuration of bonding orbitals in acetylene.[2]



p orbitals perpendicular to each other and to the linear *sp* orbitals

the two *sp* orbitals are linear

the two *p* orbitals



sigma bonds

p orbitals

two pi bonds

2.4. Significance of the bonding orbital to the composition of bitumen.

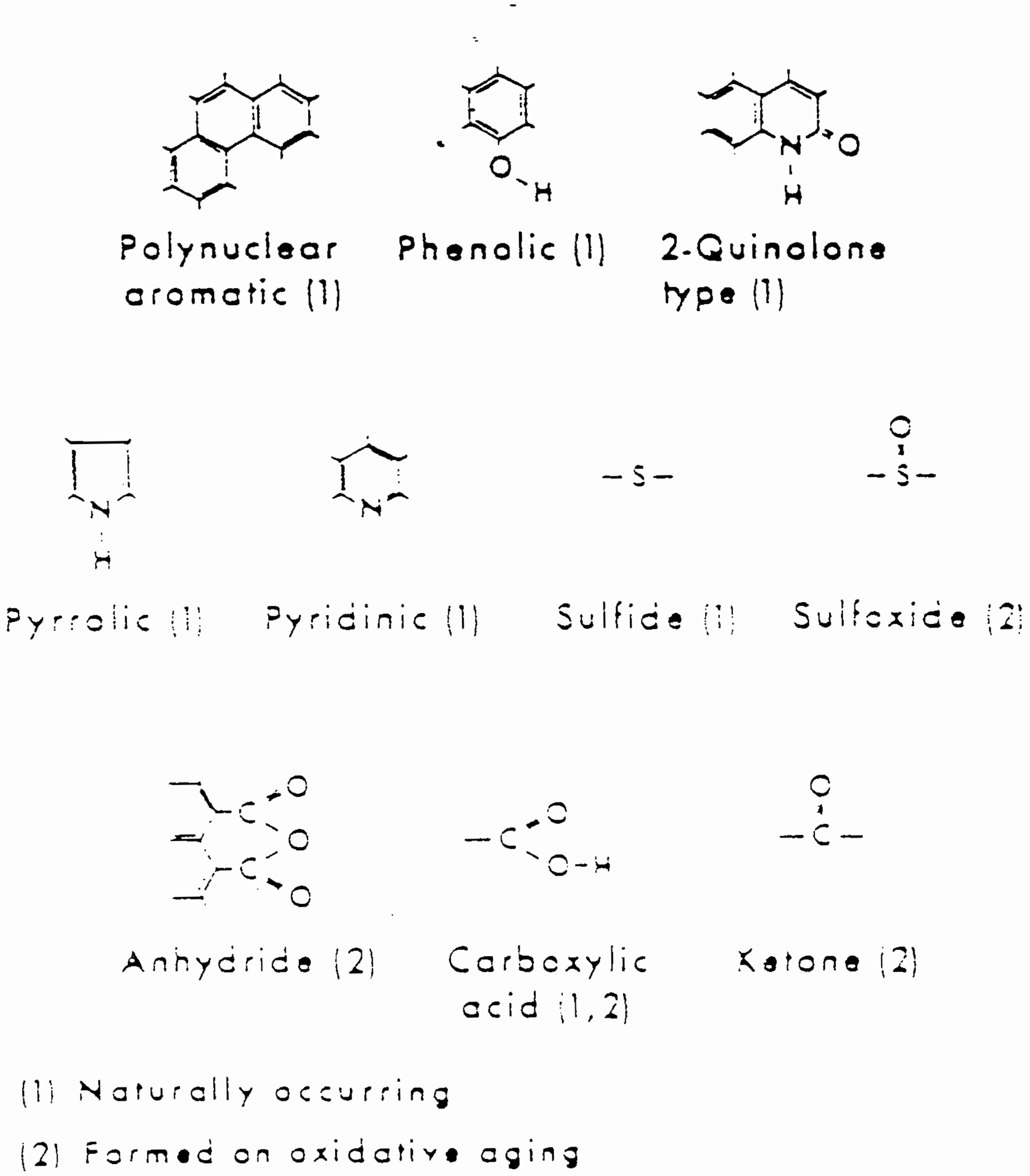
Bonding which involves sp^3 hybridisation generally results in relatively stable compounds, sp^3 bonds take very little part in organic reactions. It is the more exposed Pi bonding orbitals or other atoms, tied to the hydrocarbon molecule, which tend to be focal points of chemical reactivity. These sites of chemical activity on the molecule are called **FUNCTIONAL GROUPS.** They are of importance to the bitumen chemist because of their disproportionately large effect upon asphalt properties. Oxidative hardening, for example, is due to the atmospheric oxidation of certain bitumen molecules resulting in the formation of polar functional groups containing oxygen. Identification of the presence of such functional groups enables one to assess the suitability of such a bitumen for use as a binder.

Polycyclic ring structures which contain two or more different atoms in the ring are referred to as heterocyclic. Heterocyclic compounds may or may not be aromatic, as defined in 2.1.e above, and the non carbon atoms or molecules in the ring may or may not be functional groups.

When atoms with similar electronegativities form covalent bonds each atom exerts roughly equal attraction for the bonding electrons, such bonding is non-polar. When a covalent bond incorporates an atom, or molecule, with a large electronegativity valve then that atom, or molecule, has a greater attraction for the bonding electrons. There is , therefore, a greater electron density in the vicinity of the more electronegative atom. This phenomenon gives rise to what are known as polar covalent bonds.

Polycyclic and heterocyclic ring structures may incorporate atoms or molecules within their structure which give rise to polarisation, and hence polar functional groups. Figure 2.6. illustrates the typical polar functional groups present in bitumen.

Fig. 2.6 Important functional groups present in Bitumen[5]



2.5. The chemical composition of bitumen.

Over the last forty years there has been a vast amount of research carried out in an effort to elucidate the structure of bitumen. There is general agreement, amongst workers in the field, that it is nigh impossible to fully unravel the chemical structure of a single bitumen, at the present time, let alone the vast number of different bitumens that occur as a result of variable crude oil sources. There is no doubt, however, that full and detailed knowledge of the chemical structure of bitumen would be of considerable advantage in assessing its suitability for certain applications.

In spite of the complexity of the organic compounds present, a considerable body of information has built up which can give a broad picture of the overall chemical makeup of bitumen.

Detailed elemental analysis of bitumen, as illustrated in table 2.2., has been possible for many years, unfortunately it reveals little more than the bare proportions of elements present in bitumen.

Full molecular analysis of bitumen has proved difficult due to the wide variety of structures present. In broad outline the compounds range from non-polar non-aromatic hydrocarbons to highly aromatic structures containing varying amounts of heteroatoms, such as oxygen, nitrogen and sulphur. Heteroatoms are usually associated with polar functional groups in hydrocarbon structures. The fact that they tend to dominate the properties of the various molecules present in bitumen has led researchers to concentrate upon their identification. This approach certainly reduces the size of the compositional analysis problem and yet still allows a relationship to be established between bitumen properties and the reactively dominant functional groups.

Petersen[5] et al have developed quantitative infrared red spectrometry for the purpose of identifying key, heteroatom containing, functional groups that are present in bitumen. In this work the functional groups occurring in bitumen both naturally and as a result of oxidative ageing have been identified. Although at an early stage this work is a good example of the importance of using compositional analysis to determine binder properties.

Goodrich[6] et al identify six main analytical procedures that are currently used in compositional analysis, these are:

a) Fractionation by precipitation: solvent precipitation, chemical precipitation.

b) Fractionation by distillation: vacuum distillation, thermogravimetric analysis.

c) Chromatographic separation: gas chromatography, inverse gas liquid chromatography, (absorption, ion exchange, co-ordination, thin layer, size exclusion).

d) Chemical analysis: spectrophotometric techniques, (infrared red, ultra violet, nuclear magnetic resonance, x ray fluorescence, emission, neutron activation), titrimetric and gravimetric techniques, elemental analysis.

e) Molecular weight analysis: mass spectrometry, vapour pressure osmometry and size exclusion chromatography.

f) Indirect compositional analysis by internal dispersion stability tests.

Unfortunately the rather specialised nature of many analytical techniques have tended to place the compositional analysis of bitumen into the hands of the analytical research chemist. At the point of delivery, where the bitumen enters into engineering use, the matters of importance are compliance with specifications and suitability for application. Engineers have, over the years, preferred a simpler view of the chemical structure of bitumen, rather than a complex listing of chemical functional groups from which decisions would have to be made about the suitability of the bitumen for a particular purpose. It is probably not surprising, therefore, that over the last forty years the favoured compositional analysis technique has been to separate bitumen into broad chemical groups, which have then been used, with varying degrees of success, to try and predict physical behaviour.

2.5.1. Compositional analysis of bitumen by fractionation.

Four slightly different techniques for fractional analysis of bitumen are described by Goodrich[6] et al, it is necessary to appreciate that fractionation into broad chemical bands is an imprecise analytical technique. Not only does considerable overlap exist between the bands but each of the four techniques described produces slightly different band widths. It is usual, therefore, to specify the test method used when quoting the composition of bitumen.

The four fractionation techniques are:

1) Chemical precipitation, developed by Rostler and Sternberg: in this method separation is achieved initially with n-pentane, organic solvent. Subsequent fractions are then precipitated using sulphuric acid of increasing concentration.

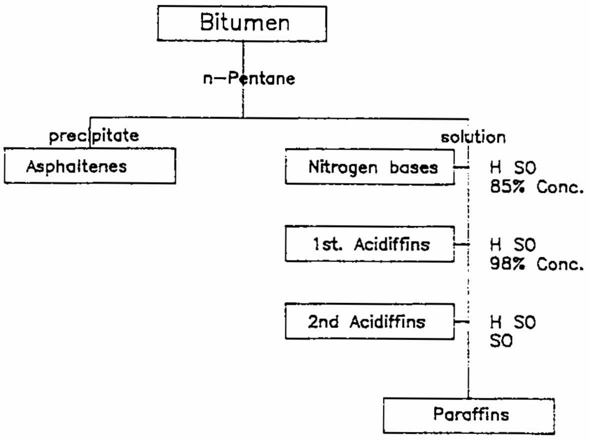
2) Solvent fractionation, developed by Traxler and Schweyer: n-butanol and acetone solvents are used along with temperature variation in order to separate and precipitate out the various fractions.

3) Fractionation and adsorption chromatography:
    a) Clay gel procedure: n-pentane is used for initial separation followed by selective adsorption on clay and silica gel.

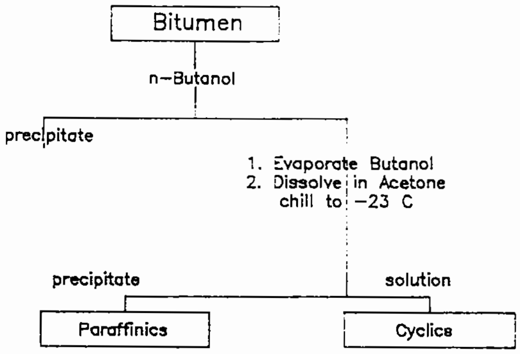
    b) Corbett procedure: probably the technique that results in the most familiar terminology for bitumen fractions. n-Heptane is used to carry out initial separation of asphaltenes followed by adsorption on alumina and subsequent desorption with increasingly polar solvents.

4) Size exclusion chromatography: separation is achieved on the basis of the size of the molecules in each of the frac-

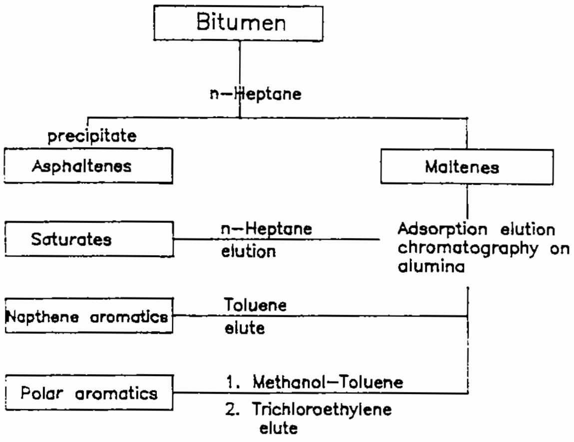
tions, analogous to sedimentation techniques used for fine soils.



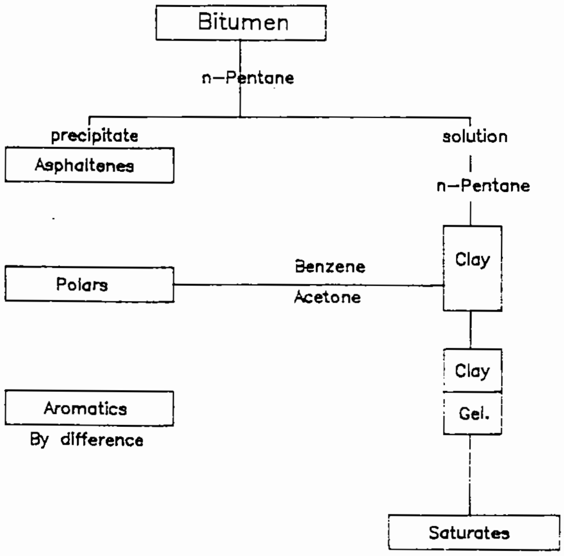
Chemical precipitation Rostler and Sternberg



Solvent fractionation Rostier and Sternberg



Corbett adsorption/desorption chromatography



Clay/gel adsorption—desorption chromatography

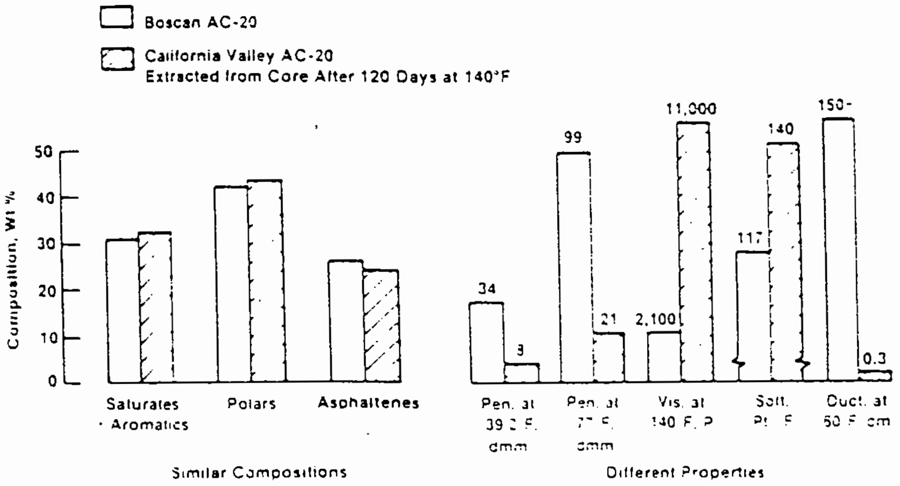
Figure 2.7 Schematic representation of the fractions obtained[6] using the various separation methods,

Table 2.2 A typical elemental analysis of bitumens from various sources[6]

Asphalt	Ni (ppm)	V (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	O (wt %)	N (wt %)	S (wt %)	C (wt %)	H (wt %)	Atomic H/C
1	21	63	39	0.2	7	6	25	0.73	0.20	3.4	81.23	9.78	1.43
2	55	102	22	0.3	39	34	159	0.37	0.38	5.3	82.21	10.16	1.47
3	42	154	141	1.5	5	7	69	0.54	0.39	5.4	82.63	10.01	1.44
4	133	1590	56	1.3	311	5	42	0.75	0.72	5.9	80.70	9.99	1.47
5	130	104	84	0.8	335	4	14	0.94	1.22	1.6	84.27	10.41	1.47
6	123	97	147	1.2	106	19	75	0.93	0.93	1.5	83.17	9.93	1.42
7	139	284	52	1.0	230	26	67	1.01	0.93	5.2	80.18	10.10	1.50
8	10	7	100	3.2	13	8	78	0.64	0.44	0.9	85.98	10.85	1.50
9	39	118	5	0.1	171	2	10	0.61	0.36	5.9	82.22	9.88	1.43
10	138	369	7	0.1	28	11	118	0.67	1.04	6.6	80.46	10.11	1.50
11	87	281	15	0.2	1	1	6	0.52	0.62	3.5	83.61	10.44	1.49
12	113	151	113	3.7	190	113	108	1.03	1.21	1.5	84.08	10.37	1.47
13	112	19	146	1.9	129	134	97	0.94	0.98	0.9	85.17	10.81	1.51
14	91	463	24	0.3	9	6	30	0.48	0.55	4.5	82.43	10.12	1.46
15	13	15	49	0.4	189	10	40	0.44	0.20	4.2	82.94	10.13	1.45

Note: Metals by inductively coupled plasma atomic absorption; C, H, N by Carlo Erba; S by Leco; and O by neutron activation.

Fig. 2.8 Bitumens with similar fractional compositions but different properties[6]



2.5.2. Critical examination of the structure of bitumen as determined by traditional fractionation methods.

The traditional view of the chemical structure of bitumen is based on fractionation techniques such as Corbett adsorption/desorption chromatography. Bitumen is considered to comprise of a colloid system with a disperse phase, composed largely of asphaltenes and high molecular weight aromatic components of maltenes, in a continuous phase made up of the low molecular weight components of the maltenes. The Corbett method divides bitumen into four fractions, asphaltenes, saturates, aromatics and polar aromatics (or resins). The latter three jointly form the maltenes.

Asphaltenes. That fraction of bitumen which is insoluble in a defined hydrocarbon solvent. Traditionally considered to comprise of complex polar aromatic compounds of molecular weight in the range 1000-100000. Recent work by Boduszynski, using field ionisation mass spectrometry, indicates that the n-Heptane asphaltene is closer to an average molecular weight of around 900 with little over 2000. Further, he established that asphaltenes had the lowest molar man of any of the Corbett fractions. Goodrich et al suggest that such findings, along with studies by Petersen of the functional groups in bitumen, indicate that a new model of bitumen can be hypothesised. This would relate the rheological behaviour of bitumen, and changes in rheological behaviour due to other effects, to interactions between molecular structures of mean molecular masses of about 1000.

Saturates. Generally comprise of sp^3 hybridised compounds such as straight and branch chain aliphatic groups and cycloparaffins. Molecular weights are in the range of 300 to 2000.

Aromatics. (As defined in 2.1.e) comprise about 40% of the total bitumen and consist of non-polar polycyclic ring structures, typically with sp^2 bonding. Molecular weight range is in the region of 300 to 2000.

Polar aromatics. These are very polar heterocyclic compounds containing small amounts of oxygen, nitrogen and sulphur in the ring structures.

Traditional compositional theory of bitumen considers the aromatic and polar aromatic content to be important in determining whether the bitumen is of a SOL or GEL type. In the presence of sufficient quantities of aromatics and polar aromatics of sufficient solvating power the asphaltenes are well dispersed and a SOL type bitumen results. SOL type bitumens are suitable for use as road binders. If the aromatic and polar aromatics are unable to fully disperse the asphaltenes then these may begin to link together to form a loose structure giving rise to a GEL type bitumen, these are unsuitable for use as road binders.

The traditional approach to composition analysis, and conclusions drawn from it, must be treated with caution. It should be borne in mind that fractionation techniques are imprecise and that there is considerable overlap between the broad bands of chemicals. In addition, the only thing that hydrocarbon compounds have in common in a given fraction may be that they are both soluble in the same solvent. Figure 2.8. illustrates how two bitumens that exhibit virtually the same fractional composition may have widely different physical properties. To summarise, fractionation techniques are a useful measure for quality control purposes, when bitumen is processed. However, it would be unwise to attempt to draw conclusions concerning the rheological properties of bitumen from them. Full analysis of bitumen is not possible at the present time and physical tests provide the only practical method for assessing the performance of bitumen.

REFERENCES

1. Franck H.G. The most recent methods for elucidating the chemical composition of tar. Reported in Bituminous materials in road construction.
2. Fessenden and Fessenden. Organic chemistry.(Brooks Cole publishing Co. Ltd.) 4th Ed. 1990
3. Dickinson E.J. The constitution of road tar. J. Soc. Chem. Ind., London 1945
4. Adam W.G. and J.S. Sach. Free carbon formation in coal tars and pitches. J. Soc. Chem. Ind., London 1929
5. Petersen J.C. Functional group analysis of asphalts using differential infrared spectrometry and selective chemical reactions-Theory and application. T.R.B. Washington D.C. 1986
6. Goodrich J.L., J.E. Goodrich and W.J. Kari. Asphalt composition tests: Their application and relation to field performance. T.R.B. Washington D.C. 1986

CHAPTER THREE

THE PHYSICAL AND RHEOLOGICAL PROPERTIES OF BITUMEN

3.1. Binders in the modern day context.

With the decline of coal gas production the use of tar as a road binder has suffered a corresponding decline. Road tar binders may still be obtained for certain specialist applications, such as car park surfacings, and they are still widely used in blends with bitumen for surface dressing. In the modern day context bitumen is the dominant material used, in various forms, for road construction and maintenance. Consequently the remainder of this report concentrates upon bitumen as a binder with the discussion of road tars confined to their use as modifiers in tar-bitumen blends.

3.2. An introduction to the concept of the ideal binder.

In any discussion of the modification of binders it is important not to overlook any of the many properties that are necessary for it to fulfil its task. If the question were asked as to which property of a binder was most important there would probably be as many different answers as there are binder applications. The introduction of the concept of an ideal binder is an attempt to draw attention to all these important properties. When considering bitumen in the role of an ideal binder its suitability must be examined in several different areas, some of which appear to be mutually exclusive.

3.3. The physical properties of the ideal binder.

a) It must be impervious to the penetration of moisture.

When a binder is incorporated into an aggregate mix, for use in a layer of road construction, or sprayed onto the surface of a road as part of a surface dressing treatment it is necessary that the resulting road is capable of resisting the penetration of moisture. If such moisture penetration were to occur it would have a deleterious effect on the sub-grade and the road foundation would effectively be undermined.

b) It should have good adhesive properties.

This is an almost self evident requirement for if a binder were unable to hold aggregates or surface coatings then they would be scattered and eroded by the action of traffic, and the road structure would be open to moisture penetration.

c) It must be fluid at mixing and spraying temperatures.

A very necessary requirement for the purpose of the manufacture of coated stone materials or for spraying the binder onto the road surface during surface dressing operations.

d) It must be Stiff and stable at high road temperatures.

The ideal binder would remain a stiff elastic solid at all temperatures except those higher temperatures required for operations related to producing bituminous mixes or spraying onto the road surface. A stiff stable binder, at all road temperatures, is required to produce materials with good load spreading characteristics which minimise the levels of stress and vertical strain in the sub-grade at formation level. Such qualities are important in order to minimise permanent deformation, or rutting of the carriageway. In addition a stiff binder reduces the level of tensile strain at a given stress level in an asphalt mix. This improves fatigue life of the mix, strain being the governing criteria.

e) It must remain ductile at very low temperatures.

In order to prevent asphalt mixes cracking at low temperatures it is necessary that an ideal binder should remain ductile during periods of cold weather.

f) It must be non-hazardous in use.

The ideal binder should be non-toxic and non- flammable.

g) The ideal binder should be capable of use in all weather conditions.

However, bearing in mind surface dressing operations and problems with very wet weather, this may be stretching the concept a little too far.

h) It should retain its properties for an indefinite period.

Ideally there should be no deleterious effects associated with ageing.

3.4. The rheology and physical characteristics of bitumen.

3.4.1. Viscoelastic behaviour..

Bitumen is a viscoelastic material and its deformation under load depends both on temperature and the rate of loading. At low temperatures and/or high rates of strain bitumen exhibits an elastic response. At high temperatures and/or low rates of strain bitumen responds in the manner of a viscous fluid. This behaviour has been classified by Van-der-Poel on the basis of the stiffness modulus at a particular temperature and loading time.

$S_{t,T}$ = stress/strain (at a stated temperature for a given loading time)

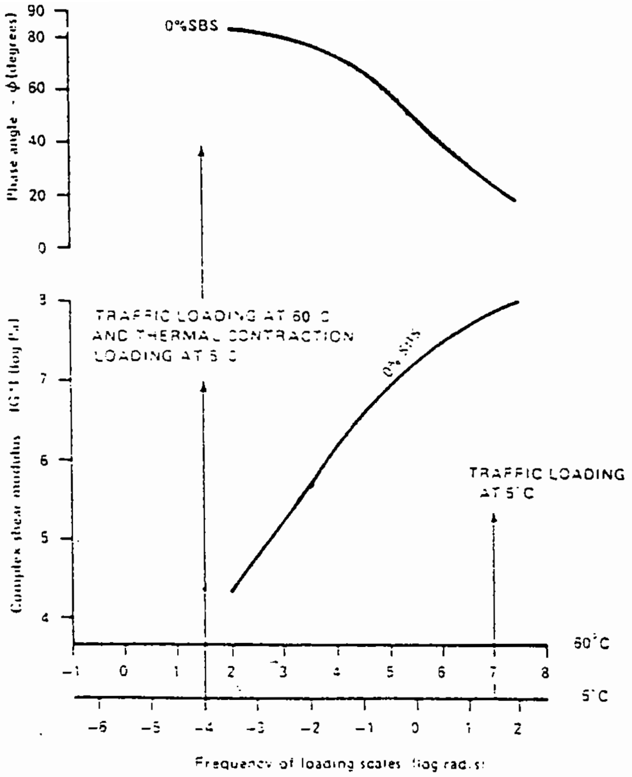
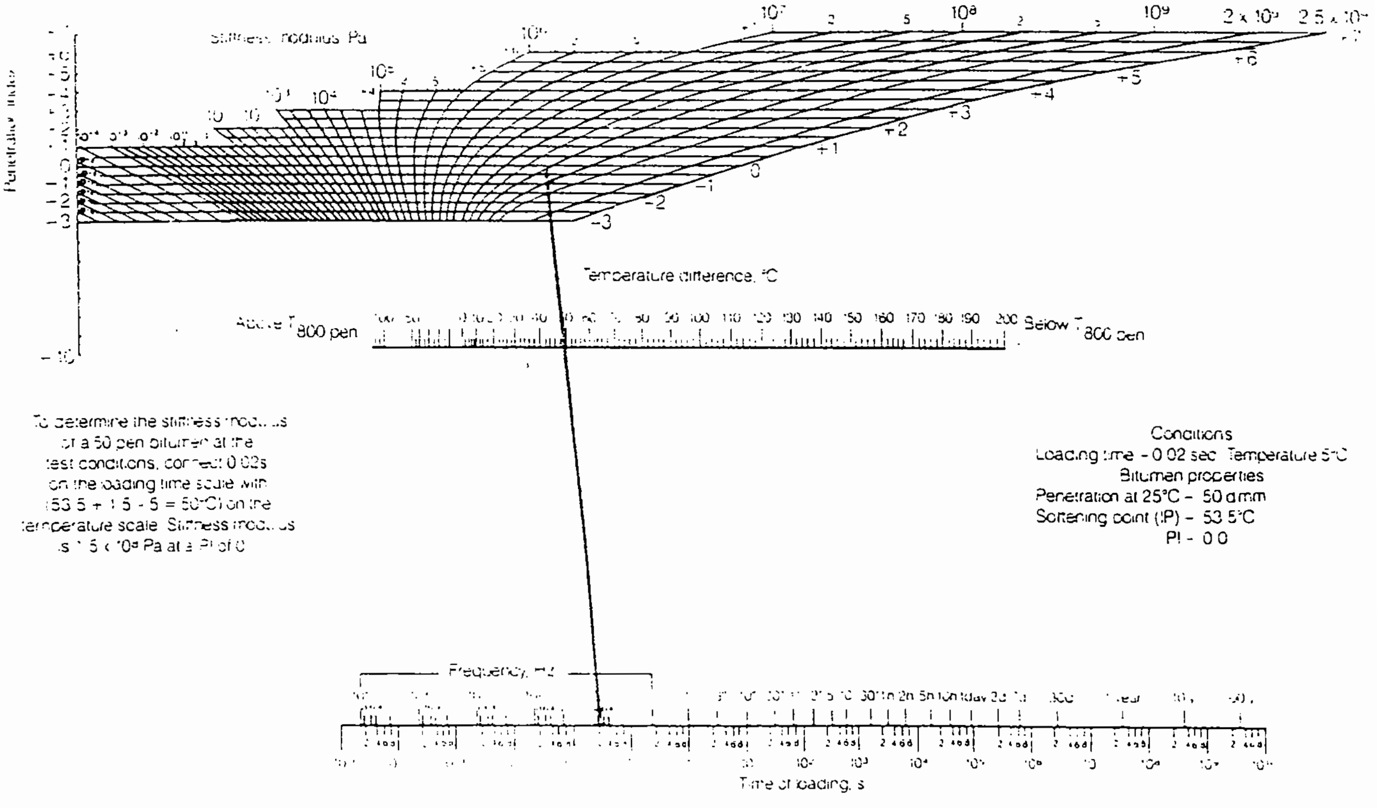


Fig. 3.1 The visco-elastic response of bitumen for various rates of loading, at high and low temperatures [1]



To determine the stiffness modulus of a 50 pen bitumen at the test conditions, connect 0.02s on the loading time scale with (53.5 + 1.5 - 5 = 50°C) on the temperature scale. Stiffness modulus is 1.5 × 10⁸ Pa at a PI of 0

Conditions
Loading time - 0.02 sec Temperature 5°C
Bitumen properties
Penetration at 25°C - 50 dmm
Softening point (IP) - 53.5°C
PI - 0.0

Fig. 3.2 Van der Poel's nomograph [2]

All bitumens exhibit thermoplastic properties, becoming progressively softer on heating. Empirical observations have shown a linear relationship between the log. of penetration and temperature.

$$\log.\text{Pen.} = AT + K$$

Pfeiffer and Van Doormaal[3] define the slope A in terms of penetration index (PI).

$$A = d\,\log.\text{Pen.}/dt = 20 - PI/((10 + PI)x50)$$

From the results of numerous creep and dynamic tests on many different bitumens Van der Poel[3] established a relationship (figure 2.9.) between stiffness modulus (G) and penetration index, temperature and loading time. He produced a nomograph for the prediction of stiffness modulus for any case of loading time and temperature. This allows the characterisation of bitumen, in terms of stiffness, on the basis of the results of routine penetration and softening point tests as:-

$$A =(\log.\text{Pen}.t_1 - \log.\text{Pen}.t_2)/(t_1 - t_2)$$

Such characterisation, whether estimated using Van der Poel's nomograph or measured directly, is important for the thickness design of bituminous pavement layers in terms of both fatigue life and permanent deformation.

Compared to the concept of an ideal binder the rheological properties of bitumen, although not straightforward, result in a material that is a stiff elastic solid at normal road temperatures under rapid traffic type loadings. And one that is capable of sufficiently fluid behaviour at high temperatures to allow spraying, and the mixing and coating of aggregates. It is at the extreme ends of the viscoelastic range where bitumen has been found lacking.In practice under the action of traffic loadings this has resulted in undue softening and rutting at high road temperatures and/or a tendency to brittle behaviour at low road temperatures. Thus, although not the ideal binder described in the model concept bitumen is nonetheless quite remarkable for its ability to perform reasonably well through a whole range of diverse functions.

3.4.2. The adhesive properties of bitumen.

Good adhesion is a fundamental requirement of a road binder. The adhesive bond between bitumen and aggregate is responsible for holding together the stone matrix which forms a bituminous layer. The adhesive bond is also vital for surface dressing operations, where chippings are effectively glued to the road by the binder prior to gradual embedment into the substrate.

In the absence of water it is the viscosity of bitumen which tends to influence the ease with which bitumen can coat the surface of aggregates or a road. Usually, once such a coating has been formed it will remain in good condition unless attacked by moisture. It is possible for the bitumen-aggregate bond to be ruptured, this may occur as a result of embrittlement due to oxidative ageing. However, it is much more likely for a cohesive failure within the bitumen itself to occur in such circumstances.

Water is the real enemy of a good adhesive bond between bitumen and road stone. It has a threefold effect, first it may hinder the formation of an effective bond - this situation usually arises if water is present in aggregate or chippings prior to mixing or surface dressing. Second, it may rain during road construction or surface dressing operations thus affecting the bond between layers. Finally, water may enter a road pavement and displace the existing bond between stone and bitumen.

It may be recalled from the discussion in 2.5. above that bitumen comprises predominantly of hydrocarbons, with a few heteroatoms contained in some of the hydrocarbon structures resulting in a number of polar functional groups. In the fractional analysis of bitumen these molecules are contained in the resin (or polar aromatic) group. They are responsible for the adhesion between bitumen and the surface of aggregates due to electrostatic interaction with the aggregate surface. Compared to the relatively few polar molecules contained in bitumen water is, by contrast, a highly polar solvent which is attracted to the charged aggregate surfaces by orientation forces. Thus, water can prevent bitumen from forming a bond with aggregates or it may displace bitumen from the aggregate surface mechanism.

A simplified view of the mechanisms operating as water displaces bitumen from a solid surface is given by the Road Research Laboratory[4]. They consider the contact angle that occurs when a globule of bitumen on a solid surface is surrounded by water. In such a situation the interfacial energies are given as Z stone/bitumen, Z stone/water, Z water/bitumen. Work (w) required to displace water from the solid surface over a unit area is given by:-

$w = Z_{sb} + Z_{bw} - Z_{sw}$ sb - solid/bitumen interface
for equilibrium $Z_{sb} = Z_{sw} + Z_{bw}\cos 0$ sw - solid/water interface
hence $w = Z_{bw}(1+\cos 0)$ bw - bitumen/water interface

Thus, the work required to displace water is related to the contact angle 0 and the bitumen/water interfacial energy. The adhesion of bitumen can be improved by increasing the contact angle, such would be the effect of increasing the quantity of certain polar hydrocarbons in the bitumen.

Returning to the concept of the ideal binder, the need is for good adhesion in any circumstance. Bitumen meets the requirements of the ideal binder in terms of dry adhesion but fails in the presence of moisture. Problems of de-bonding or stripping, due to the action of water, do not usually manifest themselves in the denser, more impervious road construction materials. However, they present a very real problem, following surface dressing operations, where open textured materials are used or drainage conditions are poor.

3.4.2.1. The relationship between the composition of bitumen and its adhesive properties.

By using differential infrared spectrometry and techniques for isolating functional groups Petersen et al[5] have identified the chemical functional groups that form the bond between bitumen and aggregate particles. In addition their relative tendency to be concentrated at the aggregate surface and susceptibility to displacement by moisture have also been identified.

Table 3.1[5]

Concentration of functional groups at the bitumen aggregate interface, and moisture susceptibility.

Functional group type	Average concentration ratio [a]	Average water displacement ratio [b]
Ketone	1.2	0.65
Carboxylic acid	30	2.1
Anhydride	14	3.5
2-Quinolone	5.4	3.1
Sulfoxide	2.6	2.5
Pyrrolic	0.27	low
Phenolic	4.1	low

[a] Concentration at asphalt-aggregate interface divided by concentration in bulk asphalt

[b] Concentration in water-displaced fraction divided by concentration at asphalt-aggregate interface

It is apparent from the figures in table 3.1. above that the functional groups that dominate the aggregate/bitumen bond also tend to be susceptible to displacement by water. Some of these functional groups are oxidation products, clearly, therefore, there is scope for modification to the adhesion properties of bitumen and its moisture susceptibility.

3.4.3. Ductility.

Ductility is an important quality for the avoidance of low temperature cracking in bitumen. Such cracking can occur as a result of stresses induced in the road by normal traffic loading or thermal movement. For binders of a given hardness maximum ductility will occur at a particular temperature. Generally this temperature will be lower for soft binders than for hard binders.

Traditional tests, involving the stretching of bitumen samples and measuring their elongation at break, are of questionable validity as a measure of ductility and cohesive strength. They tend to be unrepresentative of the real levels of strain likely to be experienced in the road and unrepresentative of the loading.

In comparing bitumen to the requirements of the model binder one is unfortunately faced with the problem that the softer bitumens that show ductility at low temperatures tend to be of low stiffness at high road temperatures. The converse is also true of the hard grades of bitumen, which tend to be brittle at low temperatures.

3.4.4. The effects of ageing on the physical properties of bitumen.

Bitumens gradually harden, and may become brittle, with age. This is due to four main factors:-

1) The oxidation of some of the hydrocarbon molecules in bitumen to form highly reactive polar functional groups. Analysis by Petersen et al has shown that the particular groups associated with oxidative ageing are sulfoxides, anhydrides, ketones and carboxylates, as indicated in figure 2.6 above.

The mechanism of hardening and embrittlement is uncertain but is probably due to a change in the internal structure of bitumen. This may involve the formation of a network of cross linked molecules, due to interaction with the oxidation products, such behaviour could be analogous to a "GEL" type bitumen, as described in the SOL-GEL theory of bitumen.

The amount and rate of oxidative hardening that takes place is dependent upon temperature and the degree to which bitumen is aerated or exposed to the atmosphere. The processes of mixing and coating are responsible for a significant initial amount of oxidation. The in service, or ageing, oxidation rate is largely dependent upon the amount of open pore space, or voids, in the mixed aggregate. Open textured materials are much more prone to oxidation, and consequent brittle failure and disintegration than dense, well compacted mixes.

2) Gradual loss of the more volatile components of bitumen, by evaporation. The greatest proportion of this loss occurs during high temperature operations such as mixing. In service, at typical road temperatures, there is a gradual loss of the more volatile oily paraffinic constituents of the bitumen in the mix. An accelerated oxidation rate at the road surface due to the effect of ultra violet radiation, higher temperature and continuous exposure to the atmosphere is responsible for the formation of hard skin on the bitumen at the road surface. Despite the effects of vehicle abrasion this skin has the effect of acting as a barrier and hindering the loss of volatiles as well as reducing the rate of oxidation in the rest of the bituminous layer.

In practice the oily components of road bitumen are not that volatile. Because of the factors mentioned above their loss and consequent hardening of the bitumen are both probably quite small.

3) Exudative hardening, as described by Whiteoak[6], occurs as a result of the absorption of low molecular weight paraffinic compounds by porous aggregates. Whiteoak explains that this occurs in circumstances where an exudative or "unbalanced" bitumen and porous aggregates are both present in a mix. He defines such a bitumen as one where "the molecular weight distribution and chemical constitution of the bitumen is unbalanced". By this he means that the chemical composition of the bitumen, as defined by fractional analysis, indicates a preponderance of one of the fractions. In the case of exudative bitumens this is most likely to be the saturate fraction.

4) Age hardening of binders. Work by Traxler and Schweyer[7] has demonstrated that bitumens harden with age only. This takes place in the absence of oxygen and is thought to occur due to the slow crystallisation of aromatic hydrocarbons. This process is reversible by the effects of heat or movement, the latter may be induced by traffic.

Brittle behaviour is undesirable in bitumen as it leads to cracking and may result in durability problems and a reduced life. Of the four factors responsible for age hardening oxidation is probably the most serious. This would imply that the less well compacted, open textured asphalt mixes present the most serious ageing problem. Such materials are also most prone to the effects of water damage, due to the concentration of moisture susceptible functional groups at the surface of aggregates, and the ease with which water can penetrate them.

The R.R.L.[4] carried out a full scale experiment to assess the effect of ageing on binder hardness. The results of this experiment, which was carried out on the Colnbrook by-pass, are indicated below in table 3.2. From these results it may be concluded that in denser mixes the combined effects of low voids, a hard oxidised skin and the action of traffic prevent undue hardening. The T.R.R.L. further concluded that the prevention of binder hardening maximised ductility at low temperatures and that for dense materials that were heavily trafficked bitumen mixes exhibited considerable durability and a long service life.

Ideally a binder should suffer no deleterious effects with age, bitumen comes close to the requirements of the ideal binder when used in well compacted dense mixes, otherwise it is prone to hardening which reduces ductility and increases a tendency to low temperature brittle behaviour.

Table 3.2 Comparison of the differential effects of voids in the age hardening of bituminous mixes[4]

The Penetrations of Different Types of Bitumen Recovered From Bitumen-Macadam Carpets after Various Intervals of Time on Trunk Road A4 (30 000 tons of traffic/day)

Type of bitumen	Pen. of asphaltic cement in binder heater	Penetration of bitumen				
		Recovered from sample from binder heater	Recovered from road before traffic	Recovered from road after		
				2 years	10 years	14½ years
Venezuelan .	52	—	46	40	27	22
Mexican . .	58	—	50	42	17	24
Californian .	56	—	58	53	—	43
Trinidad lake asphalt	65	195	138	67	30	30

Dense Bitumen Macadam

The Penetrations of Different Types of Bitumen Recovered from Rolled Asphalts after Various Intervals of Time on Trunk Road A4 (30 000 tons of traffic/day)

Type of bitumen	Pen. of asphaltic cement in binder heater	Penetration of bitumen						
		Recovered from sample from binder heater	Recovered from road before traffic	Recovered from road after				
				2 years	10 years	12 years	14½ years	17 years
Venezuelan .	60	—	47	50	60	65	55	50
Mexican .	57	—	50	49	47	—	46	41
Californian .	59	—	58	56	—	—	60	52
Trinidad lake asphalt	65	192	145	105	93	76	62	50

Rolled Asphalts

3.4.5. Physical properties relating to the general usage of bitumen.

Ideally a binder should be non-hazardous in use. Unlike road tars bitumen is non-toxic and contains only minute quantities of carcinogenic substances. The main hazards posed are skin burns due to accidental contact or splashes of hot bitumen. Bitumen fumes do not present a problem in the open air though in confined spaces there is a risk of a build up of poisonous hydrogen sulphide gas. Therefore, adequate precautions are required in terms of protection against accidental splashing, with the usual confined space precautions being taken with respect to bitumen fumes.

Whiteoak - in the shell bitumen handbook - quotes the Health and Safety Executive Guidance Note E.H.40. - Exposure limits for bitumen fumes and hydrogen sulphide in the working atmosphere.

occupational exposure limits for bitumen fumes in the working atmosphere are
Long-term exposure limit (8 h time weighted average) = 5 mg/m^3
Short-term exposure limit (10 min time weighted average) = 10 mg/m^3

occupational exposure limits for hydrogen sulphide in the working atmosphere are
Long-term exposure limit (8 h time weighted average) = 10 ppm (14 mg/m^3)
Short-term exposure limit (10 min time weighted average) = 15 ppm (21 mg/m^3)

In normal use bitumen does not pose an undue fire hazard, but the use of cut back bitumens in surface dressing operations necessitate spraying at temperatures above the flash point of the binder. Clearly in such circumstances the risk of accidental fire or explosion is high and adequate precautions are necessary. The use of cut back bitumen for surface dressing is much rarer nowadays as much for health and safety reasons as its difficulty in use.

3.4.6. Bitumen and the concept of the ideal binder.

The main areas where bitumen falls short of the performance required on the ideal binder are:-

1) In its response to temperature variations, difficulties arise in obtaining the necessary fluidity at high temperatures coupled with good stiffness at elevated road temperatures and adequate ductility at low road temperatures.

2) The aggregate-bitumen bond which is susceptible to attack by water, a phenomenon which can be aggravated by oxidation products.

3) Cohesive strength of bitumen, not in terms of its ultimate strain at break, but rather in terms of its tensile strength at modest strains representative of in service levels.

The modification of bitumen properties should, therefore, seek to address the shortcomings of bitumen relative to the requirements of the ideal binder.

REFERENCES

1. Dickinson E.J. Assessment of the deformation and flow of polymer modified paving bitumens. Australian road research, vol 11, no.3 1981.
2. Van der Poel's nomograph - reproduced from Whiteoak, the Shell Bitumen handbook. Originally reported in J. of App. Chem., vol.4,1954.
3. Pfeiffer J.P.H. and Van Doormaal. Reported in The Properties of Asphaltic Bitumen. (Elseviers Polymer Series) 1950.
4. Road Research Laboratory, Depatment of Scientific and industrial research. Bituminous Materials in Road Construction. (H.M.S.O.) 1962
5. Petersen J.C. Functional group analysis using differential infrared spectrometry. T.R.B., Washington D.C. 1986
6. Whiteoak D. The Shell Bitumen handbook. 1990
7 Traxler R.N. and H.E. Schweyer. Increase in viscosity of asphalts with time. Proc.A.S.T.M. 1936.

CHAPTER FOUR

BITUMEN EMULSIONS

4.1. Bitumen binders - alternative systems for mixing and spraying.

For whatever purpose bitumen invariably has to be initially reduced to a workable viscosity. In many cases this is achieved by heating, an alternative is to dissolve the bitumen in a volatile solvent. After mixing or spraying the bitumen hardens as the solvent evaporates. Demand for binders that could be used or applied at low temperatures also favoured the development of bitumen in water emulsions. These proved to have advantages over cut back bitumens in the following respects:-

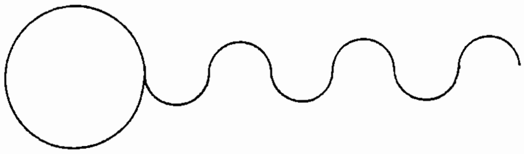
1) For applications where a rapid deposition of bitumen is necessary emulsions are safer as there is no risk associated with temperatures in excess of the solvent flash point.

2) There are no health risks associated with solvent vapours as there are with cut back bitumen.

3) Emulsions are tolerant of damp road surfaces, chippings and aggregates.

4) They are cheaper.

Figure 4.1. Diagrammatic representation of a surfactant molecule.



Surfactants may be classed as anionic, cationic or neutral, depending upon the nature of the hydrophilic groups. Soaps, with their carboxylate groups, are anionic, benzalkonium chloride is an example of a cationic surfactant (not used as a road binder emulsifying agent). Neutral surfactants are not used for producing road binders because they lack the affinity for the surface electrostatic charges that are possessed by the ionic surfactants.

4.4.1. Anionic emulsifiers.

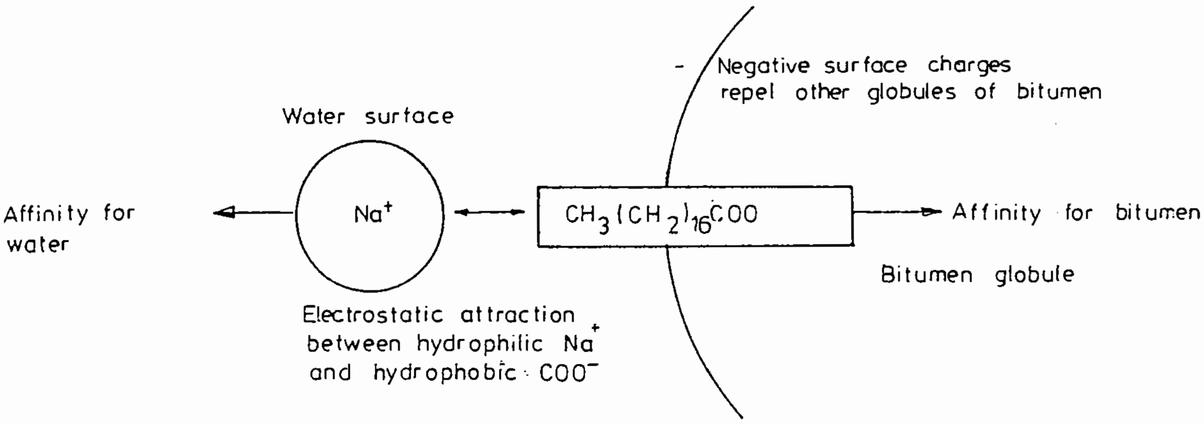
These are soaps, sodium stearate is a well known example.

$CH_3\ (CH_2)_{16}\ COO\ Na$ this ionises in water to

$CH_3\ (CH_2)_{16}\ COO^-\ Na^+$

The negatively charged stearate anion is absorbed into the bitumen (it is the hydrophobic tail) surface creating a negative surface charge. The positive sodium ions remain in the vicinity of the bitumen globule forming an electrical double layer with water, this is illustrated in figure 4.2. below.

Figure 4·2 Anionic Emulsification

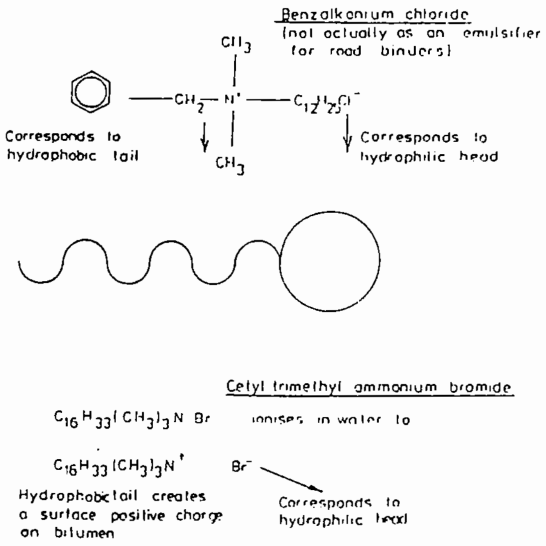


The like charges on the surface of the bitumen globules prevent them coalescing and help keep them in suspension. Emulsions prepared with metallic soap compounds are referred to as anionic because the bitumen globules have a negative surface charge and are therefore attracted to an anode.

4.4.2. Cationic emulsifiers.

Effectively operate in the reverse manner to anionic emulsifiers. Examples of compounds that act as cationic emulsifiers are illustrated in figure 4.3. below.

Figure .3 Cationic emulsifiers



Cationic emulsifiers are preferred for use in the production of road binders because it has long been thought that the surface of aggregates and road materials tend to be more electronegative. If this is true it would encourage the deposition of positively charged bitumen globules during the breaking process.

4.5. The breaking process.

The process of breaking of a bitumen emulsion can be observed in a surface dressing operation. When the binder is first sprayed onto the road surface it is a dark brown colour, as the bitumen is drawn out of the emulsion there is a change in colour to black. This occurs as the deposition of bitumen causes it to concentrate at the road surface. A considerable amount of water is then left on and around the bitumen, in normal circumstances this would seriously damage the aggregate/bitumen bond. However, the presence of the emulsifier alters the road to bitumen contact angle so that the interfacial energies favour wetting by the bitumen. In other words the charged bitumen globules are more attracted to the road surface than they are to the water and also more than the water is to the road surface.

The mechanism of break, or deposition, occurs as a result of a disturbance in the equilibrium of the electrostatic forces that hold bitumen globules in suspension. This is most readily appreciated where a cationic emulsion is attracted to negatively charged ions at the surface of aggregates, or the road. By this reasoning, however, an anionic emulsion would not break until the water phase had evaporated. There is a commonly held view that road stone aggregates have predominantly negative charges at their surface and so cationic emulsions form better bonds with the aggregate. In reality, however, it is perhaps better to consider the road or aggregate as an electrical earth, which is an infinite reservoir of both positive and negative ions, with perhaps a bias towards the latter.

4.6. Classification of bitumen emulsion by B.S. 434.

B.S. 434 parts one to three is the standard governing the types and specifications for bitumen emulsions in the United Kingdom. It applies a classification system where initially emulsions are labelled K for cationic and A for anionic. This is then followed by a number between 1 and 3, which depends upon the speed of break. One is the most rapid breaking and three the slowest. Finally a number follows which expresses the percentage of bitumen present in the emulsion. An example of the classification system would be K1-70 for a rapid breaking cationic emulsion containing 70% bitumen or A2-50 for an intermediate speed of break anionic emulsion containing 50% bitumen.

The most rapid breaking emulsions, group one, are termed labile. They are predominantly intended for surface dressing binders, tack coats and curing membranes. Group two of the classification are termed semi stable and in addition to the emulsifying agent they also contain stabilisers such as casein or potassium soaps, their main uses are for the production of coated macadams and retread processes. Group three emulsions are termed as stable, their composition is as the group two types except that higher quantities of emulsifier and stabiliser are present. Typical applications are soil stabilisation, and spray sealing of open textured wearing courses.

4.7. The importance of bitumen emulsions in the context of binder modification.

Bitumen emulsions exhibit physical properties in their own right, for example viscosity increases as the percentage of bitumen in the emulsion increases. This report is, however, mainly concerned with the behaviour of bitumen deposited by the emulsion. Despite this emulsions have received detailed attention for two reasons. First, they are very popular systems for the application of bitumen, especially surface dressing. Second, emulsions represent a modification to standard bitumen which improves adhesion between bitumen and road stones - particularly in the presence of water. Unfortunately bitumen emulsions are of limited use for coated macadam applications due to the fact that a relatively high void content is necessary to allow for the escape of water during compaction and service.

REFERENCES

B.S. 434 part 1

Whiteoak D. The Shell Bitumen Handbook. 1990

Fessenden and Fessenden. Organic chemistry. (Brooks Cole Pub. Co. Ltd.) 1990

Road Research Laboratory. Bituminous materials in road construction. (H.M.S.O.) 1962

CHAPTER FIVE.

PROBLEMS WITH BITUMEN BINDERS.

5.1. Bitumen and the concept of the ideal binder.

As a resume of the discussion in chapter three it can be stated that bitumen falls short of the requirements of an ideal binder because:-

1) Its adhesive bond with aggregates is susceptible to attack by water, the oxidation of bitumen appears to exacerbate this susceptibility.

2) The relationship between temperature and the viscoelastic behaviour of bitumen is sometimes unsatisfactory. This shortcoming manifests itself as a lack of stiffness or elastic response at elevated road temperatures, alternatively the problem may be viewed as one where bitumen exhibits sufficient stiffness or elastic response at high road temperatures but lacks ductility, and is therefore susceptible to brittle behaviour, at low temperatures. The matter of adequate stiffness, at high road temperatures, is of fundamental importance to the life of a road pavement in terms of its fatigue life and/or resistance to permanent deformation.

Plates 5.1. and 5.3. illustrates the effect of lack of binder stiffness, in this case the photograph shows failure due to permanent deformation and deformation within the asphalt layer. Mixes such as asphalts, which rely on the binder for a good deal of their stiffness, are particularly susceptible to deformation if the binder lacks adequate stiffness.

3) For certain applications, surface dressing in particular, the cohesive strength of bitumen may sometimes prove inadequate. This is most acute at sites which are subject to particularly high shear stresses at the road surface, for example tight bends or steep hills. Plate 5.2. is a good example of surface dressing failure in such circumstances, failures of this type are typified by the adhesive bond still being intact, the actual binder having failed. Clearly the temperature susceptibility of cohesive strength needs consideration in order that the shear strength within the normal working range is not exceeded.

4) In some circumstances the nature of loading may contribute to deformation and fatigue. For example, standing traffic at a road junction will cause a bitumen to react less elastically than a high speed load pulse.

When comparing bitumen with the conceptual ideal binder it is important to remember that in the vast majority of circumstances bitumen binders have proved adequate. In recent years, however, the growth in the volume and weight of traffic has begun to expose binder stiffness problems in some bituminous mixes.

In the field of surface dressing a case can probably be made for much needed improvements generally, spectacular failures on apparently ideal sites are neither new nor particularly uncommon.

In bitumen modification we seek to improve the following properties:-

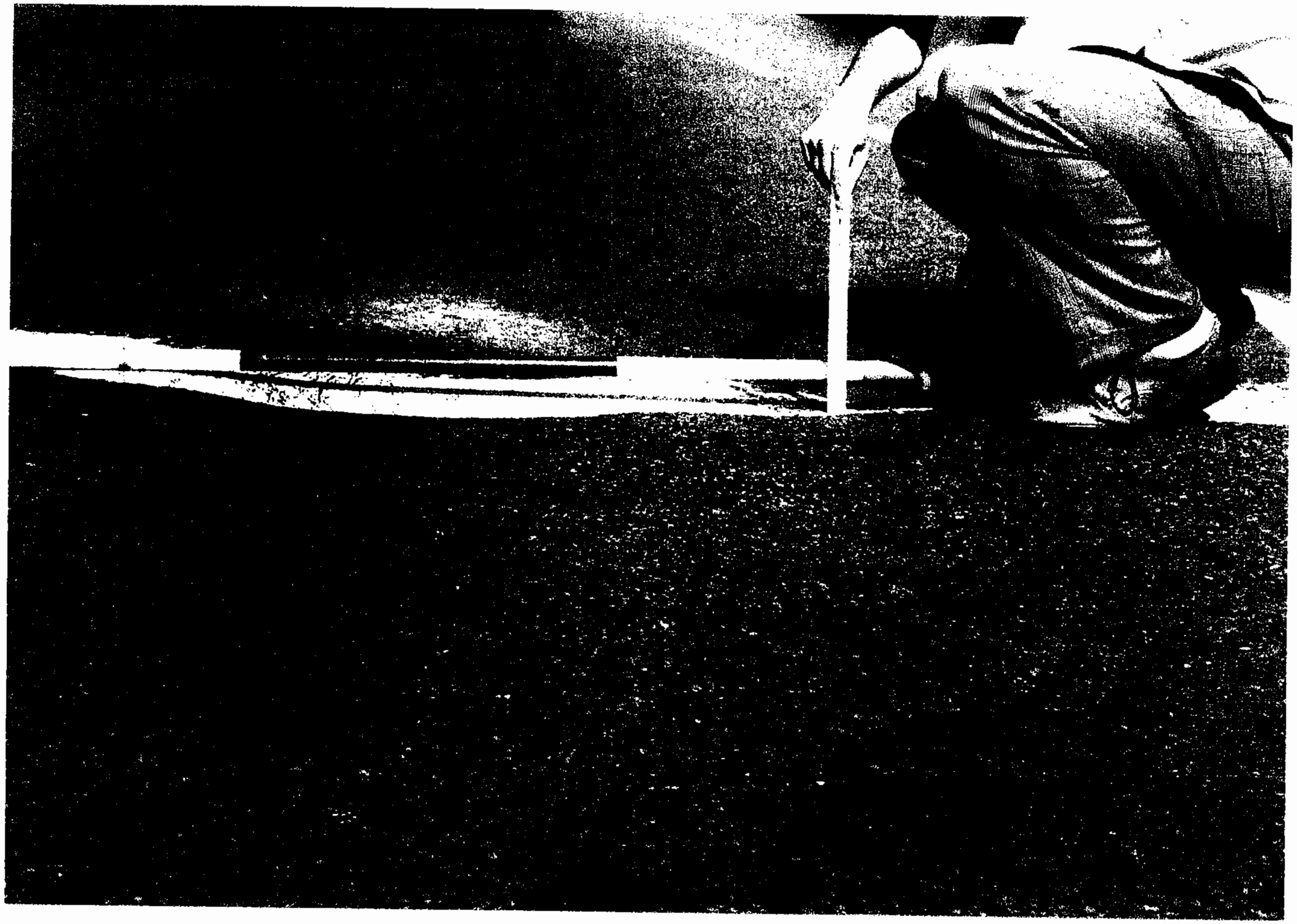


Plate 5.1 Lack of stiffness leading to rutting and deformation in rolled asphalt construction

Plate 5.2 Stripping of surface dressing on a bend due to a lack of cohesive strength in the binder

Plate 5.3 Lack of binder stiffness leading to shoving in rolled asphalt wearing course

adhesion
stiffness
ductility
and cohesive strength.

In addition, for applications such as surface dressing, it is an aim of binder modification to extend the range of climatic conditions under which such work can be carried out. This would be achieved, in theory, by improvements in the areas listed above.

5.2. Traditional test methods for characterisation of bitumen.

These are the familiar tests upon the physical characteristics of binders, rather than their composition, and comprise of the following.

5.2.1. The standard penetration test.

The test consists of allowing a standard needle to penetrate a sample of bitumen, at 25 C, under a 100g load for five seconds. The penetration value is the distance penetrated in tenths of a mm. For example, a 200 pen. bitumen is one where the needle penetrated by 20mm. This test is very sensitive to minor variations of temperature or timing. In practice automatic timing devices are used and require regular checking. (All needles must be clean and straight). Three tests are carried out and the mean value of the three results (within limits specified for variation in the three measurements) is recorded as the penetration.

The acceptable repeatability is for:-

Pen.< 50 - 0.1.mm.

Pen.> 50 - 3% of the mean of two results.

The acceptable reproducibility is for:-

Pen.< 50 - 0.4.mm

Pen.> 50 - 8% of the mean of the two results.

The penetration test is illustrated in figure 5.1.

The standard penetration test is widely used as a guide to the relative hardness of various bitumens. Empirical relationships relate penetration to viscosity. Different bitumens may have the same hardness at 25 C but very different hardnesses at other temperatures.

5.2.2. The ring and ball softening point test.

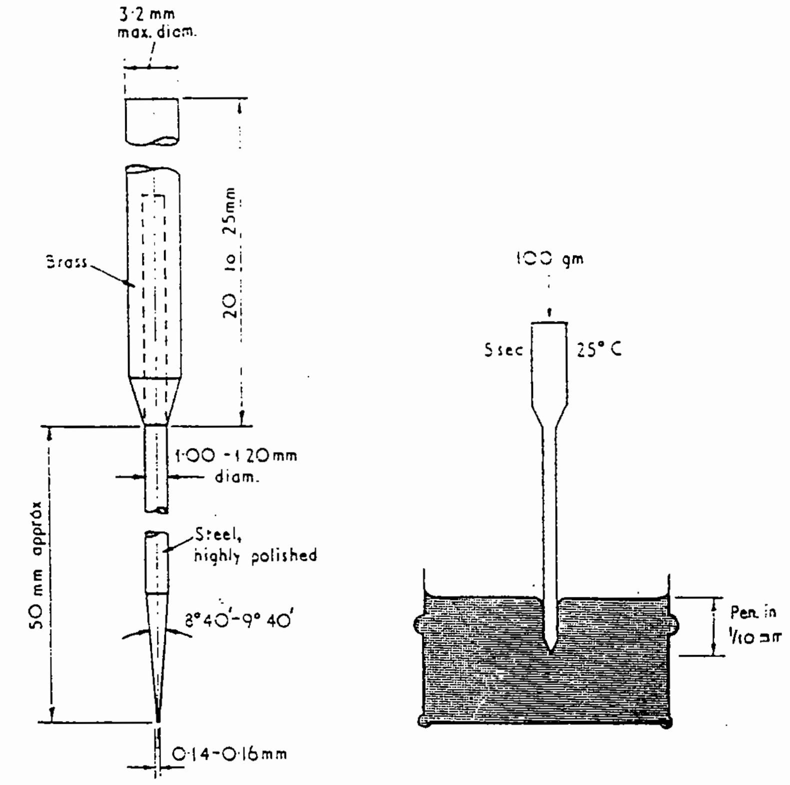
Bitumen does not melt in the ordinary sense, rather, it softens gradually as temperature rises. The softening point test, figure 5.2., establishes the temperature at which a steel ball, initially placed on the surface of a disc of bitumen, falls through as a result of the disc softening with heat.

The linear relationship between the log. of penetration and temperature for bitumens suitable for road use,

$$\text{Log. Pen.} = A.T.+K.$$

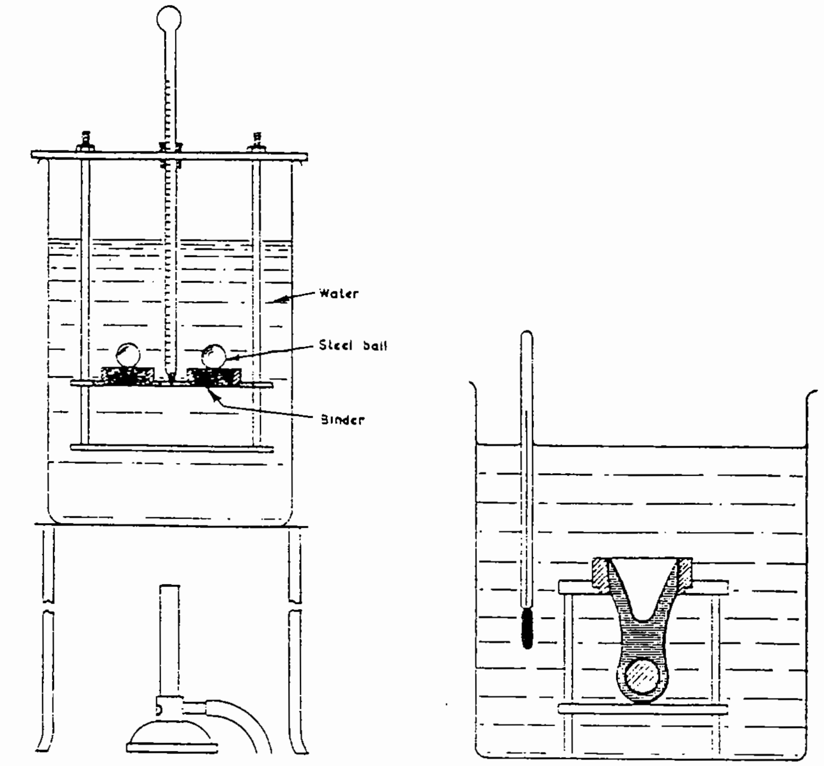
may be extrapolated to a point where it can be shown that the softening point of most bitumens equates with a penetration of around 800. Different bitumens exhibit different relationships between hardness/viscosity and temperature, and generally they are classified on the basis of their temperature susceptibility as established by penetration and softening point tests.

Fig. 5.1 The standard Penetration test [1]



(a) Diagram of needle (b) Diagram of test

Fig. 5.2 Ring and ball softening point test [1]



(a) Diagram of apparatus at beginning of test (b) Diagram showing end of test

5.2.3. The Fraas breaking point test.

This test is used to ascertain the temperature at which a bitumen is subject to brittle behaviour. It is not a commonly specified test method in the United Kingdom although it is routinely used in countries with cold climates. In the test a flexible steel strip is coated with bitumen and flexed slowly at gradually decreasing temperatures (1 C/minute). The temperature at which the bitumen cracks is the Fraas breaking point and it accords with a stiffness of about 2.1×10^9 P.a.

In the late 1960's Heukelom[3] developed the bitumen test data chart which relates both viscosity and penetration to temperature. The viscosity scale has been adjusted in order that a typical road bitumen exhibits a linear relationship with viscosity, as well as log. penetration. The results of softening point, penetration and breaking point tests, for a typical road bitumen, generally all appear along this temperature susceptibility line because the loading times for the three tests are broadly similar. The effect of loading time upon stiffness is taken into account by Van der Poel's method for the determination of stiffness modulus.

5.2.4. Viscosity tests.

British Standards and specifications tend not to express requirements for bitumen properties in terms of viscosity, but prefer indirect empirical test methods, such as penetration and softening point, for its estimation. On the other hand tars, cut back bitumens and emulsions are specified in terms of viscosity, due to their softer or more fluid nature. A whole range of fluid flow tests are used to assess viscosity, most of these comprise of timing the flow of a measured quantity of binder through a standard sized orifice. The standard tar viscometer (fig. 5.4.) is used for cut back bitumens, the Engler viscometer (fig. 5.6.) for emulsions, the A.S.T.M. prefer the Saybolt - Furol viscometer (fig. 5.5.), for cut back bitumen, which is broadly similar to the standard tar viscometer. The Redwood viscometer (fig. 5.7.) is also very similar to the standard tar viscometer except, that it has a very small orifice and is normally used for the measurement of low viscosity flux oils. Measurements of viscosity of emulsions using the Engler viscometer are expressed in degrees Engler, this is actually a ratio between the flow times for water and emulsion in the same instrument.

The tests mentioned above are used for comparative viscosity measurements, it is possible to convert the test results into fundamental units of viscosity, Pa.s (Pascal seconds). Alternatively, nowadays a sliding plate viscometer may be used to measure dynamic viscosity directly. The viscometer applies a shear stress to a thin layer of bitumen, sandwiched between two flat plates, by sliding one plate relative to the other. Viscosity is calculated by dividing the shear stress by the rate of shear strain.

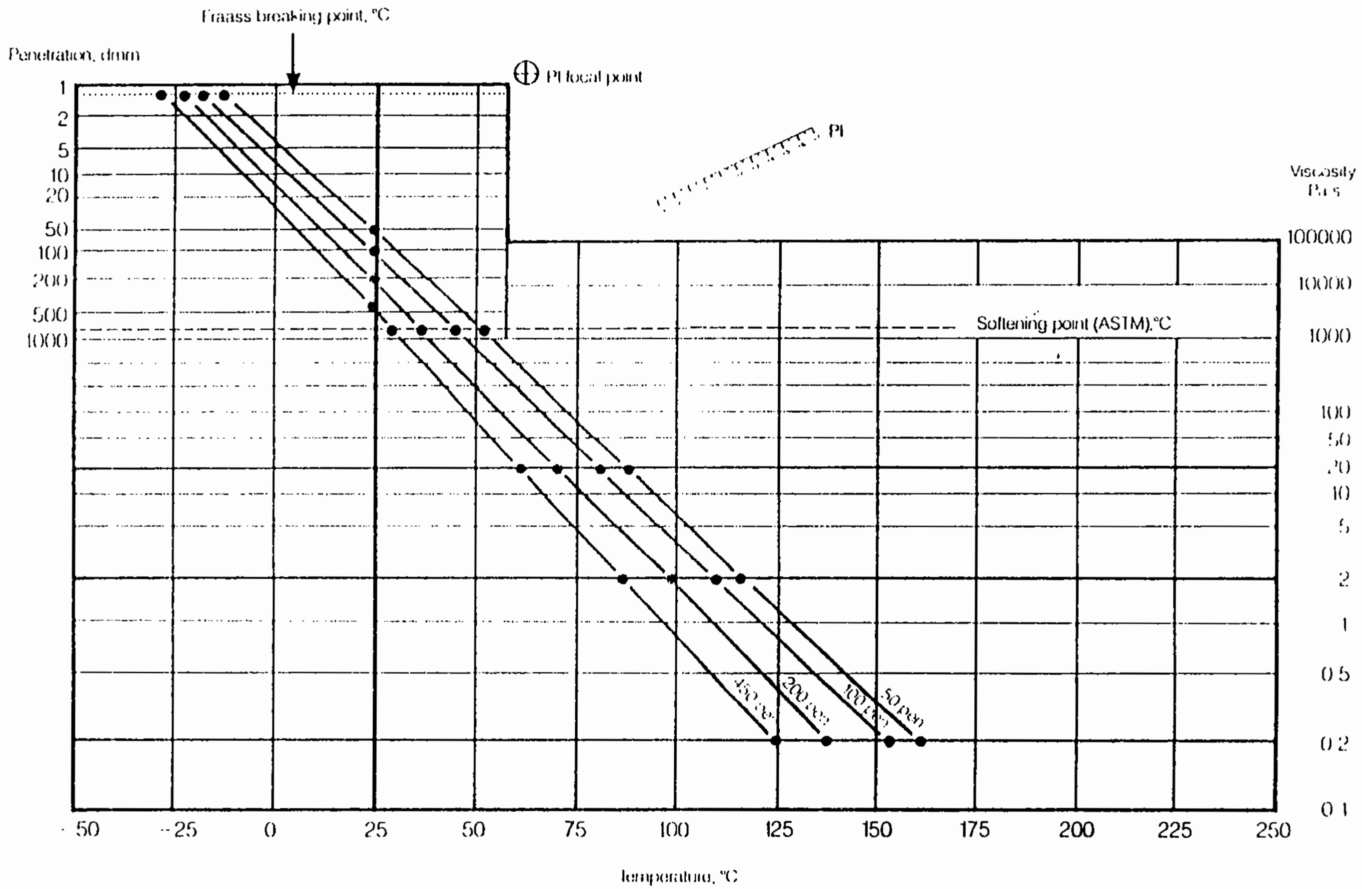
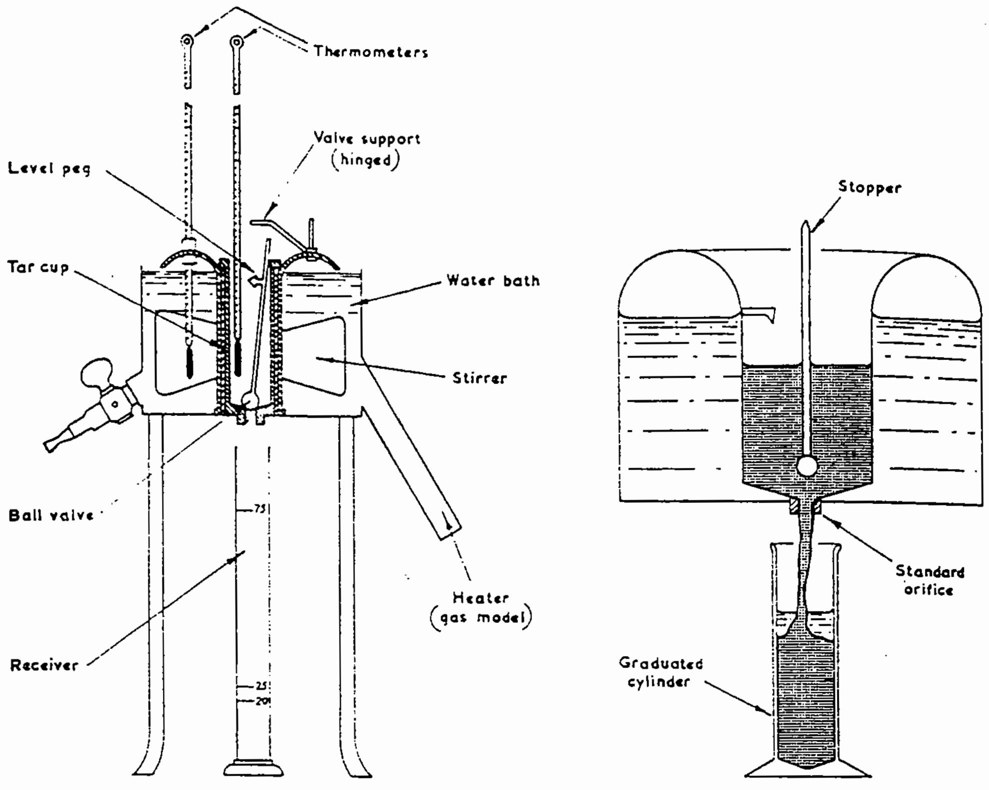


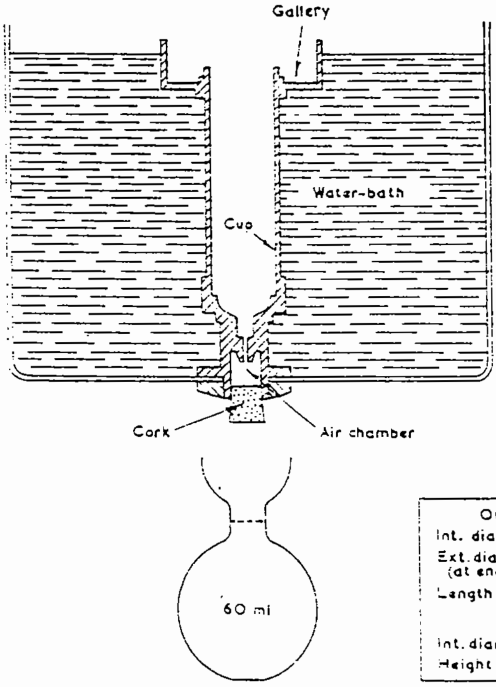
Fig. 5.3 A bitumen test data chart showing the temperature susceptibility of a number of bitumens from a single crude oil source[2]

Fig. 5.4 Diagram of the standard tar viscometer test [1]



(a) Diagram of apparatus (b) Diagram of test

Fig.5.5 Diagram of the Saybolt-Furol viscometer [1]



Outlet tube	
Int. diam.	0·315 cm
Ext. diam. (at end)	1·43 cm
Length	0·225 cm
Oil cup	
Int. diam.	2·975 cm
Height	12·5 cm

Fig.5.6 The Engler viscometer [1]

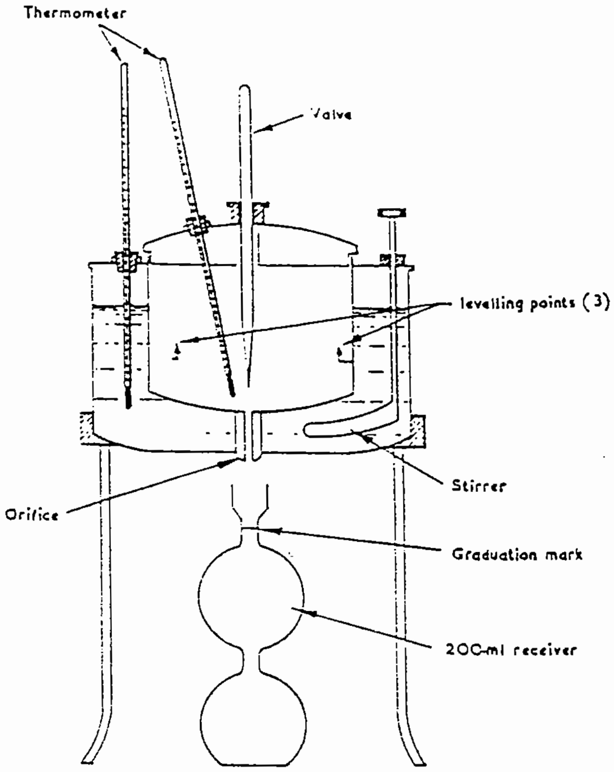
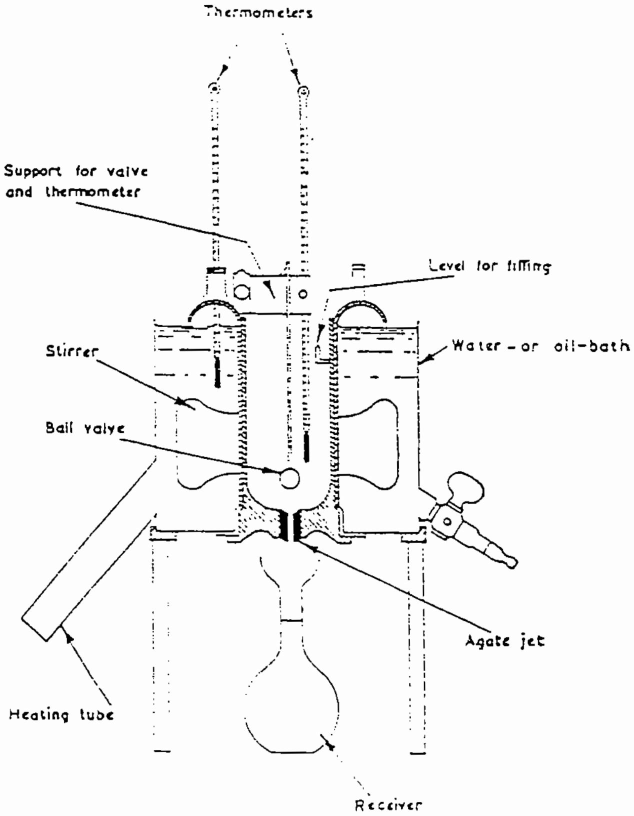


Fig.5.7 The Redwood viscometer [1]

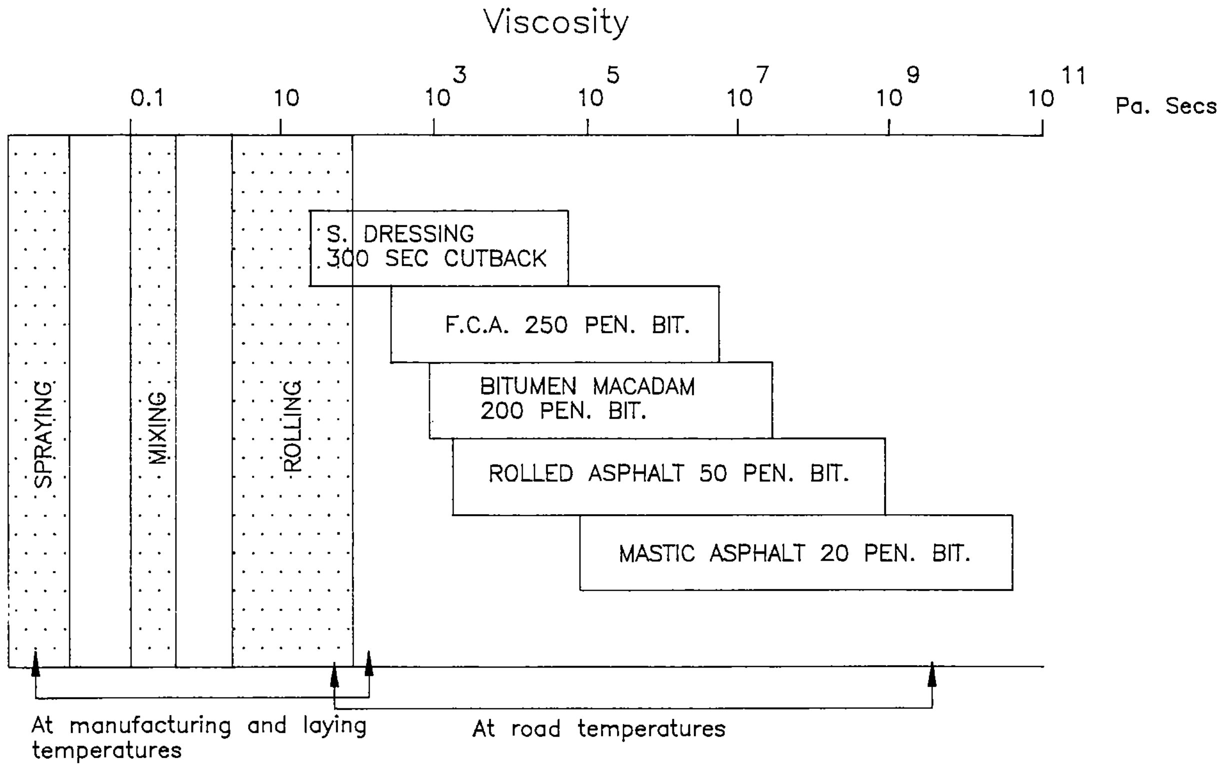


5.2.5. The importance of viscosity.

The flow characteristics of bitumens are important at the higher temperatures required for operations such as spraying, mixing and compaction. They are also important for low temperature bitumens, used in the form of emulsions or deferred set macadams. If, for example, the binder viscosity is too low then in mixing the binder will flow off the aggregate leading to separation, if too high the mix will lack workability. In the context of compaction too low a viscosity will result in an unstable material which deforms excessively when rolled, too high a viscosity will prevent sufficient workability to allow proper compaction and the mix will be weak and lack durability. In surface dressing operations incorrect viscosity may lead to chipping loss or bleeding of the binder.

Whichever method is employed to ascertain viscosity at the elevated temperatures involved in processing and handling bitumen, there can be no doubting the importance of ensuring correct viscosity for the various operations. Figure 5.9. is illustrative of the range of viscosity for particular applications of bitumen.

Figure 5.9 Range of viscosities for bitumens, used in different types[1] of mix, at high and low road temperatures



5.3. **Early attempts to modify bituminous binders.**

The earliest attempts to modify bitumens were focussed around the need to enhance their durability and stability. Additions of natural asphalt and Rosins were of benefit at a time when road treatments were primarily concerned with the waterproofing and sealing of waterbound surfaces and production of slow set macadams. The 1930's saw increased load and speed of traffic creating a need for improved stiffness of asphalts and coated macadams along with a recently appreciated need for skid resistance. At that time it was recognised that there was a trade off between the stiffness imparted by harder grades of tar and bitumen and their susceptibility to brittle failure. This concentrated attention upon the need to improve stiffness and modify the temperature susceptibility of bituminous materials.

Attempts were made to improve surface treatments, by modifying binder adhesion, in order to improve chipping retention and wet weather laying performance. The cohesive strength of surface dressing binders was also considered for improvement in order to improve chipping retention.

5.3.1. Rubberised bitumen.

In 1898 de Caudenberg took out a patent for the modification of bitumen by the addition of rubber. Difficulties in exploiting the process led to the patents lapsing. Some research work was carried out into the effects of rubber upon bitumen properties in the 1930's, primarily by the rubber industry. In the late 1930's several full scale road trials were undertaken in which ground tyre treads were used to modify rolled asphalt, although these trials were subsequently shown to have been successful the war effectively halted research. Research work resumed in the 1950's, along with full scale road trials, both of which established that rubber, in various forms, could have beneficial effects upon the physical properties of bitumen. It was also established that molecules of natural rubber were very susceptible to degradation due to heating of the bitumen rubber mix, this was responsible for undoing most of the beneficial effects initially imparted.

Traditional test methods established that rubber had a considerable modifying effect upon the properties of bitumen. It caused an increase in binder viscosity, raised the softening point temperature, reduced penetration, reduced temperature susceptibility and increased elasticity. In practice these effects meant that:-

1) The bitumen was less prone to softening at high road temperatures, this was better for retention of chippings following surface dressing, and reduced deformation of asphalt mixes during hot weather.

2) Related to point 1) above, rubber modified the visco-elastic response of the bitumen. An improved elastic response and corresponding reduction in viscous behaviour improved fatigue life due to the fact that increments of viscous deformation were smaller. It was therefore possible for a mix to sustain a larger number of load cycles before strain levels resulted in fatigue cracking.

The encouraging benefits shown by the addition of various forms of rubber to bitumen, in both laboratory tests and field trials, were not followed by widespread use and good results in practice. Problems associated with rubber degradation during heating created difficulties in handling rubberised bitumen. Little time was available at mixing and spraying temperatures before the effective rubber in solution degraded to little more than a flux oil, as the long chain rubber molecules broke down. Despite the problems experienced the use of this earliest of "polymer modified binders" served as an indicator to potential benefits to be obtained by incorporating appropriate polymers into bitumen.

5.3.2. The use of anti stripping agents.

It has long been appreciated that the bond between bitumen and aggregates was susceptible to attack by water. The nature of the attack has two basic forms. First, bitumen is unable to displace water from a damp surface and second, water is able to permeate a bitumen surface and then displace the bitumen from that surface, due to its greater polarity. Lee[4] established that higher viscosity bitumens were more resistant to stripping, in laboratory tests, than lower viscosity bitumens. Early practice therefore involved the addition of inert fillers in order to increase viscosity. Difficulties in handling high viscosity bitumen and the fact that it failed to prevent stripping in practice led to the consideration of chemically active fillers. Hydrated lime showed promise in laboratory tests, it reacted with acids in bitumen to produce weak soap compounds. This proved less effective in practice, mainly because it was not a sufficiently powerful wetting agent.

Other surface active compounds were tried, metallic soaps proved beneficial in the initial wetting of damp aggregates. They proved ineffective in the prevention of long term adhesive failure. More powerful surfactants proved too expensive at concentrations required for effectiveness, in addition some of the more powerful cationic agents used proved to be thermally unstable.

The Transport and Road Research Laboratory developed a wide variety of tests over the years for investigating the effectiveness of various adhesion modifiers. These tests ranged from a simple static immersion test, where coated stone was placed in distilled water and the amount of stripping assessed visually after a period of time, through dynamic immersion tests in which the aggregate was agitated whilst immersed, to chemical immersion and immersion trafficking tests. The former comprised of immersion in water and if stripping failed to result then coated chippings were immersed in ever increasing concentrations of sodium carbonate, fresh coated stone being used each time. The latter involved a wheel tracking test on a bituminous sample immersed in water. Stripping was deemed to have taken place when penetration of the wheel into the specimen occurred at a sudden, more rapid rate.

The Transport and Road Research Laboratory investigated the effectiveness of surfactants, in terms of their ability to coat wetted road stones, by attempting to stick chippings to bitumen whilst immersed in water. Obviously without a surfactant no adhesion could occur, the test is somewhat unrepresentative of the real coating situation due to the low temperature involved.

These early attempts to modify the adhesive properties of bitumen can best be summarised by stating that the problems were well understood and although some adhesion modifiers showed promise in the laboratory, for one reason or another , they did not achieve widespread success in practice.

5.3.3. Tar bitumen blends

Blends of tar and bitumen have been used for the production of both rolled asphalts and surface dressing binders, the latter is still a common application today. Research by Dickinson[5] et al into the way that Trinidad lake asphalt maintained its sandpaper like surface texture led to the conclusion that this was due to differential rates of oxidation , embrittlement and subsequent abrasion of the surface. From this it was hypothesised that a blend of tar and bitumen could similarly improve the texture of asphalt surfacing, as the tar oxidised more rapidly than the bitumen. This differential oxidation and abrasion, along with aggregates in the material, would produce a rougher surface texture. Full scale road trials by the Road Research Laboratory bore out this hypothesis. The logic behind the hypothesis was extended to surface dressings, the idea being that tar bitumen blends would be less prone to fatting up due to the increased susceptibility to weathering to which tar is prone.

It was also considered that the greater contact angle (or wetting power) of tar with solid surfaces would prove advantageous, in a blend with bitumen, for improving the adhesive bond with aggregates. Though this is undoubtedly the case tar bitumen blends are not suitable for use on wet materials or roads. B.S.

3690 part 3 outlines various recipes for blends of tar and bitumen in the production of binders for surface dressing, coated macadam and rolled asphalt.

REFERENCES

1. Road Research Laboratory, Department of Scientific and Industrial Research. Bituminous materials in road construction. London 1962 (H.M.S.O.)
2. Whiteoak D. The Shell Bitumen Handbook
3. Heukelom W.An improved method of characterising bitumens with the aid of their mechanical properties. Proc. assoc. asphalt paving technologists. 1969
4. Lee A.R. Adhesion in relation to bituminous road materials. J. Soc. Chem. Ind. London 1936.
5. Dickinson E.J. and Lee A.R. Improvements in bit. road surfacing materials. Pat.30456/50 1950.

CHAPTER SIX

THE MODERN APPROACH TO BITUMEN MODIFICATION

6.1. Aims and objectives

1) To increase the stiffness of bitumen at high road temperatures.

2) To improve the elastic response of bitumen and decrease the viscous (creep) response at high road temperatures.

3) To improve adhesion to the road surface, chippings and aggregates.

4) To increase the cohesive strength of binders.

5) To prevent brittle behaviour at low temperatures.

Bitumen is a relatively low cost material and it stands to reason that modifiers need to reflect the economies involved in its use. An improvement in properties at very high cost may be of interest from an academic viewpoint but of little use in practice. Similarly, methods of modification that render the bitumen dangerous to handle and use are unacceptable.

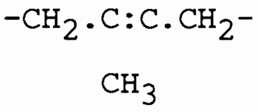
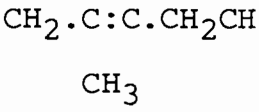
6.2 Modification by the addition of polymers

The modification of bitumen by the addition of polymers was a natural development of the technology behind rubberised bitumen. Unsatisfactory results due to problems of degradation of natural rubbers led initially to consideration of some of the newer synthetic materials that became available after the war. Early use of nitrile rubbers and styrene butadiene rubbers eventually led to consideration of newer products such as ethylene vinyl acetate and styrene butadiene styrene. The latter materials have come into widespread use over the last fifteen years. There is a wealth of literature describing the beneficial properties which these materials endow upon bitumen. The purpose of this work, among other things, is to outline a framework of specifications that avoids problems in their use.

6.2.1. Basic polymer chemistry

Polymers are large molecules built up by the repetition of small simpler chemical units. The repeating chemical unit of the polymer is usually equivalent (or nearly so) to the monomer, which is the starting material from which the polymer is fabricated.

For example:

Polymer	Repeating unit (or mer)	Monomer
Rubber	 $-CH_2.\underset{CH_3}{C}:C.CH_2-$	 $CH_2.\underset{CH_3}{C}:C.CH_2CH$
Polyethylene	$-CH_2.CH_2-$	$CH_2.CH_2$

Polymers may be linear ,where the repeating units are arranged in a chain like fashion, or they may be branched. Separate linear or branched chains may be joined together along the chains by crosslinks to give a crosslinked polymer.

6.2.2. Co-polymers

Two or more different monomers may be polymerised together to form a co-polymer. The chains of a co-polymer contain repeating units derived from each monomer, the are several ordering arrangements for the repeating units:-

1) Random - for example AABABBABAAAABBABA where A and B represent the two different repeating units.

2) Block AAAAAABBBBBBAAAAAA the repeating units are arranged in complete blocks.

3) Alternating ABABABABABABABABABA

4) Grafted - where blocks of one repeating monomer are grafted to a backbone formed by another.

```
B
B
AAAAAAAAAAAAAAAA
               B
               B
```

6.2.3. Polymers suitable for the modification of bitumen.

Polymers suitable for the modification of bitumen may be classified into two main types, these are:-

Thermosetting - where the action of the polymer is characterised by the formation of a three dimensional network due to crosslinking of the polymer. The crosslinking is strong, and may be initiated by a chemical reaction between a base constituent and a setting agent, the process is irreversible and thermosets are tough elastic materials which do not exhibit viscous behaviour. Examples of this type of material are polyurethanes and epoxy resins. Their use in modifying bitumen is somewhat restricted due to their high cost, where they are used the bitumen merely serves as an extender, they are really bitumen modified adhesives.

Thermoplastics - polymers of this type form weak crosslinked networks resulting in relatively low cohesion which can be easily destroyed by heating. Thus they soften and melt and when cooled the network reforms to give a material with temperature dependent physical properties.

Polymer chemistry has given rise to a vast range of products over the years. The number of thermoplastic polymers compatible with bitumen is, however, fairly limited. The list becomes shorter when considering only those that impart beneficial qualities. The following have been used with varying degrees of success:-

1) Two block co-polymers of Ethylene and Vinyl Acetate (E.V.A.), exhibit good compatibility with bitumen, they are characterised on the basis of their vinyl acetate content and their molecular mass. The vinyl acetate content is most significant in influencing the intrinsic mechanical properties.

2) Co-polymers of ethylene and acrylic esters.

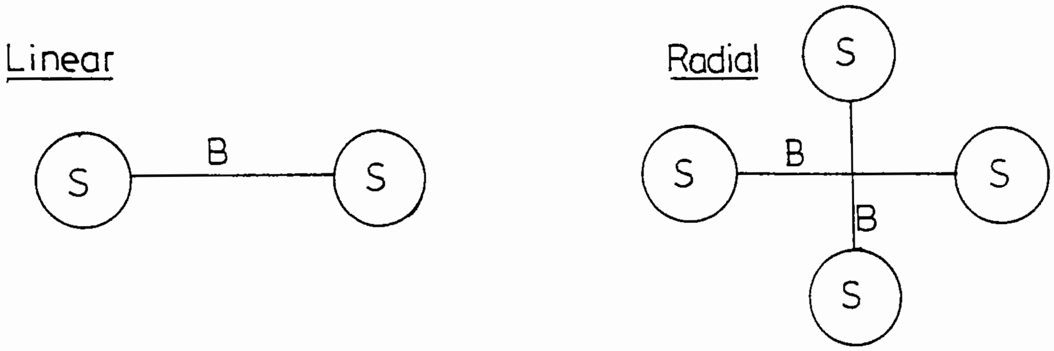
3) Co-polymers of butadiene and styrene (or isoprene), these may take one of several structural forms:-

A) They may be isotactic co-polymers such as styrene butadiene rubber.

B) They may be two block co-polymers.

C) They may be three block co-polymers of the styrene butadiene styrene (S.B.S.) or styrene isoprene styrene (S.I.S.) type, arranged in a linear or radial fashion. Linear co-polymers of this type are preferred for road bitumens, the radial type usually being found in applications such as roofing felts, employing gel. type bitumens.

Figure 6.1. Structural forms of S.B.S. or S.I.S.



4) Co-polymers of ethylene and propylene with added grafts leading to an ultimate vulcanisation, eg. ethylene propylene dienne monomer.

5) Polysulphurs - used to modify bitumens used for joint sealing.

6) Polyisoprene - natural or synthetic rubbers.

7) Polypropylenes - only the atactic variety are compatible.

8) Polybutenes, polyisobutenes.

The polymers listed may not always be used in isolation, for example ethylene vinyl acetate (E.V.A.) and certain resins may be used together. Polymers of E.V.A. and S.B.S. have been found to give the most satisfactory results, of the thermoplastic polymers, for road bitumen modification and it is mainly these which are discussed further.

6.2.4. The problem of compatibility.

One of the main problems in the modification of bitumen with polymer is that of compatibility between the polymer and the bitumen. Compatibility is associated with the chemical and physical structure of bitumen, as well as the nature and characteristics of the polymer. A polymer is said to be compatible with bitumen if it blends to produce a visually homogeneous material, though on a micromolecular scale it may well be heterogeneous. In order to influence the properties of bitumen it is necessary that there is more than just a mere incorporation of polymer molecules, they must interact in some way with the bitumen. The mechanisms of interaction are reported by most researchers on the basis of a Corbett type fractionation to describe the significant components of bitumen. From such analyses bitumen has long been theorised[1] as a colloidal system of asphaltenes and polar aromatics suspended in the oily maltenes by the aromatics. In an incompatible bitumen polymer blend the polymer competes for the solvating power of the aromatics. This leads to flocculation of the asphaltenes and bleeding (or separating) of the oily maltenes. The overall physical effect being a binder which has low cohesive strength. Clearly the explanation in terms of Corbett fractions is simplistic, the detailed mechanisms of interaction have yet to be explored.

Wolfe et al[2] carried out work which showed that the solvating power of a bitumen, table 6.1., for a styrene butadiene latex was influenced by the percentage by weight of aromatics, particularly polar aromatics. Wolfe et al were able to demonstrate, using a viscometer test, that the bitumen with the greatest solvating power for the styrene butadiene latex exhibited the greatest degree of modification. Using scanning electron microscopy the morphological characteristics indicated in this way may be related to performance of modified bitumen in practice. In the long term the researchers anticipate that modified bitumens could be tailored to suit application on the basis of morphological slides, figure 6.2. At a simple level morphological slides can give a good indication of whether a binder/modifier system is compatible.

Dickinson[3] reported work by Van Beem and Brasser (1973) which demonstrated that dispersion of S.B.S. polymers in bitumen would establish a network structure, and hence significantly influence properties, provided the bitumen had the correct aromaticity. If this was too low the polymers would not disperse and there would be incompatibility, if too high the dispersion was so effective that ordered polystyrene regions would not form. Daly et al[4] reported that polyethylene, which has a relatively low compatibility with bitumen, could be made more compatible by chlorination. This has the effect of changing and increasing the polarity of the polyethylene as well as reducing the crystallinity and increasing density to more closely match that of bitumen. Polyethylene is a potentially cheap source of modifier, in the form of waste material, and it certainly has beneficial effects upon the properties of bitumen. More widespread use will depend upon the economic feasibility of chlorination.

Co-polymers of E.V.A. are more compatible with bitumen than polyethylene and S.B.S., they blend successfully with road grade bitumens at typical concentrations required for modification.

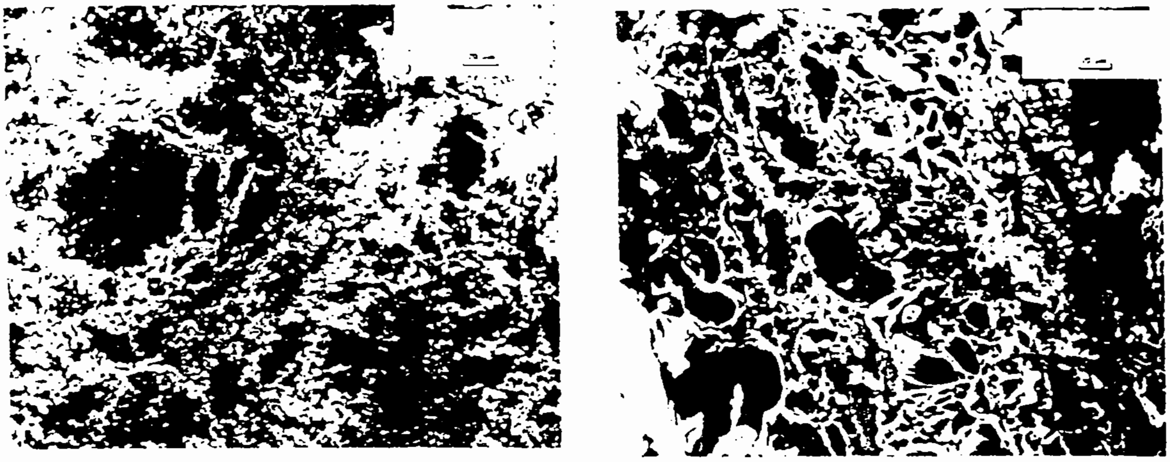
Table 6.1[2]

Fractional composition of bitumens prior to modification with SBR latex

Asphalt		Composition, Weight Percent				
Source	Grade	Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes	Loss
CC-C	AC-10	9.9	25.3	38.1	21.6	5.1
CY-W	AC-10	9.8	31.6	45.6	7.0	6.0
T-C	AC-10	11.3	33.6	37.5	14.9	2.6
T-DS	AC-10	4.0	30.1	60.6	0.2	5.1
MI-M	AC-10	9.4	33.5	38.9	16.1	2.1

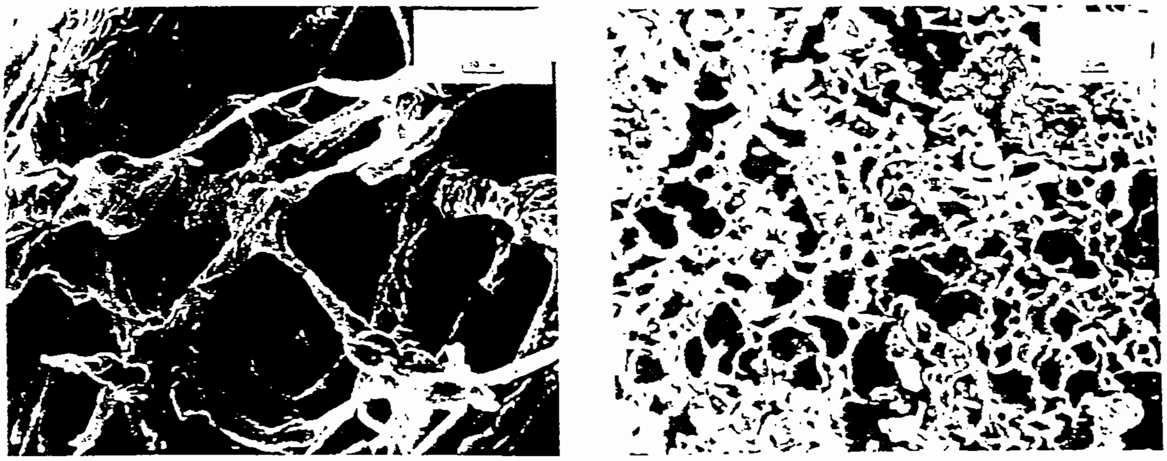
Fig. 6.2^{2}

Morphological characteristics of a styrene butadiene latex-modified bitumen established by scanning electron microscopy. See also table 6.1



CC - C AC - 10

CV - W AC - 10



T - C AC - 10

T - DS AC - 10

MI - M AC - 10

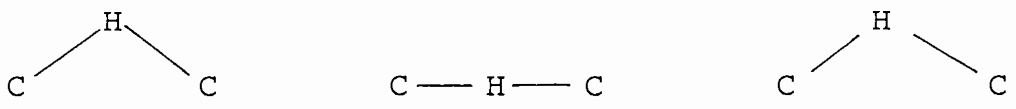
6.2.5. The properties of thermoplastic polymers which are significant in modifying bitumen.

Due to the nature of co-valent bonding it is possible for free or partially restricted rotation about carbon single bonds. Thus polymer molecules may adopt many different configurations. In a given sample of amorphous polymer the chains may be twisted, coiled and intertwined. Below the glass transition temperature the material is rigid and glassy, the polymer chains are frozen into a set configuration. Above the glass transition temperature the polymer chains are capable of rapid movement with continual changes in configuration.

When a stress is applied to a thermoplastic polymer its response may be divided into:-

1) A rapid reversible elastic response, this corresponds to bond stretching and deformation of bond angles in the chain.

Figure 6.3 Reversible deformation of covalent bond angles.



2) A delayed elastic response, typically characterised by reversible extension of several hundred per cent. This behaviour is associated with straightening out and orientation of coiled chains, the speed at which it takes place is influenced by the viscosity of the medium.

3) Viscous flow, this is characterised by the melt viscosity of the polymer.

In terms of bitumen modification, property 1) above is important for improvement for overall stiffness, 2) is important in terms of resistance to brittle behaviour and accommodation of thermal movement, 3) is important at high temperatures associated with mixing and spraying.

Thermoplastic polymers are sometimes subdivided, according to their visco-elastic behaviour, into elastomers and plastomers. The former have a characteristically high elastic response and resist deformation by stretching and recovering after removal of stress. Such behaviour is typical of natural and synthetic thermoplastic rubbers. Plastomers on the other hand form a more rigid entanglement of polymer chains. Polymers such as E.V.A. exhibit tough plastic behaviour but are more susceptible to brittle fracture at high strains.

6.2.6. Properties exhibited by bitumen after modification by addition of thermoplastic polymers.

6.2.6.1. Ethylene vinyl acetate.

Research by T.R.R.L. established the following effects upon bitumen as a result of the addition of E.V.A., containing 18% vinyl acetate, to 50 and 70 pen. bitumens.

1) A reduction in penetration.

2) A significant increase in the softening point, as measured by the ring and ball softening point test. The research indicated that this increase was approximately linear in relation to the quantity of E.V.A. added and that for every 2.5% increase in E.V.A. there was a corresponding 50°C increase in the softening point temperature.

3) Over a typical range of temperatures experienced on the road E.V.A. modified bitumen showed increased stiffness and slightly more elasticity than unmodified bitumen.

4) An increase in viscosity at high, mixing and spraying, temperatures, though not to the extent indicated by the increased softening point due to an increase in shear susceptibility.

E.V.A. has the following effect on rolled asphalt mixes:-

1) Reduced wheel tracking rate.

2) An increase in Marshall stability, although results are difficult to interpret due to limitations of the test method.

3) Higher wheel tracking rates are achievable at lower Marshall stabilities.

Table 6.2 The effect of E.V.A. grades 150/19 and 45/33 on binder and hot rolled asphalt wearing course properties[5].

Binder	Binder properties		Marshall properties			Wheel-tracking rate at 45°C, mm/h
	Penetration at 25°C, dmm	Softening point (IP), °C	Stability, kN	Flow, mm	Quotient, kN/mm	
70 pen	68	49.0	6.3	3.3	1.9	4.4
70 pen + 5% EVA 150/19	50	65.5	7.6	3.2	2.4	0.8
70 pen + 5% EVA 45/33	57	58.0	8.0	2.7	3.0	1.0

Note the grading of E.V.A. is based upon the melt flow index and the vinyl acetate content. Grade 150/19 has a melt flow index of 150 and a vinyl acetate content of 19%. It is thought that E.V.A. modifies bitumen by forming close packed ordered crystalline regions linked by amorphous vinyl acetate regions. The crystalline regions enhance the stiffness of bitumen whilst the amorphous regions impart a degree of elasticity.

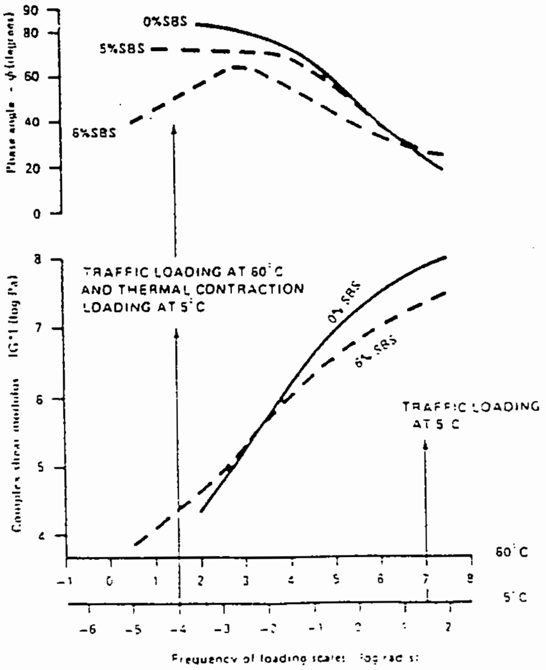
6.2.6.2. The effect of E.V.A. in practice

E.V.A. has been employed mainly in the production of hot rolled asphalt wearing course materials. These gap graded materials rely upon bitumen for stiffness and E.V.A. improves the overall stiffness and resistance to deformation of the mix at high road temperatures. The improved stability due to E.V.A. allows the use of a softer base bitumen than would otherwise be the case, this can help to reduce low temperature brittle behaviour.

6.2.6.3 Styrene butadiene styrene

The viscoelastic response of bitumens modified by the addition of styrene butadiene styrene has been investigated widely, Dickinson[3] compared the viscoelastic response of normal and modified bitumens at various rates of loading and temperature.

Figure 6.4 The viscoelastic response of normal and modified bitumens[3]



From figure 6.4 it may be observed that the presence of the polymer is less significant at high road temperatures/rates of loading. Dickinson found that elastic recovery, with a dispersion of 5% S.B.S., gave a moderate improvement in elastic recovery whereas 6% S.B.S. gave very significant improvement. Dickinson also reported that S.B.S. modified bitumen took longer to reach a similar level of strain than ordinary bitumen.

6.2.6.4. The effect of S.B.S. in practice.

1) Bitumen viscosity is increased, this may be disadvantageous for surface dressing binders .

2) Cohesive strength (elasticity/stiffness) is maintained at high road temperatures, to a reduction in temperature susceptibility. This is important for the avoidance of damage to surface dressings in high summer temperatures.

3) The elastic range of visco-elastic behaviour is improved at high road temperatures and cases where low frequency loading occurs, for example thermal movement. The latter point is important for the production of mixes to be used as overlays where reflective cracking has been a problem.

4) Resistance to shear deformation is improved along with elastic recovery. This is important where surface dressing is carried out on sites subject to large shearing forces from traffic, for example, tight bends, approaches to pedestrian crossings, etc.

5) Research by Biczysko suggests that the addition of S.B.S. to bitumen in hot rolled asphalt mixes can improve low resistance to brittle behaviour at low temperatures. The reasons for this are not clear, as previous research by Dickinson[3] suggested that the polymer did not significantly alter visco-elastic behaviour at low temperatures. It may be that S.B.S. modified bitumens are less prone to low temperature brittle behaviour due

to an increased strain limit.

6.2.7. Properties exhibited by bitumen after modification with thermosetting polymers.

The main thermosetting polymer used for bitumen modification is epoxy resin, this is normally produced by mixing two components, a resin and a hardener which react chemically to form a strong three dimensional polymer network in the bitumen. In reality it would be more accurate to consider binders modified in this way as bitumen modified epoxy resin, since the bitumen merely extends the resin and the mix displays the characteristics of the resin.

The characteristics of a bitumen extended epoxy binder are virtually no temperature susceptibility, limited time for handling once the two components of the epoxy are mixed, purely elastic behaviour (not viscous). Epoxy binders exhibit good durability and a very high stiffness modulus, extremely good fatigue behaviour, and great resistance to permanent deformation. In extended form they produce the ideal binder, the drawbacks are difficulty in handling, health risks associated with their use and very high cost. Indeed their cost is something like ten times that of a thermoplastic polymer modified binder.

6.2.8. Summary of polymer modification of bitumen.

In recent years various studies have shown that polymer modification can be a successful method for improving the performance of bituminous mixes and surface dressings. The two most commonly used thermoplastic polymers are E.V.A. and S.B.S., the former enhancing bitumen with the qualities of a tough plastomer and the latter providing rubber like elastic characteristics. A thermosetting polymer adhesive, epoxy resin, may be used to modify bitumen and provide the characteristics of the ideal binder, its main drawback is its high cost.

REFERENCES

1. Nellensteyn F.J. Chem. weekblad.1939 reported in Pfeiffer J. Properties of Asphaltic Bitumen (Elsevier) 1950
2. Wolfe et al, Crude source effects on the chemical, morphological and viscoelastic properties of SBL modified asphaltic cement. T.R.B. 1096, Washington D.C. 1986
3. Dickinson E.J. assessment of the deformation and flow properties of polymer modified paving bitumens. A.R.R. 1981
4. Daly et al,preparation and characterisation of asphalt-modified polyethylene blends.
6. Whiteoak D. The shell bitumen handbook.

CHAPTER SEVEN

OTHER ASPECTS OF BITUMEN MODIFICATION

7.1. Adhesion modification.

In dry dust free conditions the adhesive bond between bitumen and road stone is perfectly acceptable, indeed it usually exceeds the cohesive strength of bitumen. Modification techniques are mainly focussed on achieving and retaining this bond in the presence of water. The traditional approach to this problem has been to modify the interfacial energy of bitumen with respect to aggregates. Different aggregates can also play a part in this bonding mechanism for unbalanced surface charges on some may help to tip the balance of interfacial energies in favour of bitumen or water. Properties of aggregates such as porosity, presence of surface dust, moisture content, shape and surface roughness also have an influence on the adhesive bond with bitumen. However, examples of adhesive bond failure, or stripping, can be found with most types of aggregate, although it is claimed[1] that it is less common with limestone and blast furnace slag. The overriding common denominator in adhesive failure of bitumen is water. It is important to draw a distinction between adhesive and cohesive failure at this point, failures in bond to cold conditions are more likely to be due to a cohesive failure as a result of binder embrittlement. The only part played by water may be as an expansive freeze thaw mechanism which causes additional disruptive tensile forces in the binder.

7.1.1. Adhesive failure mechanisms.

Several hypothetical mechanisms have been widely reported[2,3] to explain adhesive failure. All these mechanisms depend upon the greater affinity of water over bitumen for the surface of aggregates or chippings. The first of these mechanisms is the straightforward displacement of bitumen by water, the second is detachment of a coating of binder due to the entrapment of a thin film of water. Another mechanism has been demonstrated experimentally by Hughes et al[4]. It involves the actual permeation of a thin binder film by water in liquid or gaseous form, it is most easily demonstrated by painting a sheet of steel with a thin layer of bitumen and noting how rust forms below the surface of the bitumen. Porous bituminous mixes may also be prone to erosive effects as a result of high pore pressures generated as water is forced into voids by vehicle tyres.

In the case of surface dressing damp chippings prevent adhesion until they have dried out. Chipping loss will occur during this drying period, due to the action of traffic. If rain should fall shortly after surface dressing, whilst the binder is still fluid, the rain water will effectively wash the bitumen from the chippings. Subsequent chipping loss will then expose patches of bitumen which may be picked up by vehicle tyres along with other chippings, resulting in serious damage.

7.1.2. The problem of adhesive failure in perspective.

Regular maintenance by surface dressing and the use of dense low void content mixes combined with good drainage effectively deny sufficient access by water to cause damage. More porous open textured materials are prone to water damage due to the fact that water may enter the pores and may reside for long periods due to the tortuosity of the pore structure, which hinders free drainage. In terms of the manufacture of coated materials such operations are usually carried out in dry controlled conditions, aggregates may be dried by pre-heating, adhesive failures are extremely rare and occurrence would normally be due to a fault at the plant. Surface dressing operations are very susceptible to wet weather damage, the use of damp chippings may also cause problems in cool conditions. Once surface dressing has been established and trafficked to the point where it has become embedded into the substrate below it is resistant to moisture attack for many years. Normally a cyclic routine of surface dressing is carried out every five to ten years in order to maintain this protection.

In essence therefore it is surface dressing operations and open textured bituminous mixes that are prone to water damage. The former at the point of initial adhesion and the latter in the long term.

7.1.3. Modern methods of preventing adhesive failure.

There are several approaches to the problem of adhesion modification which depend upon whether one is dealing with the need for a good adhesive bond in the presence of moisture, as is the case with surface dressing. Or the longer term problem that arises of water displacement of binder from mix aggregates.

In the former case modification of interfacial energies to favour wetting by bitumen would appear to be the only possible approach. Traditionally this has been achieved using wetting, or anti-stripping agents, most recently cationic organic amines. There are two main drawbacks with modern cationic wetting agents. First, they are thermally unstable at high temperatures and secondly there is something of a dilemma presented by their use in that in wet conditions they render the bitumen susceptible to emulsification by water. They could therefore, in certain conditions, be suspended in water and washed from chippings. Functional group analysis of bitumens, as detailed earlier, with reference to table 3.1. indicates that phenolic functional groups have a low tendency to be displaced by water but tend to concentrate in small amounts at the bitumen/aggregate interface. The U.S. Transportation Research Board in its Strategic Highway Research Programme (S.H.R.P.) has investigated the use of phenolic resin additions in order to improve adhesion. The resin may be added to bitumen, used to coat chippings or both. Early indications are that incorporation of such resin is economic and laboratory testing (Texas boiling test) indicates an increase in bitumen/aggregate adhesion.

Table 3.1. also points the way to a modification method in which the long term stability of the bitumen aggregate bond may be improved. From the work by Petersen[5] functional group analysis of bitumen indicated that carboxylic acid and anhydride groups are formed with oxidative ageing, the former also being present in bitumen in smaller quantities prior to oxidation. Both of these functional groups occur in very high concentrations at the bitumen/aggregate interface and both are susceptible to displacement by water. It stands to reason therefore that a two fold

benefit may be achieved by prevention of oxidation, the first is a reduced tendency to embrittlement which results from hardening of bitumen due to these functional groups, secondly a reduction in susceptibility to stripping. Clearly a bitumen low in carboxylic functionalities in the first instance is also necessary.

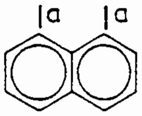
Prevention of oxidation can be achieved in two ways, first by using only dense mixes with low void contents to which atmospheric oxygen can gain little access, second, by the use of anti-oxidants. The R.R.L.[6] reported early research by Walther[7] and Dubrisay[8] which produced evidence from laboratory tests that showed the oxidation retarding effects of small quantities of hydroquinone and b-napthol. The extent to which incorporation of anti-oxidants has been explored by the Strategic Highways Research Project (S.H.R.P.) is at the present time not known, it is certainly a promising area for future research.

The techniques mentioned above, in which functional group modification is used to improve adhesion, remain as yet unproven in practice. Presently porous asphalts and open textured macadams are subject to durability problems. Surface dressing adhesion in damp conditions is variously improved using cationic emulsions of bitumen and water, where relatively low temperatures do not degrade the emulsifying surfactant, and also by heating the chippings. Surface dressing remains weather dependent, however, in that even with appropriate interfacial energies rapid cooling of bitumen, due to cold or rain, would cause such a rapid increase in viscosity that chippings would not be wetted by the bitumen.

7.2. The modification of bitumen with manganese.

A manganese additive marketed by Chemkrete Technologies inc., offers benefits of reduced temperature susceptibility in bitumen. The extent of modification is such that a softer grade of bitumen will exhibit improved stiffness at high temperatures and less low temperature stiffness, than an unmodified harder grade of binder, for quantities of up to 0.2% of Mn by weight. The modifier catalyses a reaction between atmospheric oxygen and hydrocarbon side chains on aromatic rings - mostly at the alpha carbon positions -

Figure 7.1.



Alpha carbon positions on aromatic rings

to form a transitory oxidation product which decomposes to form either a diketone or an anhydride. The creation of diketone and anhydride functional groups is initially rapid gradually levelling off with time. It is thought that these diketone and anhydride compounds then form stable compounds with the manganese, which link up and tie together the hydrocarbon molecules present in bitumen. The increase in the quantities of the diketone and anhydride functional groups are accompanied by a corresponding increase in resilient modulus and viscosity at the appropriate temperatures. Thus there is an initial curing or stiffening period during which asphalt layers must not be subject to overloading, figs. 7.2. and 7.3. illustrate the development of stiffness and creation of chemical functionalities with curing time, a fuller discussion of the chemical mechanisms involved can be found in ref. Epps[9] et al.

7.2.1. The effect of Chemkrete modification upon bitumen properties.

Following investigatory work by Jon Epps et al the effects of Chemkrete modification can be reported as follows:-

1) At very low temperatures there was a decrease in stiffness of the bitumen and thus no increase in a tendency to brittle behaviour.

2) An increase in viscosity of bitumen at high temperature.

3) An increase in stiffness and usually an increase in tensile strength at high road temperatures coupled with a reduction in temperature susceptibility.

Modifications by the use of Chemkrete appears to throw up a number of paradoxes. To begin with the rate at which curing takes place in practice will be dependent upon accessibility to atmospheric oxygen. For dense mixtures the curing time could be quite long and it may be some time before the mix develops its full stiffness. In the meantime significant rutting may have occurred. Another aspect of oxygen accessibility is that porous mixes should exhibit most rapid curing when Chemkrete is added. However, Chemkrete modification creates a form of accelerated oxidative ageing and although it is claimed that the type of oxidation initiated by the modifier does not result in embrittlement there is evidence that the presence of anhydride functional groups may increase susceptibility to moisture damage. Epps[9] et al report that this moisture susceptibility reduces stiffness and strength in laboratory test samples following exposure to water. However it was noted that this loss of strength, relative to dry samples still exceed that of unmodified test specimens. In asphalt materials with a high voids content, such as pervious macadam, the risk of normal oxidative ageing would still exist alongside the possibly increased susceptibility to stripping.

Chemkrete modification would probably be of little benefit for surface dressing due to the fact that the time when the dressing is in its most vulnerable state, which is soon after laying, would be during the curing period when the bitumen was not at full strength.

There is no doubt that considerable benefits are to be obtained by using appropriate catalysts to modify and promote interaction between hydrocarbon molecules present in bitumen. It is an area in which the compositional analysis of bitumen may have a significant part to play, by enabling potentially beneficial reactions to be identified.

7.3. The modification of bitumen by the addition of sulphur.

In the U.K. sulphur has been used in small quantities to extend bitumen and in larger quantities it has been used as a plasticiser or workability aid. Whiteoak reports work by Petroni et al and Lee which shows that sulphur reacts predominantly with the napthenic aromatics fraction of bitumen. In so doing it is reported to combine with the ring structures to cause an increase in the polar aromatic fraction, this is somewhat puzzling in view of the fact that the sulphur has the same electronegativity as carbon. It is further reported that sulphur may also oxidise napthenic aromatics, removing hydrogen to produce hydrogen sulphide. This oxidative reaction increases rapidly at temperatures above 150°C to produce an increase in the size of the asphaltene fraction, this is similar to the effect of air blowing hot bitumen at the refinery and may result in a bitumen with a gel. structure.

Dispersions of greater than 15-18% sulphur in bitumen result in a temporary suspension of free sulphur during mixing. At high temperatures the low viscosity of this excess sulphur helps to produce a very workable fluid mix which is pourable and does not require compaction. At typical road temperatures the excess sulphur helps to fill voids in the asphalt mix and increases interparticular friction thereby increasing stability, as measured in the Marshall test. The stability gradually increases over a number of days as sulphur slowly crystallises out of the bitumen. The general behaviour of sulphur modified bitumens is that in small quantities it tends to create a gel. type structure in bitumen whilst in higher concentrations in a mix it acts as a plasticiser at high temperatures and a mouldable filler at low temperatures. In both cases it causes an increase in the stiffness of a mix with a probable increase in low temperature brittle behaviour. Refer to figs. 7.2. and 7.3.[9]

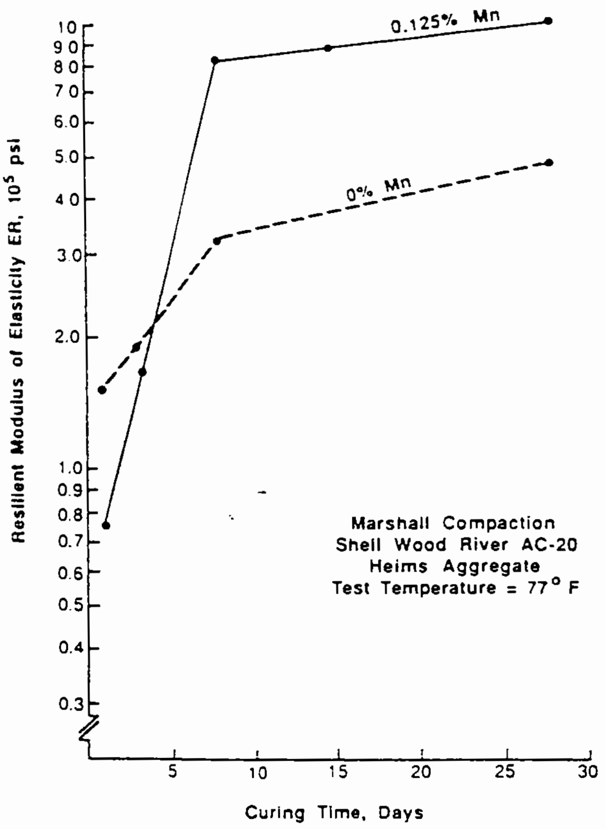


Fig. 7.2 The development of stiffness with curing time in bitumen[9] modified by the addition of Chemkrete

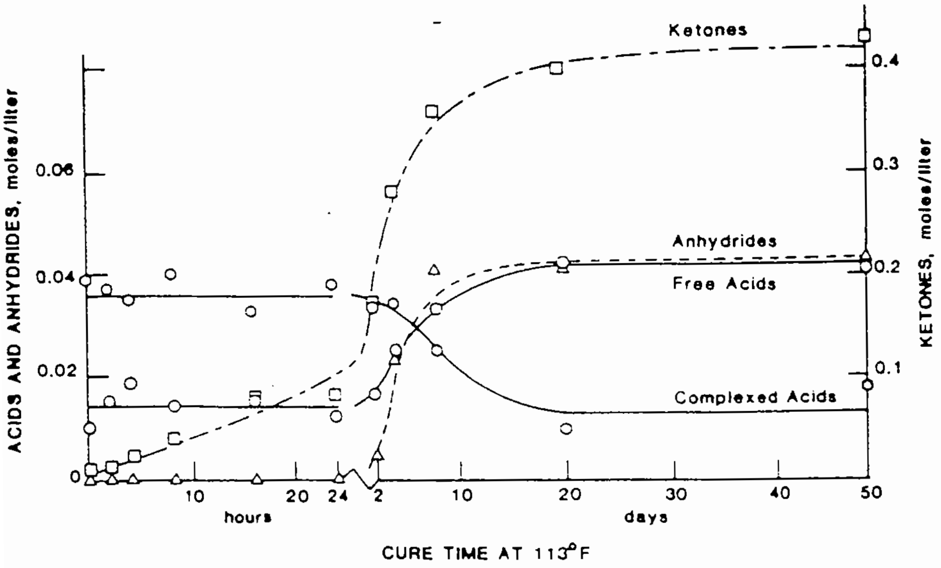


Fig. 7.3 The creation of chemical functionalities with curing[9] time in bitumen modified with Chemkrete

7.4. The modification of bitumen by the addition of carbon black.

Dispersions of 10-15% carbon black in bitumens have been shown[10] to increase viscosity at typical high road temperatures (60°C) and at mixing temperatures (135°C). Penetration tests at 25°C indicated that the particular carbon black additive marginally reduced the penetration whilst at 4°C it remained virtually the same as an unmodified bitumen. The implications of this are that carbon black improves resistance to permanent deformation of a mix at high road temperatures. However, resistance to low temperature brittle behaviour is reduced. Care would be necessary in establishing whether the use of a softer grade of bitumen modified by carbon black would sufficiently reduce low temperature brittle behaviour whilst maintaining the improved high temperature stiffness.

The Texas Transport Institute also reported that infrared spectrometry, used to determine concentrations of functional groups both before and after ageing, indicated that carbon black absorbed free carboxylic acids. It was also noted that carboxylic acid salts were also absorbed upon oxidative ageing. Other oxidation products such as ketones and anhydrides were also reduced in quantity compared to unmodified bitumen. The study noted that although carbon black did reduce the presence of certain functional groups, either by absorption or suppression of the oxidation process, it did significantly alter the ageing index ie the ratio of 60°C viscosity before and after ageing. However, on the basis of recent research carried out at the same time, upon the moisture susceptibility of certain functional groups by Petersen et al there may be grounds for considering carbon black as an agent for reducing long term adhesive failure due to moisture.

REFERENCES

1. Whiteoak D. Shell Bitumen handbook, 1990 (Shell Bitumen U.K.).
2. Wilhelm R. and K. Schultze. Interface phenomena in the system water - bituminous binders and their importance in road construction. Bitumen, Teere, Asphalte, Peche 1954 and reported in Bituminous Materials in road construction 1962.
3. Lee A.R. and J.H. Nicholas. Adhesion in the construction and maintenance of roads. Adhesion and adhesives fundamentals and practice, London, 1954 (Soc. Chem. Ind.).
4. Hughes R.I. et al. Adhesion in bitumen macadam, J. Appl. Chem., London, 1960.
5. Petersen J.C. Quantitative functional group analysis of asphalt using differential infrared spectrometry and selective chemical reactions, theory and application. T.R.B. 1096, Washington D.C., 1986.
6. Road Research Laboratory. Department of Scientific and industrial research. Bituminous materials in road construction. London, 1962 (H.M.S.O.).
7. Walther H. The chemical processes during the oxidation of bitumen. Mitteilungen aus der Dachpappen industrie, 1938. Berlin, 1938 (Allgem. Industrie Verlag Knorre and Co.), pp. 135 - 52. Farb. Zeit., 1938, 43 (52), 1375; Brit. Paint Res., 1939, 12 (67), 39.
8. Dubrisay R. Ageing of asphalt in the atmosphere. C.R. Acad. Sci., Paris. 1955, 241, 1139 - 41.

9. Epps J. et al. Chemistry. rheology and engineering properties of manganese - treated asphalts and asphalt mixtures. T.R.B. 1096, Washington D.C. 1986.

10. Texas Transport Institute. Investigation of asphalt additives. Report F.H.W.A./R.D. - 87/001, Nov. 1986.

CHAPTER EIGHT

PRACTICAL PROBLEMS IN THE SPECIFICATION AND USE OF MODIFIED BITUMENS

8.1. Specification and practice.

In the U.K. the construction and maintenance of most roads is carried out, either directly or indirectly, under a general framework of specifications and standards laid down by Central Government. Within a typical set of U.K. contract documents there will usually be widespread adoption of the Department of Transports own specification for Highway works along with references to appropriate British Standards. This standardised approach stems from the fact that it is central government, through the Department of Transport, which bears responsibility, both directly and through various agencies, for the highway network.

Within the current specifications and standards there is little guidance on the use and performance of modified bitumens. However, there is general recognition by government agencies of the benefits of modified bitumens for road use. This recognition has manifested itself through the issue of many laboratory test reports and guidance notes, by the Transport Research Laboratory, upon the performance and use of modified bitumens. Increasing awareness of the benefits of bitumen modification has also shown up in greater usage by local authorities.

The rather tentative and cautious approach to the wholesale acceptance of modified bitumens, by the Department of Transport, is justified. Benefits or otherwise of these materials have still to be proved in practice. In spite of the wealth of literature, laboratory test reports and specific trial sites which indicate the positive benefits of modification, most engineers will have encountered cases of indifferent performance in practice not to mention occasional failures. Drastic failures are usually confined to surface dressing where the effects of any binder deficiency, particularly at a demanding site, show up very rapidly. The behaviour of mixes made with modified bitumen will take longer to evaluate.

The lack of an appropriate British Standard, or guidance on a specification, may cause contractual problems and disputes between customers, contractors and material suppliers. Such a situation is made more likely due to the absence of an effective basis for ensuring that a modified binder is fit for the purpose for which it is intended. Bearing in mind that modified bitumens are more expensive than unmodified a potential user would need to be satisfied on three counts:-

1) Has the bitumen been modified.

2) Is the modifier properly incorporated.

3) Does the modified bitumen meet the desired performance requirements.

These three questions generate another question, which is how best to approach the whole problem of specifying and testing modified binders.

8.2. The specification and testing of modified bitumen.

There are two general approaches to specification and testing. The first is to specify the modified bitumen in terms of its constituents, with appropriate compositional testing to ensure compliance. Whereas the second, is to outline a set of physical criteria which the modified binder shall be required to meet, the physical criteria then being measured by suitable tests. In view of the fact that no one modification technique provides a universal panacea, in producing an ideal binder from bitumen, it will be necessary to consider different specifications with different test regimes for applications.

8.3. The compositional, or recipe, approach to specification.

As has been mentioned above potential users of modified bitumen will be interested in whether the product they are paying for actually contains performance enhancing additives, whether the additive is compatible with the base bitumen and whether the modified material will meet their performance requirements. The recipe approach to specification ensures that performance criteria are met by concentrating on the questions of compatibility and the presence of the correct amount of modifier.

The problem of compatibility usually arises with polymers, for example polyethylene, S.B.S. and E.V.A. Polyethylene resins are not actually very soluble in bitumen, and therefore not considered compatible, high speed, high shear mixing is necessary at high temperatures in order to effect dispersion. Bitumens that are considered compatible with polymers, such as S.B.S. and

E.V.A. are, generally required to have an appropriate aromaticity, as established by fractionation techniques, this is not so difficult, but establishing the concentration of S.B.S. and E.V.A. present in bitumen requires quite sophisticated differential infrared spectrometry. The method, developed by western research institute, is used to assess the quantities of various functional groups that result from the modifying additives - for example the presence of a carbonyl bond in the case of E.V.A., or the presence of reactive olefinic double bonds in the case of S.B.S. It is submitted that the precision of such a method must be questionable in a complex substance such as bitumen. For modifiers such as carbon black and sulphur it is relatively straightforward to assess quantities present - this may be carried out by elemental analysis before and after modification or by solvent separation techniques. Modification by catalysts such as Chemkrete may be assessed by analyses of the functional groups promoted as a result of the catalytic reactions induced, typically ketones and anhydrides. Alternatively the proportion of manganese present may be detected. Again sophisticated differential infrared spectrometry is required.

Modifiers that promote adhesion, emulsifiers and anti-stripping agents are mainly amines or chemical compounds containing amines. Tarrer et al[1] have developed a straightforward method for the detection of amine based anti- stripping agents. It involves measuring the induced basicity of bitumen, as a result of the amine, by titrating the asphalt (in a solution of chloroform, isopropyl alcohol and water) with an acid such as HCl the concentration of the additive is then deduced from the difference between the basicity of the bitumen sample without the additive and the basicity of the one with it. The accuracy of the method varies but is typically capable of detecting to within about 20%.

The susceptibility of bitumen to ageing or long term loss of adhesion due to moisture can be assessed by examining the composition of bitumen before and after accelerated ageing (by rolling thin film oven test). Products of oxidative hardening, which cause embrittlement, plus the moisture susceptible functional groups, that tend to concentrate at the surface of aggregates, may be detected by the techniques developed by Petersen et al involving differential infrared spectrometry and selective chemical reactions. The same method would also be necessary for the detection of phenolic resin additives in bitumen.

Differential infrared spectrometry, fractionation techniques, elemental analysis and even the relatively simple titrimetric method for detection of amine based anti-stripping agents all require sophisticated laboratory equipment and expert interpretation. The methods are a far cry from simple physical tests such as penetration or softening point. As such it is necessary to recommend that the recipe approach to specification is not chosen, but that the methods used continue as a research tool, in order to extend the knowledge of bitumen composition and methods of improving its performance.

8.4. <u>The physical approach to specification.</u>

This approach is concerned with outlining a set of performance criteria for a modified bitumen. Compliance with the criteria may then be assessed by physical testing. The approach therefore answers questions regarding the presence of a modifier or compatibility in an indirect fashion. A physical approach to specification and testing has several advantages over the recipe approach:-

1) Physical test methods can be made relatively straightforward and representative of conditions in reality.

2) Difficulties can arise in compositional analysis, where several modifiers are used in the same bitumen, due to masking by, or interaction of, the modifiers affecting spectroscopic absorption. Physical tests are not interested in the chemistry of the mix, only the end result.

3) There is a considerable body of experience in specification and testing of bitumen using this approach.

8.4.1. Specifications for modified binders.

The range of modifications that are available for bitumen necessitate that several different specifications are available for various bitumen applications. In terms of the model binder the specifications will endeavour to create a binder which produces the most suitable properties for that particular application. For example, in a surface dressing application the dominant requirements are good adhesive properties, an extended season in terms of cold and damp weather, high cohesive strength and good spraying and wetting characteristics. Matters such as resistance to oxidative ageing and high stiffness modulus are less important, although they may be a by product of some of the more desirable properties.

It is submitted that there are four general material applications for modified bitumens which will require different specifications. These are:-

1) Applications in dense mixes such as rolled asphalt and dense bitumen macadam.

2) Porous macadams and open textured materials.

3) Surface dressing applications.

4) Surface overlays on roads subject to reflective cracking or thermal movement.

8.4.1.1. The specification of modified bitumens for rolled asphalts and dense macadams.

Rolled asphalt materials rely heavily upon the bitumen binder for their stiffness, consequently the stiffness and temperature susceptibility of the binder is reflected in the behaviour of the mix. Dense bitumen macadams are not so dependent upon the bitumen for stiffness, relying to a greater extent upon aggregate interlock. There are circumstances, however, where a particularly heavy duty macadam may be required in which case a modified binder may contribute to producing a stiffer mix.

The overall aim of bitumen modification, in these circumstances, is to produce a road pavement which has a higher fatigue life and greater resistance to rutting, both due to excessive sub-grade strain and lack of stiffness within the mix. These improvements in stiffness through the working temperature range must not be accompanied by an increase in a tendency to brittle behaviour at low temperatures. Factors that are somewhat less important are:-

1) Oxidative ageing - due to the dense, low void content of the mixes, which effectively denies access to oxygen.

2) Moisture susceptibility and long term stripping - due to the fact that mixes are dense and it is difficult for water to penetrate. Further, because oxidation is also retarded by the low void content fewer moisture susceptible functional groups are produced.

3) Initial adhesion to aggregates - asphalt and macadam mixes are prepared under controlled dry conditions using heated aggregates, consequently the adhesive bond between bitumen and the aggregate is good. There is, therefore, no need for additives which assist bitumen to adhere to the aggregate.

In order to obtain the properties desired polymer additives such as E.V.A. or catalytic modifiers such as Chemkrete may be specified. The main problem in producing a specification for such a modified bitumen is in characterising the temperature/stiffness relationship under traffic loading. For unmodified bitumens this is possible from two simple test measurements, penetration at 25 C and the ring and ball softening point. However, the relationship between temperature and stiffness for a modified bitumen may be quite different to that for ordinary bitumen. For this type of mix it will, therefore, be necessary to specify the temperature/stiffness relationship of the bitumen as well as having the means to measure it. It is recommended, therefore, that the specification for bitumens of this type should contain a graph of temperature versus stiffness obtained under repeated load applications which simulate traffic loading. Clearly some research will be necessary in order to establish the relationship, this may be carried out by testing bitumen samples at a range of temperatures using a <u>Nottingham asphalt tester</u>, which has been specifically adapted to test pure bitumen samples. Alternatively the new <u>Dynamic shear rheometer</u>, which is a product of the U.S. Strategic Highway Research Program (SHRP), may be employed. The stiffness range should extend to very low temperatures, where a limiting value of may be established at a point somewhere above the <u>Fraas breaking point of the modified material.</u> Once a specification has been established in this way compliance testing may be carried out, with one of the test methods mentioned above, on samples of modified bitumen at various temperatures.

In view of the fact that modifiers may increase viscosity at mixing temperatures it will be necessary to specify certain viscosities at these temperatures, these may be tested using an efflux viscometer. For modification using Chemkrete it will be necessary to indicate a stiffness temperature relationship for the modified binder both prior to full curing and after the bitumen has gained its full strength.

For the designer of a road pavement a standard specified stiffness range will enable the direct assessment of mix stiffness and thickness of pavement layers when using a modified bitumen. The purpose of the specification in this case is simply to ensure that the temperature susceptibility is a known quantity and replace the method of assessment of binder stiffness based upon penetration, softening point and Van der Poel's nomograph.

8.4.1.2. The specification of modified bitumens for porous asphalts and open textured macadams.

Porous asphalts are open textured materials which absorb both noise and water producing a quiet running surface with a reduction in the amount of spray. Water is able to drain away through the open pore structure of the material and then enter the normal road drainage network. When used as a wearing course the main structural layers of the pavement are designed on the assumption that the porous asphalt contributes little to the strength of the pavement. Stiffness, therefore, is only a requirement for this material in order to maintain its stability. Open textured macadams are generally only used as basecourse materials in footways or lightly trafficked roads the material is not used, or designed for use, in situations where a high stiffness is required. The greatest drawback with both these materials is lack of durability due to the large percentage of voids. These allow free penetration by water and atmospheric oxygen, resulting in a high rate of oxidative hardening and consequent embrittlement, with the attendant risk of stripping.

Bitumens for use in open textured materials should therefore be specified which have a low susceptibility to oxidative ageing and which exhibit resistance to long term moisture damage. It is recommended that a specification for a low oxidative ageing criteria should be based upon a stated allowable increase in binder stiffness following a 75 minute rolling thin film oven test at 163 C. The approach taken in the SHRP is somewhat different in that it involves subjecting binder to an ageing process (representative of the short term effects of high temperature mixing) and then preparing a mix with the aged binder. The mix specimen is then baked, to simulate long term ageing. Relative stiffness tests before and after ageing are then made on the asphalt sample. It is submitted that both approaches are similar but that the SHRP method is geared to producing a mix design specification rather than a modified bitumen specification.

Several tests are available for compliance testing of bitumens modified with anti stripping agents. Examples of test procedures in addition to those mentioned in 5.3.3 above are, the Vialit[3] plate test, the Texas boiling test[4] and the SHRP net absorption/desorption test. the Texas boiling test is preferred because the test procedure involves heating bitumen to 163 C for 24-26 hours, in order to simulate the heating and mixing phase of mix production. Any anti stripping agents which are thermally unstable will, therefore, be shown up by the test. In outline the test, which is described fully by Lee and Al Jarallah[4], involves mixing hot bitumen with pre-heated aggregates in order to produce coated stone. These are allowed to cool for two hours and are then boiled in distilled water for ten minutes. Stripped bitumen is periodically removed from the surface of the water during the test and upon completion the amount of stripped bitumen is assessed. It is recommended that the percentage of modified bitumen retained should be not less than, say, 80% of the original mass.

Clearly adhesion tests are as much a test of the adhesive properties of the aggregate as they are of the binder. It is recommended therefore that the type of aggregate used in the test should be the same as that used in the mix. A case could be made to extending adhesion tests to include aged, bitumens in order to show up potential stripping problems. Further research is needed in this area in order to ascertain if such an approach is actually valid.

Summary of an outline specification for a modified bitumen for mixes with a high void content.

1) The temperature susceptibility under traffic loading shall be specified in terms of a stiffness/temperature relationship throughout a full range of likely road temperatures. For example -25°C to 50°C. It is accepted that where modification does not involve the viscoelastic behaviour of bitumen such a detailed approach to the specification of temperature susceptibility may not be necessary. However, it is better to adopt a standard approach which could be applied to all types of bitumen and it is suggested that the specification outlined would ensure more reliable products than the traditional approach.

Compliance tests shall be as outlined in 8.4.1.1 above.

2) Viscosity at mixing and laying temperatures shall be as specified and tested as outlined in 8.4.1.1.

3) The stiffness of the modified bitumen shall increase by no more than a factor of - say 1.2 - following ageing in a rolling thin film oven test for 75 minutes at 163°C.

Compliance may be tested by a modified Nottingham asphalt tester or the new SHRP dynamic shear rheometer.

4) The percentage of bitumen retained, following a Texas boiling test using specified aggregates, shall be not less than -say 80% - .

8.4.1.3. The specification of modified bitumens for surface dressing

The predominant requirements for a high performance bitumen based surface dressing binder are:-

1) Low viscosity at spraying temperature.

2) Good wetting and adhesion to ensure initial chipping retention.

3) High tensile strength (cohesion), with good elastic recovery following application of strain, in order to resist high shearing forces due to traffic.

4) Low temperature susceptibility, including some resistance to brittle behaviour. To prevent bleeding and chipping loss at high temperatures and chipping loss due to low temperatures during the after care period.

5) High stability in order to ensure that repeated cycles of heating and cooling do not cause degradation.

Factors that are less important are:-

1) Oxidative ageing, because in the long term chippings will become embedded into the road surface layer, which contains sufficient binder to resist oxidation until the next cycle of treatment.

2) Long term resistance to stripping, as in 1) above, the repeated cycles of surface dressing preclude this problem, in any event a bitumen with good wetting and adhesive properties will probably have good long term resistance to stripping.

3) A high stiffness at high road temperatures, is not a requirement for a surface dressing binder but would probably be imparted by a low temperature susceptibility. Low temperature brittle behaviour is important in extending a surface dressing season into the colder weather, however, the main function of the binder is to retain the chippings until they are embedded into the road surface. Once this has taken place low temperature brittle behaviour will be less of a problem.

In producing a specification which addresses the requirements of a high performance surface dressing binder it is likely that samples of bitumen emulsion are more likely to meet the criteria of the adhesion test due to the fact that less thermal degradation of anti-stripping agents will occur at the lower spraying temperatures for emulsion. Unless, of course, a supplier opts for an alternative non heat susceptible agent such as slaked lime.

A typical model specification for a modified bitumen surface dressing binder should contain the following:-

a) A stiffness temperature relationship for the full range of (road) working temperatures.

b) Stated viscosities at spraying temperatures.

c) Rate of elastic recovery at specified levels of strain.

d) Not less than 80% retention of binder following Texas boiling test.

e) Bitumen emulsion shall be required to comply with the present requirements of B.S. 434 in terms of particle charge and viscosity.

f) For bitumen emulsion the base binder shall comply with the requirements a to d.

The testing regime for the above specification will be as follows:-

1) The stiffness/temperature relationship is to be stated for the full range of road temperatures. As before it is envisaged that compliance testing will be with the Nottingham Asphalt Tester or dynamic rheometer on samples of modified bitumen. Low temperature brittle behaviour will be avoided by specifying a

limiting value for stiffness - established initially by Nottingham Asphalt and Fraas breaking point tests or the new SHRP dynamic rheometer and the low temperature direct tension tests. The tensile strength of bitumen at, high road temperatures, is difficult to measure due to the unrepresentative levels of strain that occur during testing. In practice, bearing in mind that bitumen is viscoelastic, it may be advisable not to specify tensile strength directly but rather achieve it through specifying stiffness and elasticity. The latter can be estimated with the sliding plate rheometer test[5].

2) Viscosities at spraying temperatures shall be measured using an efflux viscometer, such as the standard tar viscometer. For modified bitumen emulsions the Engler and Redwood II viscometers may be used in accordance with the current recommendations in B.S. 434.

3) The elasticity of the bitumen shall be measured in a sliding plate rheometer. This test comprises of shearing a 10mm thick prism of bitumen between two parallel plates. The rate of recovery of deformation, initially applied under a specified load at a stated temperature, should assist in assessing the cohesive strength of the binder.

4) The Texas boiling test is not representative of the typical conditions that an asphalt mix will experience in reality. The new SHRP environmental conditioning test is arguably better. What the Texas boiling can do though is reveal any thermal instability in wetting agents. For surface dressing binder

the test is more appropriate than the SHRP test methods, though for bitumen emulsions a thermal degradation test is perhaps less important.

8.4.1.4. The specification of modified bitumens for surface overlays subject to reflective cracking.

The physical requirements for materials of this type is that they are resistant to deformation, that they are capable of absorbing movement in the pavement layers below, and that they contribute to the overall strength of the pavement structure. For such a material the modified bitumen will need to be specified and tested in the following areas:-

1) The temperature stiffness relationship, in order to ensure that the bitumen produces a mix that is intrinsically stiff and makes a worthwhile contribution to the overall pavement structure.

2) Elastic recovery criteria in order to withstand imposed strain without distress.

3) Resistance to oxidative hardening, in order that the overlay may continue to accommodate movement.

4) Related to 3) above, long term adhesion in the presence of water, in order to resist stripping.

5) Viscosity at mixing temperatures.

8.4.2. Summary of the physical parameters contained in the outline specifications and appropriate compliance tests

A) The temperature stiffness relationship

Test with Nottingham asphalt tester or SHRP dynamic rheometer, range typically -25°C to 50°C.

B) High temperature viscosity

Standard tar viscometer for modified bitumens, temperature range typically 120° - 165°C

Redwood II and Engler viscometer for emulsions at 85°C and 20°C respectively.

C) Elastic recovery at high road temperatures

Sliding plate rheometer.

D) Oxidative hardening and resistance to long term stripping

Rolling thin film oven test plus stiffness tests in A) above or

SHRP ageing test.

E) Adhesion and resistance to long term stripping

Texas boiling test or

SHRP environmental conditioning/net adsorption tests.

CHAPTER NINE

CONCLUSION

9.1. The history of the modification of bitumen, in order to improve its performance as a road making material, is about as long as the history of its use in road construction. Of the wide range of additives that are available, for the modification of bitumen today, none is a universal panacea. It is necessary to select a particular modifier to suit a specific application. In some cases more than one modifier may be necessary in order to achieve a desired end result.

At present in the U.K. there are no properly detailed specifications and complementary test methods specifically for modified binders. Consequently there can be wide variability in what are allegedly the same materials, obtained from different sources. It is intended that, amongst other things, this work will serve as a guide both to the drafting of specifications and the design of an appropriate test regime. In 1987 the U.S. Congress initiated a $150 million research programme in order to improve the performance, safety and durability of U.S. roads. This Strategic Highways Research Program (SHRP) was completed in 1993 and some of the details of this extensive investigation are now being published. Details that have come to light in respect of bitumen are largely centred on a new physical performance specification. The specification is designed around different performance requirements for binders in various applications. The specification enables the selection of both normal or modified bitumens and it will be interesting to see how well the recommended materials perform in practice. A number of new test methods have been developed under the SHRP, those that are relevant to modified binders have been mentioned in this study.

From the point of view of pure research it will be clear from this work that not enough is known about the mechanisms of chemical and physical interaction between bitumen and various additives. Further work to elucidate the structure of bitumen will be beneficial in developing more sophisticated performance enhancing additives.

REFERENCES

1. Tarrer A.R. et al. Detection of amine based anti-stripping agents in asphalt cement. T.R.B. 1228. Washington D.C. 1989.
2. Whiteoak D. Shell Bitumen handbook 1990. (Shell Bitumen U.K.).
3. Vaniscote J.C. and B. Brule. Characterisation of polymer modified binders for surface dressing. 68th meeting of T.R.B. 1987.
4. Lee K.W. and M.J. Aljarallah. Utilisation of Texas boiling test to evaluate effectiveness of anti-stripping additives in Saudi Arabia. T.R.B. 1096. Washington D.C. 1986.
5. Dickinson E.J. Assessment of the flow and deformation of bituminous binders. Australian road research, Vol. 2, No.3 1981.