

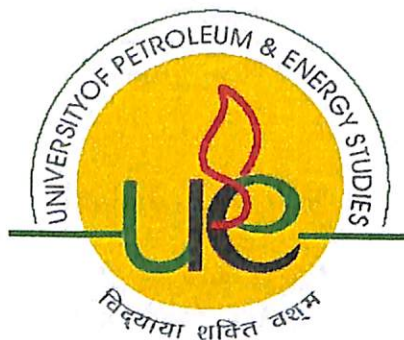
STUDIES ON THE CHEMISTRY FOR THE PRODUCTION OF HIGH QUALITY BITUMEN

A thesis submitted in partial fulfillment of the requirements for the Degree of
Master of Technology
in
Refining & Petrochemical Engineering

By
ANUJ TOMAR
R080207006

Under the guidance of

Dr. R. P. BADONI
Distinguished Professor
COE, UPES



College of Engineering
University of Petroleum & Energy Studies
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Dr. SHRIHARI

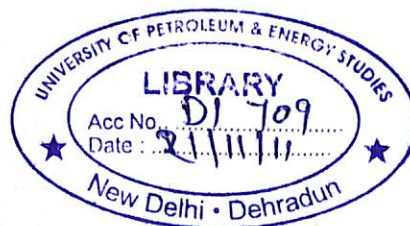
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CERTIFICATE

This is to certify that the work contained in this thesis titled "STUDIES ON THE CHEMISTRY FOR THE PRODUCTION OF HIGH QUALITY BITUMEN" has been carried out by Mr. ANUJ TOMAR (Roll No. R080207006) under my supervision and has not been submitted elsewhere for a degree.

R.P. Badoni

Dr. R.P. BADONI May 07, 2009
Distinguished Professor
College of Engineering

Office:
Sons Education & Research Society
PHD House,
stitutional Area
ranti Marg, New Delhi - 110 016 India
11-41730151-53 Fax: +91-11-41730154

Main Campus:
Energy Acres,
PO Bidholi Via Prem Nagar,
Dehradun - 248 007 (Uttarakhand), India
Ph.: +91-135-2102690-91, 2694201/ 203/ 208
Fax: +91-135-2694204

Regional Centre (NCR) :
SCO, 9-12, Sector-14,
Gurgaon 122 007
(Haryana), India.
Ph: +91-124-4540 300
Fax: +91-124-4540 330

Regional Centre (Rajahmundry):
GIET, NH 5, Velugubanda,
Rajahmundry - 533 294,
East Godavari Dist., (Andhra Pradesh), India
Tel: +91-883-2484811/ 855
Fax: +91-883-2484822

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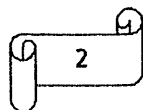
Anuj Tomar
ANUJ TOMAR
RO80207006

ABSTRACT

Bitumen is a heavy petroleum fraction mainly used in road construction. It has high viscosity and at normal temperature its adhesion to macadam is very good. But the road scenario has been changed from older days due to increase population of vehicles, heavy duty trucks, traffic jams etc. As well as the load running on the road is going high, the demand of high quality bitumen become necessary. By using the normal bitumen it is tough to meet the new revised road specifications. This work is understanding the chemistry of bitumens and how it is changed on modification. The modifiers are polymers, crumb rubber which enhance the property of bitumen and modified bitumen is known as Polymer Modified Bitumen (PMB), Crumb Rubber Modified Bitumen (CRMB). This bitumen can accept high load, high temperature susceptibility, low traffic speed. The experimental exercises shows that how the property changes in high quality Bitumen and are responsible for good life of roads with good crack and rut resistance.

CONTENTS

• Chapter 1		
	1. Intoduction to bitumen	1
	2. Uses of bitumen & its consumption	2
• Chapter 2		
	1. Bitumen constitution	3
	2. Bitume structure	6
	3. Rheology and structure	9
	4. Relationship between composition and properties	10
• Chapter 3		
	Bitumen production process	12
• Chapter 4		
	1. Penetration Test	14
	2. Ductility Test	15
	3. Softening Point Test	16
	4. Rolling Thin Film Oven Test	17
	5. Marshall stability Test	18
• Chapter 5		
	1. Bitumen Specifications and Quality	20
	a) Penetration Grade Bitumen	20
	b) Oxidised bitumens	23
	c) Hard bitumens	24
	d) Cutback bitumens	25
	2. Bitumen quality	26
	a) Rheology (flow behaviour)	26
	b) Cohesion	27
	c) Adhesion, Durability & Elasticity	29
	d) Stiffness	30



• **Chapter 6**

1. Modified bitumens	31
2. The role of bitumen modifiers in bituminous mixes	32
3. The modification of bitumen	34
a) The modification by the addition of sulphur	35
b) The modification by the addition of rubbers	36
c) The modification by the addition of Organo-manganese compound	36
d) The modification by the addition of thermoplastic polymers	38
e) The modification by the addition of thermoplastic rubbers	41
4. The influence of bitumen constitution on thermoplastic rubber/bitumen blends	42
5. The manufacture of thermoplastic rubber/bitumen blends	45
6. Epoxy Asphalt	47

• **Chapter 7**

1. Experimental Work	
a) Experiment No. 1 (with Results & Discussion)	48
b) Experiment No. 2 (with Results & Discussion)	60
c) Experiment No. 3 (with Results & Discussion)	61

List of Figures

- Figure 1: Chromatographic separation of constituents
- Figure 2: Different types of Aromatic Hydrocarbons
- Figure 3: Saturates
- Figure 4: Gel Type Bitumen
- Figure 5: Sol Type Bitumen
- Figure 6: Asphaltenes Structure
- Figure 7: Flow diagram of Bitumen production
- Figure 8: Penetration Test
- Figure 9: Ductility Test
- Figure 10: Softening Point Test
- Figure 11: Rolling Thin Film Oven Test Apparatus
- Figure 12: Marshall Stability Test Apparatus
- Figure 13: The Penetration grade QUALAGON
- Figure 14: Typical Force vs elongation for Modified Binders (force – ductility)
- Figure 15: Visco-elastic response to static loading
- Figure 16 :Visco-elastic response to a moving wheel load
- Figure 17: Effect of sulphur content on Marshall properties
- Figure 18 : Packing of the polyethylene in EVA
- Figure 19 : Linear and branched thermoplastic rubber
- Figure 20 : Phase structure of thermoplastic rubber
- Figure 21: Typical Viscosity vs Polymer Content Relationship
- Figure 22: Compatible & Incompatible systems
- Figure 23: Influence of bitumen constitution on bitumen/thermoplastic rubber blends
- Figure 24 : Effect of polymer content on softening point for diff. Modifiers.

List of Tables

- Table 1: Constituents of bitumen
- Table 2: BS 3690 : Part 1 Specification for penetration grade bitumen
- Table 3: BS 3690: Part 2 Specification for oxidized grade bitumens
- Table 4: BS 3690 : Part 2 Specification for hard grade bitumens
- Table 5: BS 3690: Part 1 Specification for cutback bitumens
- Table 6: Comparison between epoxy asphalt and conventional asphalt
- Table 7: Feedstock Analysis
- Table 8: Experimental work with FEEDSTOCK B (Modification with SBS)
- Table 9: Experimental work with FEEDSTOCK B (Modification with CRUMB RUBBER)
- Table 10 : Experimental work with FEEDSTOCK A (Modification with SBS)
- Table 11: Experimental work with FEEDSTOCK A (Modification with CRUMB RUBBER)
- Table 12: Comparative study of Modifier in FEEDSTOCK B
- Table 13: Comparative study of Modifier in FEEDSTOCK A
- Table 14: Requirement of POLYMER MODIFIED BINDERS (PMB)
Under IRC:SP:53-2002
- Table 15: Requirement of CRUMB RUBBER MODIFIED BINDERS (CRMB)
Under IRC:SP:53-2002
- Table 16: Effect of EVA grade 150/19 and 45/33 on Bitumen
- Table 17 : Polymer Content and Softening Point of different modified Bitumen

NOMENCLATURE

- IRC –Indian Road Congress
- TRRL – Transportation & Road Research Laboratory
- BS - British Standard
- TR- thermoplastic rubbers
- SBS- styrene-butadiene-styrene
- (SIS)- styrene-isoprene-styrene
- MFI- melt flow index
- EVA- ethylene vinyl acetate
- GLC- Gas liquid chromatography

1.0 INTRODUCTION

It is widely believed that the term 'bitumen' originated in Sanskrit where the word 'jatu' meaning pitch and 'jatu-krit' meaning pitch creating, referred to the pitch produced by some resinous trees. The Latin equivalent of it is claimed by some to be originally 'gwitu-men', (pertaining to pitch) and by others, 'pixtu-men' (bubbling pitch), which was subsequently shortened to 'bitumen' (then passing via French into English).

1.1 BITUMEN

Bitumen is manufactured from crude oil. It is generally agreed that crude oil originates from the remains of marine organisms and vegetable matter deposited with mud and fragments of rock on the ocean bed. Over millions of years, organic material and mud accumulated into layers hundreds of meters thick, the immense weight of the upper layers compressing the lower layers into sedimentary rock. Conversion of the organism and vegetable matter into the hydrocarbons of crude oil is thought to be the result of the application of heat from within the earth crust, pressure applied by the upper layer of sediments, possibly aided by the effects of bacterial action and radioactive bombardments.

The four main oil producing areas in the world are in U.S.A, the Middle East, the countries around the Caribbean and U.S.S.R. Crude oils differ both as to their physical and chemical properties. Physically they vary from viscous black liquids to free-flowing straw coloured liquids. Chemically they may be predominantly, naphthenic or aromatics, with combinations of the first two being common.

BS3690: part 1: 1989 defines bitumen as "a viscous liquid, or solid, consisting essentially of hydrocarbons and their derivatives, which is soluble in trichloroethylene and is substantially non-waterproofing and adhesive properties. It is black or brown in colour and possesses water proofing and adhesives properties. It is obtained by refinery processes from petroleum, and is also found as natural deposits or as a component of naturally occurring asphalt, in which it is associated with mineral matter".

1.2 THE EARLIEST USES OF BITUMEN BINDERS

In the vicinity of subterranean crude oil deposits surfaces seepages may occur at geological faults

.the amounts and nature of this naturally occurring material depends on a number of natural processes which will modify the properties of the material. This product may be considered to be a 'natural' bitumen, often being accompanied by mineral matter, the amount and the nature of which will depend on the circumstances which cause such an admixture to occur. For over 5,000 years bitumen in one form or another has been used as a waterproofing agent; the recorded use was by the Sumerians around 38000 B.C. At Mohenjo Daro in the Indus valley there is a particularly well preserved water tank which dates back to around 3,000 B.C.

1.2.1 USES:

- As a paving material: construction of highway, air port run ways, taxiways, parking lots, drive ways foot path construction and also in railways sleepers.
- In Agriculture: Disinfectants, Tree paints, wind -water erosion control, Fence post coat, protecting tanks vats irrigation channels etc.
- In industries: In electrical industries mainly for insulation purposes such as: cable protection particularly of small diameter cable, armature carbon, winding battery boxes, under seal etc.
- In buildings: Floors, Damps proofing and waterproofing, roofing purpose, masonry coating, wall boards etc.
- Recreation activities: Paved surfaces for dance in pavilions, running tracks, tennis courts etc.

1.3 GROWTH OF CONSUMPTION IN INDIA

Demand from the market on the quality of bitumen has been continuously growing in view of the developments taking place over the country in the transport segment. Bitumen demand for renewal programme of existing national highways, state highways and rural roads, was estimated to be 3.36 MMT by 2005. In addition to this, the proposed East- West, North-South corridors and Golden quadrangle construction (four lane having total length of 62300 kms) is expected to consume over 4 MMT of very high quality bitumen. With increasing demand of premium grade bitumen in the country coupled with complete shift from 80/100 softer grade bitumen to 60/70, 30/40 grade bitumen being a certainty, a need was felt to relook at the bitumen manufacturing facilities in Indian refineries.

Chapter 2

2.0 BITUMEN CONSTITUTION

The configuration of the internal structure of a bitumen is largely determined by the chemical constitution of the molecular species present. Bitumen a complex chemical mixture of molecules

of a predominantly hydrocarbon nature with a minor amount of structurally analogous heterocyclic species and functional groups containing sulphur, nitrogen and oxygen atoms. Bitumen also contains trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium which occur in the form of inorganic salts and oxides or in porphyrine structures. Elementary analysis of bitumens manufactured from a variety of a crude oil shows that most bitumens contain

Table 1: Constituents of bitumen

Carbon	80 - 82 %
Hydrogen	8 - 11%
Sulphur	0 - 6 %
Oxygen	0 - 1.5
Nitrogen	0 - 1%

The precise composition varies according to the source of the crude oil from which the bitumen

originates and the subsequent modification induced by semi-blowing and blowing during manufacture and subsequent ageing in service. The chemical composition of bitumen is extremely complex: thus, a complete analysis of bitumen would be extremely laborious and would produce such a large amount of data that correlation with the rheological properties would be impossible. However, it is possible to separate bitumen into two broad chemical groups called asphaltenes and maltenes. The maltenes can be further subdivided into saturates, aromatics and resins. The four groups are not well defined and there is inevitably

some overlap between in the groups. However it does enable bitumen rheology to be compared with broad chemical, composition.

The methods available for separating bitumens into fractions can be classified as follows:

- solvent extraction;
- adsorption by finely divided solids and removal of unadsorbed solution by filtration;
- chromatography;
- molecular distillation used in conjunction with one of the above techniques.

Solvent extraction is attractive because it is a relatively rapid technique , but the separation obtained is generally poorer than when using chromatography where a solvent effect is combined

with selective adsorption. Similarly simple adsorption methods are not as effective as column chromatography in which the eluting solution is constantly re-exposed to fresh adsorbent and different equilibrium conditions as it progresses down the column. Molecular distillation is lengthy and has limitations in terms of how far type separation and distillation of high molecular weight components of bitumen can be effected.

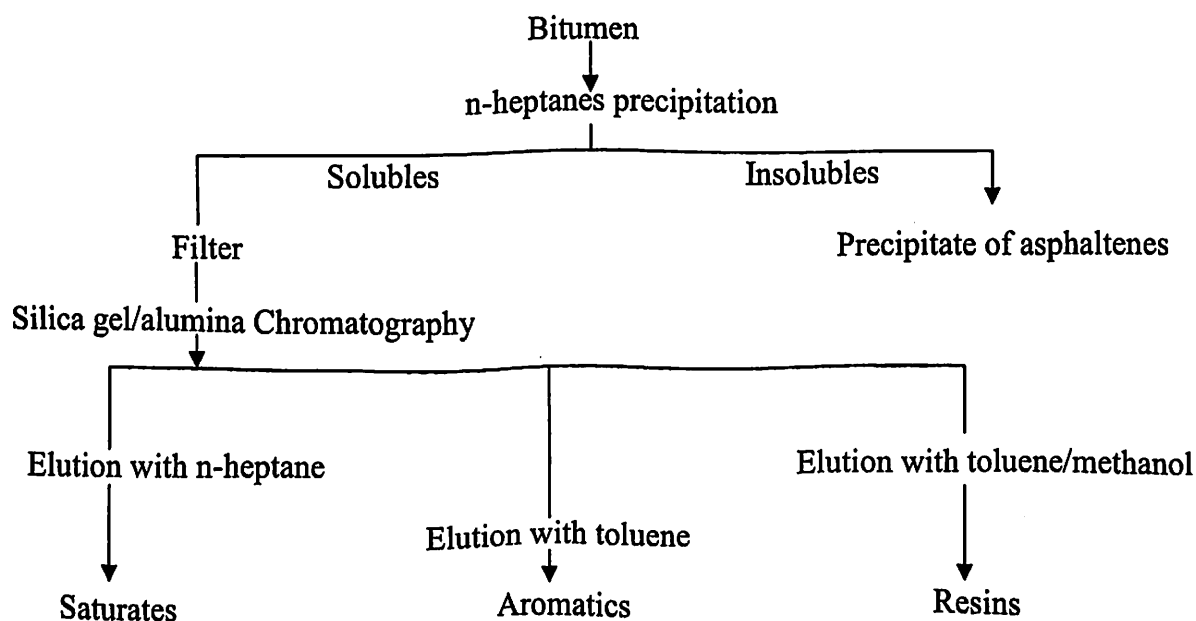


Figure 1: Chromatographic separation of constituents

Chromatographic techniques have therefore been most widely used to define bitumen constitution. The basis of the method is to initially precipitate asphaltenes using n-heptane followed by chromatographic separation of the remaining material. Using this technique bitumens can be separated into the four groups: asphaltenes, resins, aromatics and saturates.

The main characteristics of these four broad component groups are as follows:

2.0.1 ASPHALTENES: These are n-heptane insoluble black or brown amorphous solids containing in addition to carbon and hydrogen, sulphur and oxygen. Asphaltenes are generally considered as highly polar and complex aromatic materials of fairly high molecular weight. The molecular weight of asphaltenes range from 1000- 100000 they have a particle size of 5nm, to 30 nm and hydrogen carbon atomic ratio of about 1:1. The asphaltene content has a large effect on the rheological characteristics of bitumen. Increasing the asphaltene content produces a harder bitumen with lower penetration, higher softening point and consequently higher viscosity. Asphaltenes constitute 5% to 25% of the bitumen.

2.0.2 RESINS: Resins are soluble in n-heptane; like asphaltenes they are largely composed of hydrogen and carbon, and small amounts of oxygen, sulphur and nitrogen. They are dark brown in colour, solid or semi-solid, and very polar in nature. This particular characteristic makes them strongly adhesive. They are dispersing agents or peptisers for the asphaltenes and the proportion of resins to asphaltenes governs to a degree the solution (SOL) or gelatinous (GEL) type character of the bitumen. Resins separated from bitumen are found to have molecular weights ranging from 500 to 5000, a particle size of 1 nm to 5nm and an H/C atomic ratio of 1:3 to 1:4.

2.0.3 AROMATICS: Aromatics comprise of lowest molecular weight naphthenic aromatic compounds in the bitumen and represents the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 40% to 60% of the dark brown viscous liquid. The average molecular weight range in the region of 300 to 2000, they consist of non polar carbon chains in which the unsaturated ring system dominates, and they have a high dissolving ability for other high molecular weight hydrocarbons.

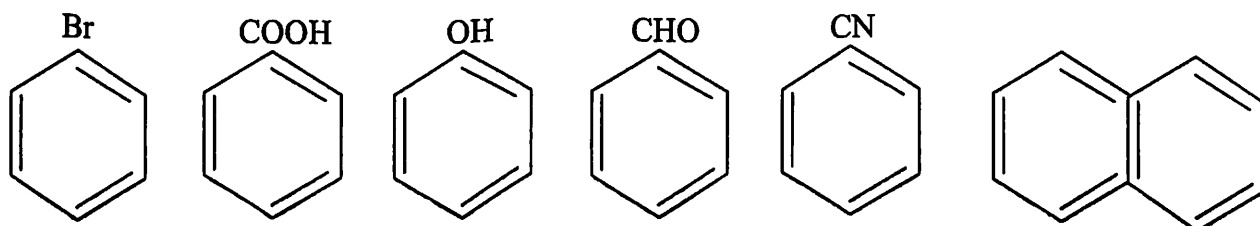
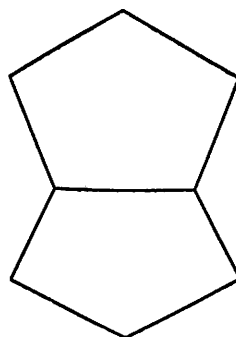
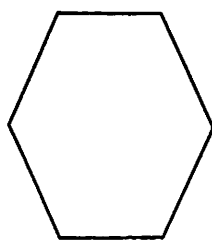
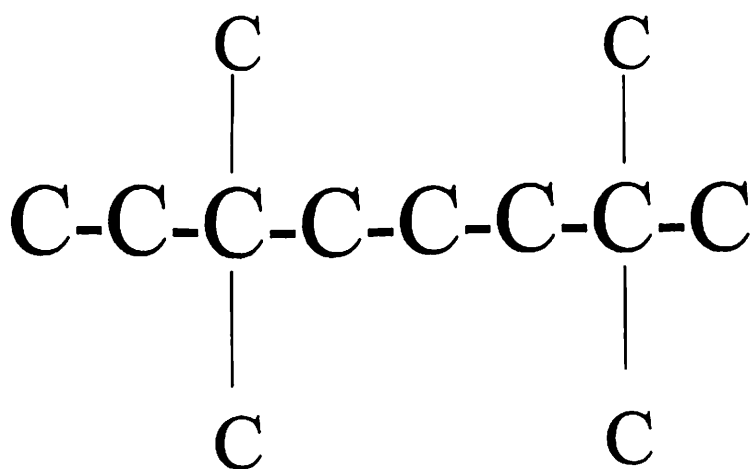


Figure 2: Different types of Aromatic Hydrocarbons

2.0.4 SATURATES: Saturates comprise straight and branched chain aliphatic hydrocarbons together with alkyl-naphthenes and some alkyl-aromatics. They are non polar viscous oils which are straw or white in colour. The average molecular weight range is similar to that of aromatics and the components include both waxy and non waxy saturates. This fraction 5% to 20% of the bitumen.

**Figure 3: Saturates****2.1 BITUMEN STRUCTURE:**

Bitumen is traditionally regarded as a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltenes together with an absorbed sheath of

high molecular weight aromatic resins which acts as a stabilising solvating layer. Away from the centre of the micelle there is a gradual transition to less polar aromatic resins, these layers extending outwards to the less aromatic oily dispersion medium.

In the presence of sufficient quantities of resins and aromatics of adequate solvating power the asphaltenes are fully peptised, and the resulting micelles have good mobility within the bitumen. These are known as solution or 'SOL' type bitumens, If the aromatic/resin fraction is not present in sufficient quantities to peptise the micelles. or has insufficient solvating power, the asphaltenes can associate further together. This can lead to an irregular open packed structure of

linked micelles, in which the internal voids are filled with an intermicellar fluid of mixed constitution. These bitumens are known as gelatinous or 'GEL' type bitumens, the best examples being the blown or oxidised grades used for roofing purposes. In practice most bitumens are of intermediate character. The colloidal behaviour of the asphaltenes in bitumens results from aggregation and solvation. The degree to which they are peptised will considerably influence the resultant viscosity of the system.

Such effects decrease with temperature and the GEL character of certain bitumens may be lost when they are heated to high temperatures. The viscosities of the saturates, aromatics, and resins depend on their molecular weight distributions. The higher the molecular weight the higher the viscosity. The viscosity of the continuous phase, ie the maltenes, imparts an inherent viscosity to the bitumen which is increased by the presence of the dispersed phase, ie the asphaltenes. The saturates fraction decreases the ability of the maltenes to solvate the asphaltenes, because high saturates contains can lead to marked agglomeration of the asphaltenes. Increasing in GEL character and a lower temprature dependence for bitumenes, therefore, not only results from the asphaltene content but also from the saturates content .

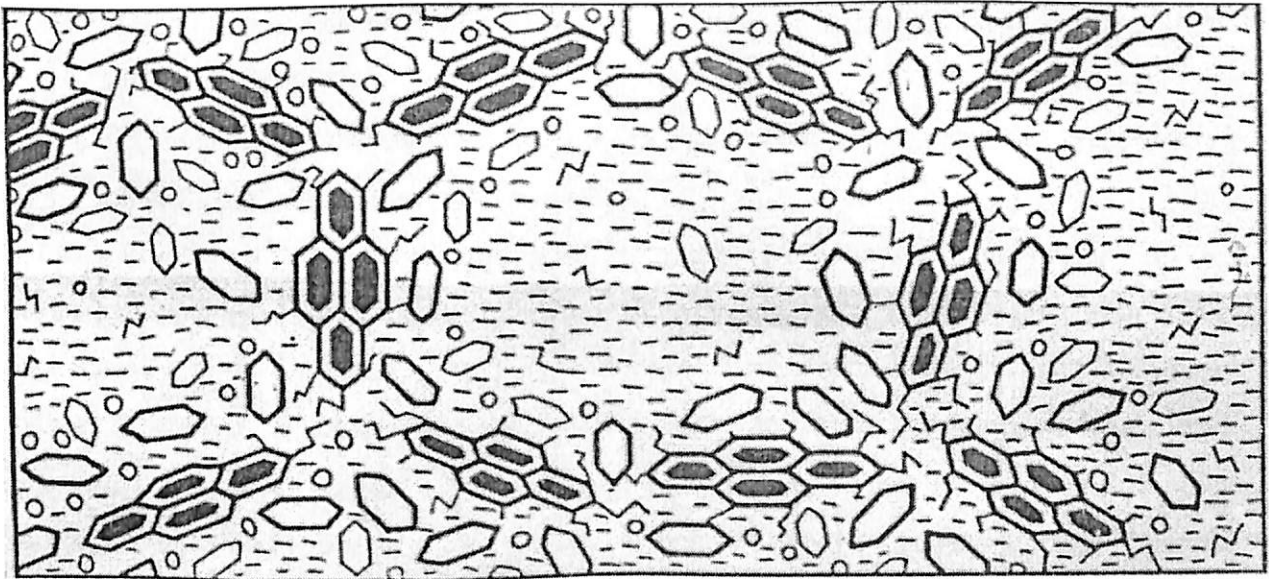
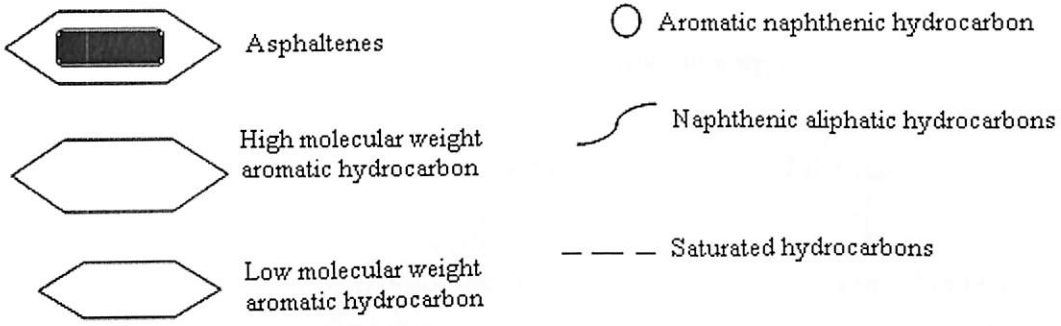


Figure 4: Gel Type Bitumen (Courtesy: I.I.P.)

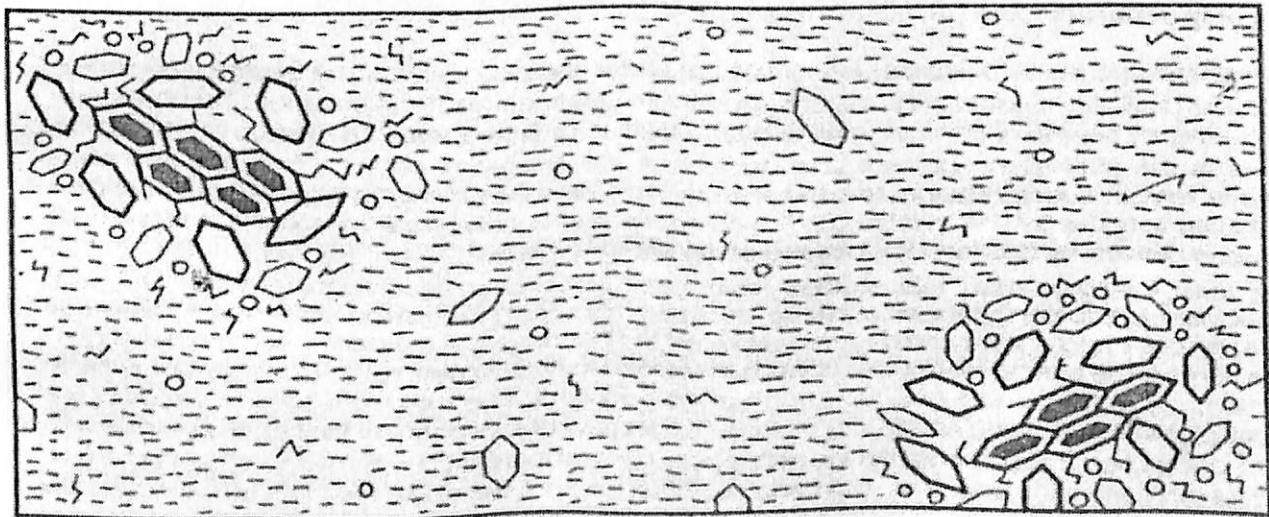


Figure 5: Sol Type Bitumen (Courtesy: I.I.P.)

2.2 Rheology and structure

Systematic blending of saturates, aromatics, resins and asphaltene fractions separated from bitumen has demonstrated the dependence of rheology on constitution. By holding the asphaltene content constant, and varying the concentration of the other three fractions, it has been demonstrated that :

- Increasing the aromatics content at a constant saturate of resins ratio has little effect on rheology, other than a marginal reduction in shear susceptibility;
- Maintaining a constant ratio of resins to aromatics and increasing the saturates content softens the bitumen;
- The addition of resins hardens the bitumen, reduces the penetration index and shear susceptibility but increases the viscosity.

It has also been shown that the rheological properties of bitumens depend strongly on the asphaltene content. At constant temperature the viscosity of a bitumen increases as the concentration of the asphaltenes blended into the parent maltenes is increased. The increase in viscosity, however, is substantially greater than would be expected if the asphaltenes were spherical, non-solvated entities. This suggests that the asphaltenes can interact with each other and/or the solvating medium. Even in a dilute toluene solution the viscosity increase observed when increasing the asphaltene content corresponds to a concentration of non-solvated spheres, some five times higher than the amount of asphaltenes used. Bitumen asphaltenes are believed to be stacks of plate-like sheets formed of aromatic/naphthenic ring structures. The viscosity of a solution, in particular a dilute solution, depends on the shape of the asphaltene particles. Size is important only if shape changes significantly as size increases. At high temperatures the hydrogen bonds holding the sheets/stacks together are broken, resulting in a change in both the size and shape of the asphaltenes. Dissociation of the asphaltene entities continues until the limiting moiety, the unit sheet of condensed aromatic and naphthenic rings, is reached. Consequently, viscosity falls as temperature increases. However as a hot bitumen cools, associations between asphaltenes occur to produce extended sheets. These, in turn, interact with other chemical types present (aromatics and resins) as well as stacking together to form discrete asphaltene particles.

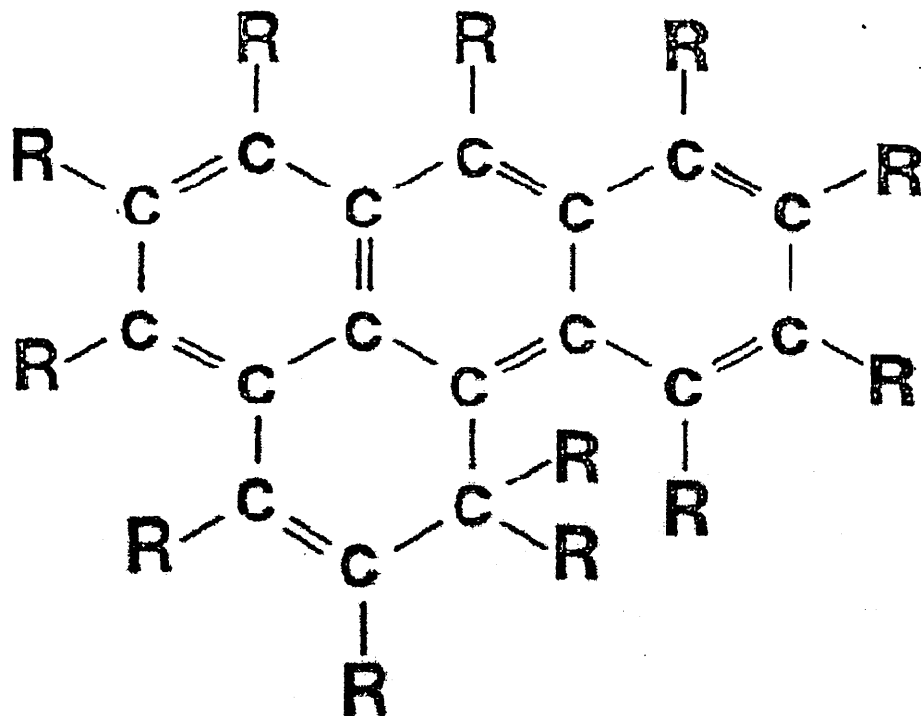


Figure 6: Asphaltenes Structure

The marked increase in non-newtonian behaviour as a bitumen cools is a consequence of the inter and 'intra-molecular attractions between asphaltenes and other entities. Under shear these extended associations will deform or even dissociate. In a way not adequately described by classical Newtonian concepts. Consequently, at ambient and intermediate temperatures, it can be reasonably concluded that the rheology of bitumens is dominated by the degree of association of asphaltene particles and the relative amount of other Species present in the system to stabilise these associations.

2.3 The relationship between broad chemical composition and physical properties

Atmospheric and vacuum distillation removes the lighter components from the bitumen feedstock. The loss of distillates leads to the preferential removal of saturates and concentration of asphaltenes. Air blowing of bitumens from a given vacuum residue or fluxed vacuum residue considerably increases the asphaltene content and decreases the aromatics content. Saturate and resin contents remain substantially of the same order as before commencing blowing of the same feedstock.

Long term full-scale road trial studies have been undertaken to determine if the chemical composition of bitumen changes with time. using a full range of practical conditions, ie different mix types, different aggregates and bitumen contents. The major changes in viscosity are associated with the mixing and laying process. Changes in the viscosity of the binder are small with time. For the chemical composition the asphaltene content increased with mixing and has shown a gradual increase with time. The resin and aromatic content decreases with time. Although little change was expected in the saturates content. some increase has been noted, probably due to oil spillage from vehicles on the road. Overall changes after mixing are very small even though the initial void contents of the mixes studied were relatively high 5% to 8% ,recovered bitumen samples were obtained from the top 3 mm of cores extracted from the test Sections and service temperatures were high.

Whilst chemical composition can be related to physical properties given specific components, it should be noted that bitumens of very different chemical compositions can have very similar , physical properties. It is, therefore, Impossible to describe bitumens generally in terms of chemical component concentrations, and defining individual components, such as a minimum asphaltene content ,has little ,if any relevance.

Reference : Shell Bitumen Hand Book ,chap. 6, page 89-97;

Chapter 3

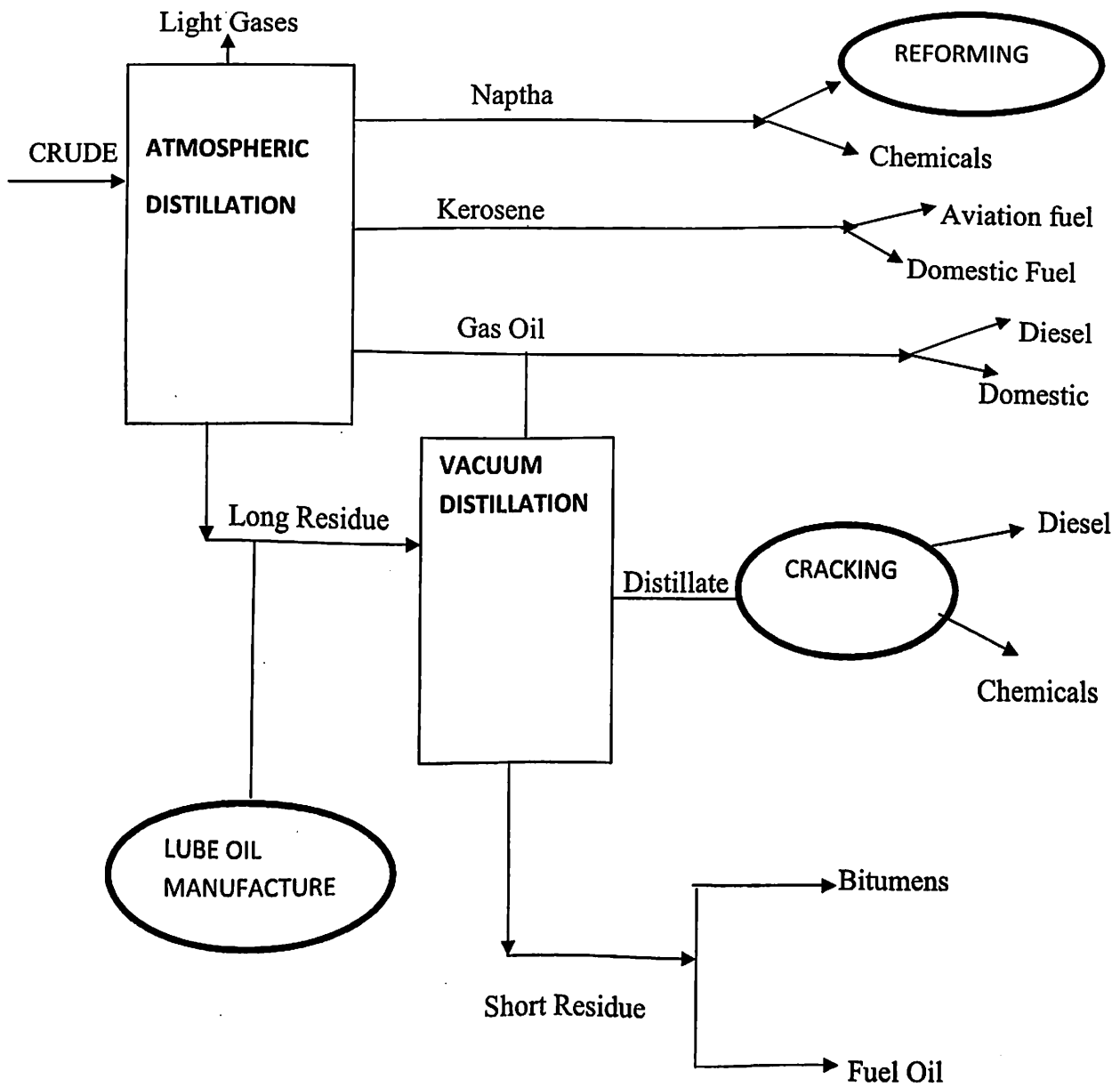
3.0 BITUMEN PRODUCTION PROCESS:

Fractional distillation of crude oil- The first step in processing of all crude petroleum is straight reduction by distillation. Fig shows the distillation principle which principle which is used to separate various crude fractions which have different boiling ranges. Because bitumen is primarily made up of the highest boiling fractions, it becomes residue from the vacuum tower. The crude oil is heated in large furnace to about 650°C and partially vaporized. Then it is introduced into a distillation tower where the lightest components vaporize, rise to the top cool, condense, and are drawn off for further processing. At various heights in the tower different fractions reach their boiling point and then, as the temperature is reduced, condense on tray inside tower

The intermediate components are taken out at different levels and are treated to make jet fuel, kerosene and diesel fuel after proper treatment. The residuum from this distillation is usually fed

into a vacuum distillation' unit where heavier gas oils are produced .The reduced pressure (typically 55 mm Hg .1 psi) in the vacuum tower assists in the flashing these oils at lower temperatures to prevent thermal cracking of the asphalt. In cracking, asphalt molecules are thermally broken apart .often steam is added to the bottom of the tower to further reduce the pressure from 50 mm Hg to about 12mm Hg, 24psi.

The bottom fraction from this unit is called vacuum processed, steam-refined bitumen. The grade of bitumen, where it is measured by penetration or viscosity, is controlled amount of heavy oil removed. All of this is done by a continuous flow operation.



Reference: Petroleum refining technology by Dr. Ram Prasad

Chapter 4

4.0 CONSISTENCY TESTS

To define the quality and determine the property of Bitumen several tests are followed. The main tests are given below :

4.1 Penetration test

It measures the hardness or softness of bitumen by measuring the depth in tenths of a millimetre to which a standard loaded needle will penetrate vertically in 5 seconds. BIS had standardised the equipment and test procedure. The penetrometer consists of a needle assembly with a total weight of 100g and a device for releasing and locking in any position. The bitumen is softened to a pouring consistency, stirred thoroughly and poured into containers at a depth at least 15 mm in excess of the expected penetration. The test should be conducted at a specified temperature of 25⁰c. it may be noted that penetration value is largely influenced by any inaccuracy with regards to pouring temperature, size of the needle, weight placed on the needle and the test temperature. A grade of 40/50 bitumen means the penetration value is in the range 40 to 50 at standard test conditions. In hot climates, a lower penetration grade is preferred. The Figure shows a schematic Penetration Test setup.

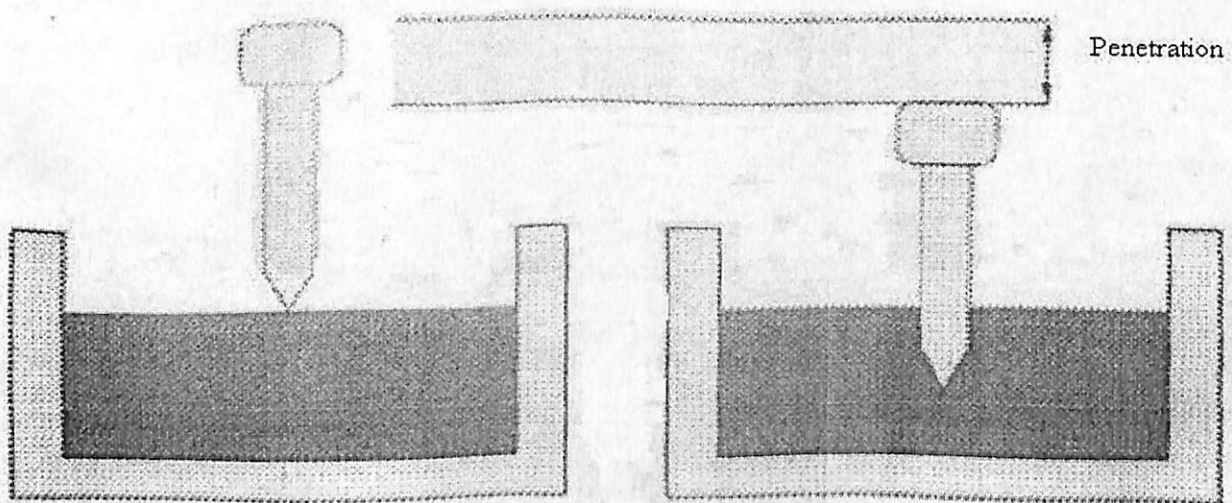


Figure 8: Penetration Test

4.2 Ductility test

Ductility is the property of bitumen that permits it to undergo great deformation or elongation. Ductility is defined as the distance in cm, to which a standard sample or briquette of the material will be elongated without breaking. Dimension of the briquette thus formed is exactly 1 cm square. The bitumen sample is heated and poured in the mould assembly placed on a plate. These samples with moulds are cooled in the air and then in water bath at 27°C temperature. The excess bitumen is cut and the surface is leveled using a hot knife. Then the mould with assembly containing sample is kept in water bath of the ductility machine for about 90 minutes. The sides of the moulds are removed, the clips are hooked on the machine and the machine is operated. The distance up to the point of breaking of thread is the ductility value which is reported in cm. The ductility value gets affected by factors such as pouring temperature, test temperature, rate of pulling etc. A minimum ductility value of 75 cm has been specified by the BIS.

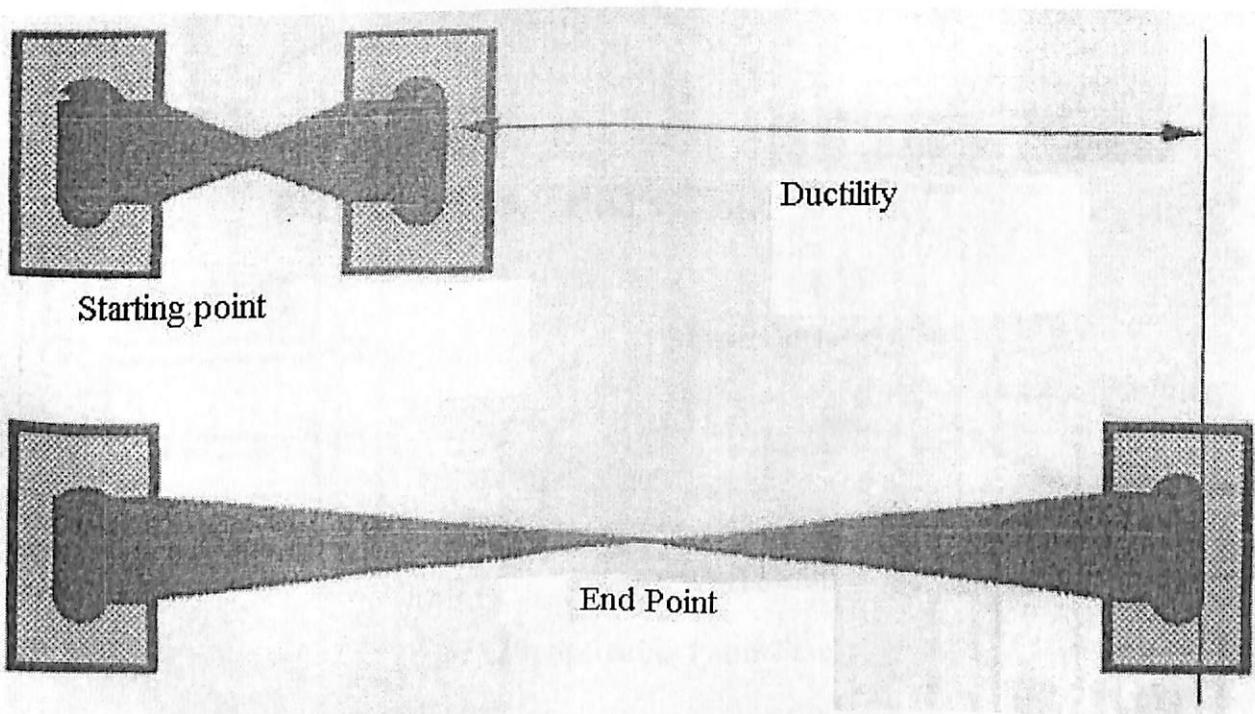


Figure 9:Ductility Test

4.3 Softening Point Test:

Softening point denotes the temperature at which the bitumen attains a particular degree of softening under the specifications of test. The test is conducted by using Ring and Ball apparatus.

A brass ring containing test sample of bitumen is suspended in liquid like water or glycerine at a

given temperature. A steel ball is placed upon the bitumen sample and the liquid medium is heated at a rate of 5°C per minute. Temperature is noted when the softened bitumen touches the metal plate which is at a specified distance below. Generally, higher softening point indicates lower temperature susceptibility and is preferred in hot climates. Figure shows Softening Point

test setup.

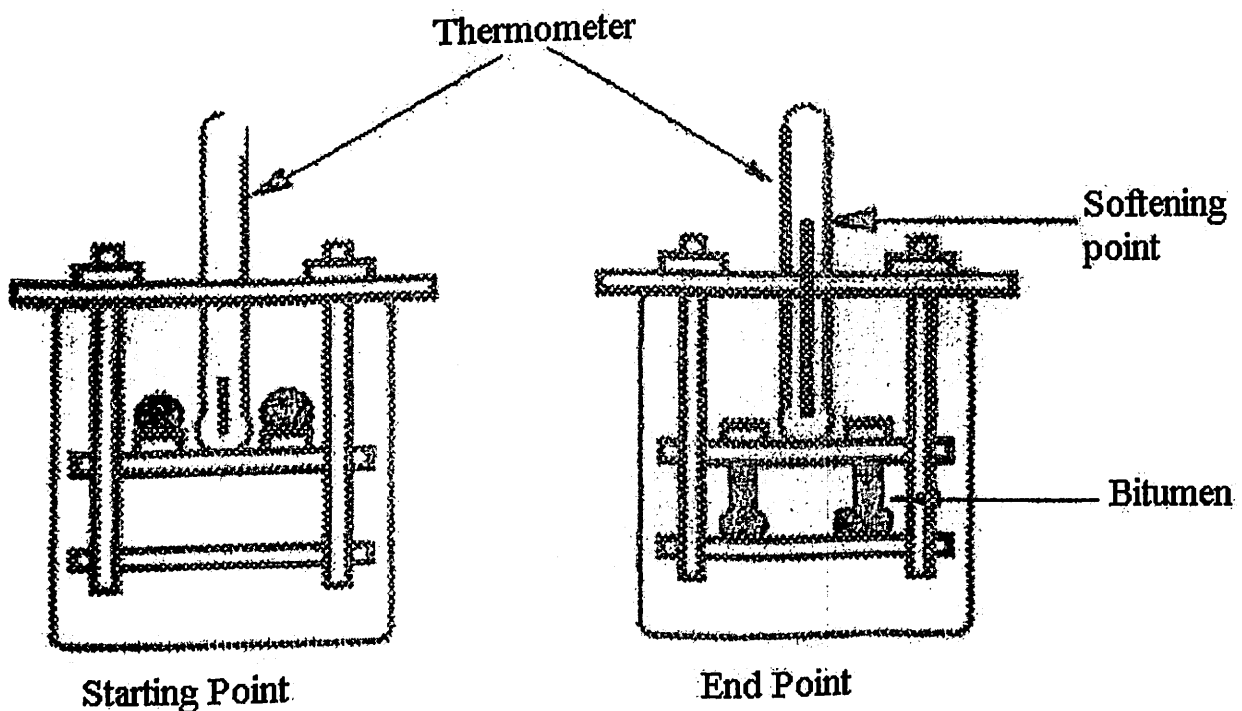


Figure 10: Softening Point Test

4.4 Viscosity Test:

Viscosity denotes the fluid property of bituminous material and it is a measure of resistance to flow. At the application temperature, this characteristic greatly influences the strength of resulting paving mixes. Low or high viscosity during compaction or mixing has been observed to

result in lower stability values. At high viscosity, it resists the compactive effort and thereby resulting mix is heterogeneous, hence low stability values. And at low viscosity instead of providing a uniform film over aggregates, it will lubricate the aggregate particles. Orifice type viscometers are used to indirectly find the viscosity of liquid binders like cutbacks and emulsions. The viscosity expressed in second, is that time taken by the 50 ml bitumen material to pass through the orifice of a cup, under standard test conditions and specified temperature. Viscosity of a cutback can be measured with either 4.0 mm orifice at 25°C or 10 mm orifice at 25 or 40°C.

4.5 Rolling Thin Film Oven Test:

This is a modified/accelerated version of TFOT and can be carried out in 75 minutes in spite of

300 minutes using same temperature to make bitumen of same consistency. A variation of thin

film oven test is in use by agencies in the United States, although it has the same purpose. It is described in ASTM D2872.

A specified amount of asphalt is poured into a bottle, which is placed in a rack in the oven maintained at 163°C. The rack rotates at a prescribed rate around a horizontal axis. The rack rotates at a prescribed rate around a horizontal axis. The rotating bottle continuously explores fresh asphalt. The orifice of the sample bottle passes in front of an air jet during each rotation. The heated air from the jet purges the vapours accumulated in the sample bottle. After 75 min the sample is taken from bottle and further test like soft. point, penetration etc. are done to see the effect of this test on bitumen. This test creates the actual working condition of bitumen where it has to work and after this test we can observe its life and workability.

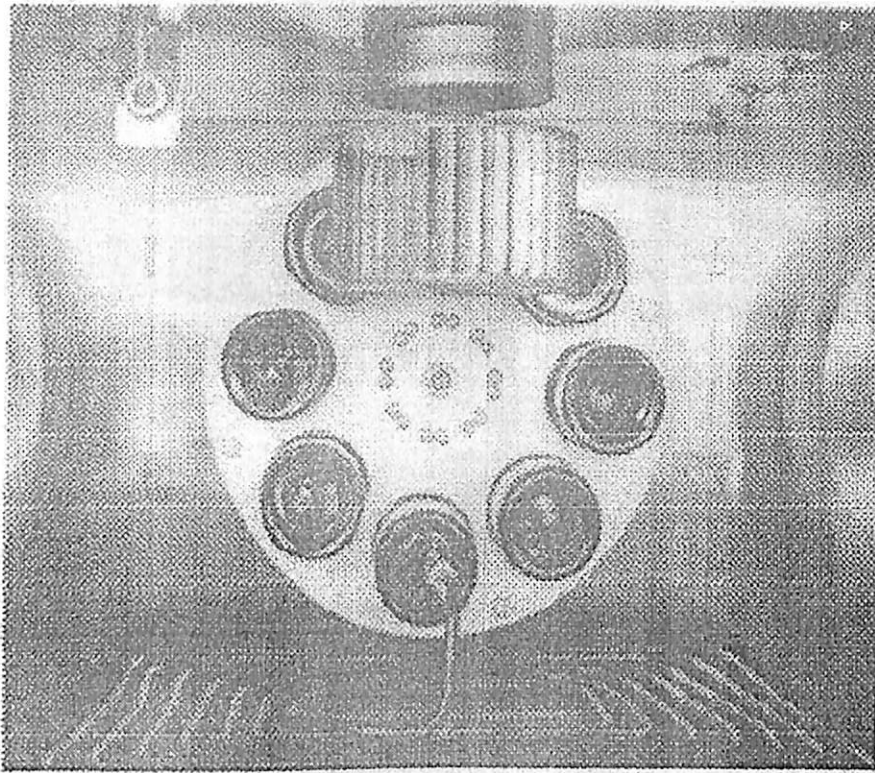


Figure 11: Rolling Thin Film Oven Test Apparatus

4.6 Marshall stability Test:

Take aggregates and bitumen separately and heat it upto 170°C and 163°C respectively After mixing thoroughly, shift the mixed material to the compaction mould arranged on the compaction pedestal. Give 75 blows on the top side of the specimen mix with a standard hammer (45cm, 4.86kg). Reverse the specimen and give 75 blows again. Take the mould with the specimen and cool it for a few minutes. Gently remove the specimen from the mould. Mark this test specimen and cure it at room temperature, around 12 hrs. A series of specimens are prepared by a similar method with varying quantities of bitumen content, with an increment of 0.5% (3 specimens) or 1 bitumen content. Before testing of the mould, keeps the mould in the water bath having a temperature of 60°C for half an hour. Now observe the stability of the mould on the Marshall stability apparatus.

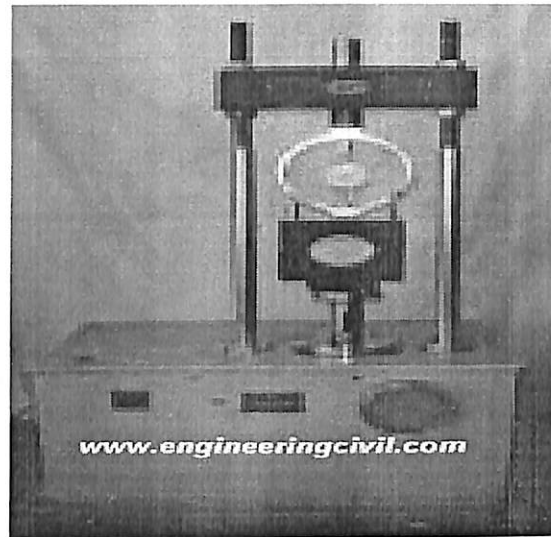


Figure 12: Marshall Stability Test Apparatus

- References :*
- 1.American Society of Testing Materials, Philadelphia, 1935, page 775*
 - 2.Shell Development Company U.S.A, Penetration of Bituminous Material, Methods series CT 32/55*
 - 3. www.engineeringcivil.com*

5.0 Bitumen specifications and quality

In the U.K. bitumens are manufactured to British Standard (BS) 3690 Part 1 covers bitumens for road purposes, part 2 covers bitumens for industrial uses and part 3 covers blends of bitumen with coal tar, and with lake asphalt or pitch. Four types of bitumen are manufactured mainly which are characterised by a combination of penetration, softening point and viscosity, viz:

1. Penetration grades - penetration and softening point;
2. Oxidised and hard grades - softening point and penetration;
3. Cutback grades - viscosity

In addition to the tests specified in BS 3690, Shell Bitumen U.K. carry out a further range of laboratory tests to ensure that the quality of the bitumen is maintained to a consistent standard and to ensure total suitability for purpose.

5.0.1 Penetration grade bitumens

Penetration grade bitumens are specified by the penetration and softening point test. But are designated by penetration only, eg 100 pen bitumen has a penetration of 100 ± 20 and a softening point of $46 \pm 5^\circ\text{C}$. The grades range from 15 pen through to 450 pen, with corresponding softening point ranges for each grade. In addition to penetration and softening point, limits are given for solubility in trichloroethylene, loss on heating and for grades used in the manufacture of hot rolled asphalt wearing course, ie 35 pen, 50 pen, 70 pen, 100 pen and HD 40, there is a minimum permittivity requirement. The loss on heating test ensures that there are no volatile components in the bitumen that could result in excessive hardening during storage, application or in service. The solubility limit ensures that contaminants such as carbon (coke) and mineral matter are kept to negligible proportions.

In the permittivity test the space between two plates in a parallel plate capacitor is filled with bitumen and a potential difference is applied across the two plates. The permittivity of bitumen is defined as the ratio of :

$$\frac{\text{(The capacitance of a capacitor with the bitumen as the dielectric)}}{\text{(The capacitance of the same capacitor with a vacuum as the dielectric)}}$$

The Transport and Road Research Laboratory showed that the ability of bitumens to weather under the combined effects of ultra-violet light in sunlight, oxygen, rain and oil deposition from traffic was related to the permittivity or dielectric constant of the bitumen .

The majority of penetration grade bitumens is used in road construction, the harder grades, 35 pen to 100 pen, being used in asphalt where bitumen stiffness is of primary importance and the softer grades, 100 pen to 450 pen, in macadams where the lubricating properties during application and bonding of the aggregate in service are more important.

Table 2: BS 3690 : Part 1 Specification for penetration grade bitumen

PROPERTY	Test Method	Grade of Bitumen									
		15 pen	25pen	35pen	40 pen HD	50 pen	70 pen	100 pen	200 pen	300 pen	450 pen
Penetration at 25°C dmm	BS 2000 (Part 49)	15 \pm 5	25 \pm 5	35 \pm 7	40 \pm 10	50 \pm 10	70 \pm 10	100 \pm 20	200 \pm 30	300 \pm 45	450 \pm 65
Softening point °C min.	BS 2000 (Part 58)	63	57	52	58	47	44	41	33	30	25
		max	76	69	64	68	58	54	51	42	39
Loss on heating for 5 hr.at 163°C a) loss by mass % b) drop in penetration	BS 2000 (Part 45)	.1	.2	.2	.2	.2	.2	.5	.5	1.0	1.0
		20	20	20	20	20	20	20	20	20	25
Solubility in trichloroethylene %by mass min.	BS 2000 (Part 47)	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5
Permittivity at 25 °C and 1592 Hz Min.	BS 2000 part 357	-	-	2.630	2.630	2.630	2.630	2.630	-	-	-

5.0.2 Oxidised bitumens

Oxidised bitumens are used almost entirely for industrial applications, eg. roofing, flooring, mastics, pipe coatings, paints, etc, and are specified and designated by both softening point and penetration tests, eg 85/40 is an oxidised grade bitumen with a softening point of $85 \pm 5^\circ\text{C}$ and a penetration of 40 ± 5 . Oxidised bitumens also have to comply with solubility and loss on heating criteria. Table 3 of BS 3690: Part 2, details the specification requirements for the six U.K. oxidized grade bitumens. The softening points of oxidized grades of bitumen are much higher than those of the corresponding penetration grade bitumen and therefore the temperature susceptibility ie penetration index is much higher, ie + 2 to +8.

Table 3: BS 3690: Part 2 Specification for oxidized grade bitumens

PROPERTY	Test Method (BS 2000)	Grade of Bitumen					
		75/30	85/25	85/40	95/25	105/35	115/15
Soft. Pt. $^\circ\text{C}$	Part 58	75 ± 5	85 ± 5	85 ± 5	95 ± 5	105 ± 5	115 ± 5
Pen. at 25°C Dmm	Part 49	30 ± 5	25 ± 5	40 ± 5	25 ± 5	35 ± 5	15 ± 5
Loss of heating for 5 hr. at 163°C loss by mass % max.	Part 45	0.2	0.2	0.5	0.2	0.5	0.2
Solubility in trichloroethyl.% mass min.	Part 47	99.5	99.5	99.5	99.5	99.5	99.5

5.0.3 Hard bitumens

Hard bitumens are also used entirely for industrial applications, eg coal briquetting, paints, etc. They are also specified by both softening point and penetration tests but are designated by a softening point range only, and a prefix H, eg H 80/90 is a hard grade bitumen with a softening point between 80°C and 90°C. The penetration index varies from 0 to +2. Table 4 of BS 3690: Part 2, details the specification requirements of hard grade bitumens.

Table 4: BS 3690 : Part 2 Specification for hard grade bitumens

PROPERTY	Test Method (BS 2000)	Grade of Bitumen	
		H 80/90	H 100/120
Softening Pt. °C	Part 58	85±5	110±10
Penetration at 25 °C dmm	Part 49	9+3	6+4
Loss of heating for 5 hr, at 163 °C loss by mass % max	Part 45	0.05	0.05
Solubility in trichloroethylene % by mass min	Part 47	99.5	99.5

5.0.4 Cutback bitumens

Cutback bitumens are manufactured by blending either 100 pen or 200 pen bitumen with kerosene to comply with a viscosity specification. In the U K. cutback bitumens are specified and designated by the flow time through a standard tar viscometer. Three grades are available, 50 seconds, 100 seconds and 200 seconds. The majority of cutback bitumen is used in surface dressing but a significant amount is also used for the manufacture of both standard and deferred set macadams.

Table 5: BS 3690: Part 1 Specification for cutback bitumens

PROPERTY	Test Method (BS 2000)	Grade of Bitumen		
		50 secs.	100 secs.	200 secs.
Viscosity (STV) at 40 °C, 10 mm cup, secs.	Part 72	50±10	100±20	200±40
Distillation a) distillate to 225 °C, %Vol. (max.) 360 °C, %Vol. b) penetration at 25 °C of residue from distillation to 360 °C, dmm	Part 27	1	1	1
		10±3	9±3	7±3
	Part 49	100 to 350	100 to 350	100 to 350
Solubility in trichloroethylene, % by mass (min.)	Part 47	99.5	99.5	99.5

Table 5 of BS3690 Part1 details the specification requirements of cutback bitumens. In addition to STV and solubility, cutback bitumens have to comply with a distillation

specification and a penetration requirement on the residual bitumen. This ensures that during application and in service the diluent will evaporate at a consistent and predictable rate and that the residual bitumen will have the appropriate properties in service.

The suffix X on the SHELPHALT range of cutback bitumens indicates that they have been doped with a specially formulated heat stable passive adhesion agent. This additive assists 'wetting' of the aggregate and resists stripping of the binder from the aggregate in the presence of water

5.1 Bitumen quality

For many years researchers has been investgating the relationship between laboratory measured

properties of penetration grade bitumens and their performance in asphalt mixes on the road. With increasing traffic loadings and more demanding performance requirements the need to be able to predict long-term behaviour is essential performance on the road depends on many factors, including the design, application and the quality of the individual components. Although bitumen is, in terms of its volume, a relatively minor component of a bituminous mix, it has a crucial role acting as a durable binder and conferring viscoelastic property to the mix. Essentially, satisfactory performance of bitumen on the road can be ensured if four properties are controlled:

- Rheology
- Cohesion
- Adhesion
- Durability

5.1.1 Rheology (flow behaviour)

Rheology is the study of the flow and deformation of materials. Bituminous binders behave as viscoelastic materials, with their behaviour influenced by the loading time as well as the temperature. In most instances, the addition of a polymer results in the binder having a lower moduli at low temperatures, and is therefore more flexible. At high temperatures, however, the binder exhibits an improved stiffness when compared to the unmodified bitumen. The most common way of measuring rheological properties is through the use of the Dynamic

Shear Rheometer (DSR), which applies a range of shear stresses at various frequencies (loading time) and temperatures. These results are compiled in diagrams that explain the behaviour of the binder for a variety of loading and temperature conditions. Typical parameters used for design purposes are the Dynamic Stiffness (G^*) and the Phase Angle (δ). The phase angle measures the relative elastic and plastic components of the binder's behaviour at the test conditions

The rheology of the bitumen at service temperature is adequately characterised by penetration and penetration index . By studying correlations between field performance and measured properties of experimental and commercial bitumens a set of laboratory tests has been developed which can assess the quality of a bitumen. The set of tests include six on the bitumen itself and three on a bituminous mix. For ease of assessment these nine results are presented on a regular polygon which is called the bitumen QUALAGON. Within the QUALAGON are tests which cover the three remaining key performance elements:

- cohesion –low temperature ductility
- adhesion –retained Marshall
- durability – rolling thin film oven test (oxidation stability)
true boiling point-gas liquid chromatography (volatility)
exudation droplet test (homogeneity)
Field trails (oxidation stability)

5.1.2 Cohesion

Cohesion is a measure of the tensile stress required to break the bond between molecules of the binder. For conventional bitumen the low temperature ductility test is used to measure this property. Thus, a binder with high cohesion will require higher tensile stress to cause failure, while a binder with a low cohesion will break easily. Test for cohesive strength of a modified binder is the force-ductility test, which measures the peak force generated during the test as well as the force versus elongation (ductility) relationship, shown in Figure 14 . The area under the curve, before the initial peak, is called the "elastic" phase while the total area under the curve can be used to calculate the toughness of the binder. This is a good indicator of the energy required to extend the binder, and thus its resistance to cracking. In summary, the cohesive properties of a modified binder influence how soon a surface seal can be opened to

traffic after completion, as well as its ability to withstand the expected shear stresses imparted by heavy traffic

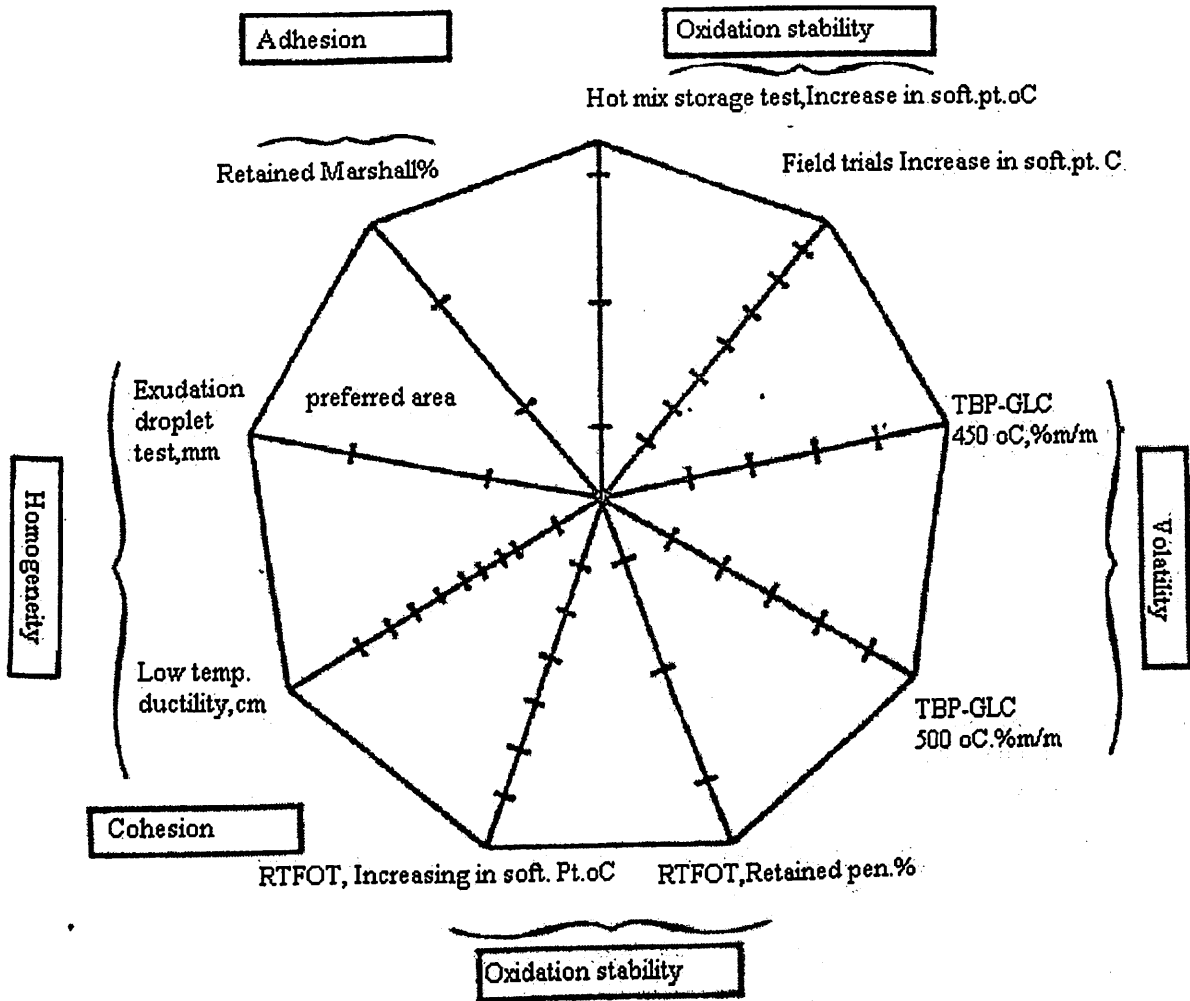


Figure 13: The Penetration grade QUALAGON
(courtesy: Shell Bitumen U.K.)

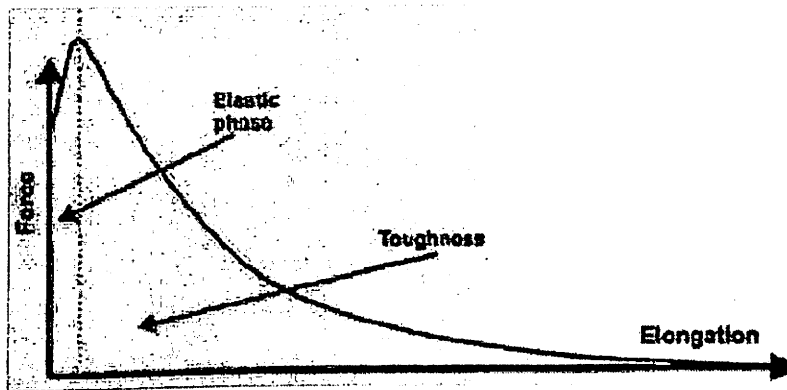


Figure 14: Typical Force vs elongation for Modified Binders (force – ductility)
(Courtesy: A.R. Thermosets)

The cohesive strength of penetration grade bitumens is characterised by low temperature ductility. In this test three dumb-bells of bitumen are immersed in a water bath and stretched at a constant speed of 50 mm per minute until fracture occurs. The distance the specimen is stretched before failure is reported as the ductility. The test temperature is adjusted depending on the penetration of bitumen, Under these conditions the test has been found to discriminate between bitumens of different cohesive strengths.

5.1.3 Adhesion

Adhesion is a measure of the stresses required to break the bond between the binder and aggregate. Bitumen adheres well to most types of road aggregate provided that they are clean and dry. In general, hot modified binders develop increased cohesive strength at the expense of a concomitant increase in adhesion, and are consequently less able to initially wet and adhere to the aggregate particles. It is, however, recommended that the Modified Vialit test be carried out to predict the adhesion of the binder to a particular aggregate. A number of additional subjective tests, such as the Pull-out test or Pliers test may be useful in predicting early binder/aggregate adhesion characteristics.

5.1.4 Durability

This is determined by volatility, oxidation, homogeneity test. These tests give its performance at working conditions, so that its life can be calculated. By GLC its true boiling point is determined, which gives that at what limit it should be operated. In rolling thin film test air,

temp, motion is applied to the sample and after some specified period the sample is again tested and the deviation in properties is checked which gives an idea about effect of working condition on bitumen.

5.1.5 Elasticity

Elastic behavior indicates that the binder recovers most or all of its initial shape when the load that caused the deformation is removed. The elastic recovery of a binder is commonly used to measure the fatigue resistance of a binder or its ability to absorb large stresses without necessarily cracking or deforming. For example, SBS forms a three-dimensional network of highly elastic, butadiene chains connecting stiff styrene domains, resulting in very high elastic recoveries. SBR has random styrene/butadiene molecules, resulting in relatively lower elastic recovery. EVA forms a rigid three dimensional network, imparting no elastic recovery properties to the base binder but a high stiffness. The elastic property of a binder is generally influenced by the type of modifier as well as the degree of modification and is determined by measuring the recovery of a sample which has been extended in a low temperature ductilometer. This property may also be categorised by means of a torsional recovery procedure, that has been introduced as a tentative quality control tool. In general, there is a direct relationship between elastic recovery and the degree of modification.

5.1.6 Stiffness

Stiffness is an engineering property that indicates the strain (deformation) a material will exhibit under a particular stress (load) condition. The stiffness modulus of bitumen is a function of the load size, the loading time and the loading temperature. There is a direct correlation between the stiffness of a binder and the permanent deformation that repetitive loading induces in an asphalt. Binders having a higher stiffness should therefore be used for asphalt layers subjected to high and/or slow moving, heavy, traffic loading

- References :*
- 1. British Standard (BS:3690) Part 1,2.*
 - 2. Shell Bitumen Hand Book , chap. 3, page 35-39*

Chapter 6

6.0 Modified bitumens

On the majority of our roads conventional bituminous materials perform satisfactorily. However, demands made upon roads increase year by year. Ever increasing numbers of commercial vehicles with increased axle loads take their toll and as we look forward to the year 2000, it is clear that this trend will continue. To enable the highway engineer to meet this growing challenge there now exists a wide range of road-proven modified bitumens.

Good basic design, stage construction and timely maintenance enable asphalt roads not only to withstand all the demands made, but also to provide the high standards of safety and comfort which have become synonymous with bitumen-bound surfacing. However, certain areas of road are, predictably, much more highly stressed than others and therefore, if the entire length is to perform satisfactorily during the design life, these areas may require special attention. We are all aware of the need for special materials on bridge decks for example, but the needs of other Critical areas can often be overlooked during construction or maintenance. It is clearly advantageous that maintenance or strengthening work be required along the entire length at a given point in time rather than repeated work being required at certain 'black spots' at shorter intervals. Disruption to traffic flow during maintenance work is a considerable cost to society. The closure of one lane of a UK motorway in 1987 was estimated to cost the community £20,000 per day and this is probably a conservative estimate.

The use of modified bitumens offers one solution to reduce the frequency of maintenance required at 'black spots' and provides much longer service life for maintenance treatments at difficult sites. To optimise the cost effectiveness of modified bitumens, they are best used in combination with high quality aggregates, in unusual mixes such as pervious macadam, or in areas requiring exceptional resistance to fatigue and deformation. The degree of improvement required, and hence the cost, will depend upon needs of the site to be treated. Modest improvements in deformation resistance can be achieved using reclaimed tyre rubber. Moving up-market, sulphur, organo-manganese compounds and thermoplastic polymers can improve both the workability of the asphalt during compaction and its deformation resistance in service. Moving further up-market, thermoplastic rubbers improve both deformation

resistance and fatigue characteristics. Thermosetting systems offer the ultimate performance of exceptional deformation resistance coupled with outstanding flexibility.

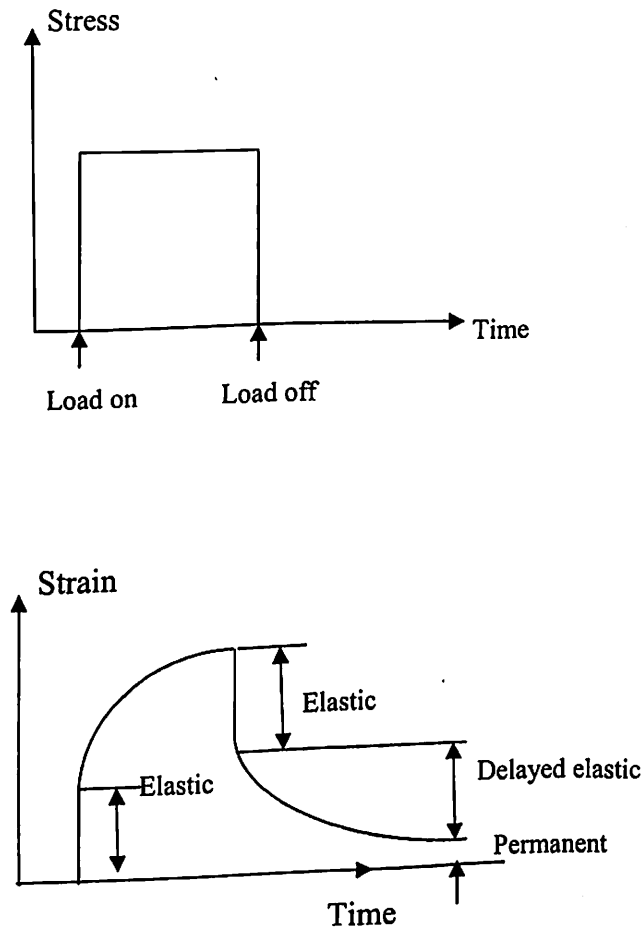


Figure 15: Visco-elastic response to static loading

6.1 The role of bitumen modifiers in bituminous mixes

As the bitumen is responsible for the visco-elastic behavior characteristic of all bituminous materials. It plays a large part in determining many aspects of road performance resistance to permanent deformation and cracking are typical examples. In general the proportion of any induced strain in a bituminous material that is attributable to viscous flow i.e. non recoverable, increases with both loading time and temperature. The effect is shown in figure 15. The strain resulting from the applied loading shows an instantaneous elastic response

followed by a gradual increase in strain with time until the load is removed. The change in strain with time is caused by the viscous behaviour of the material. On removal of the load the elastic strain is recovered instantaneously and some additional recovery occurs with time.

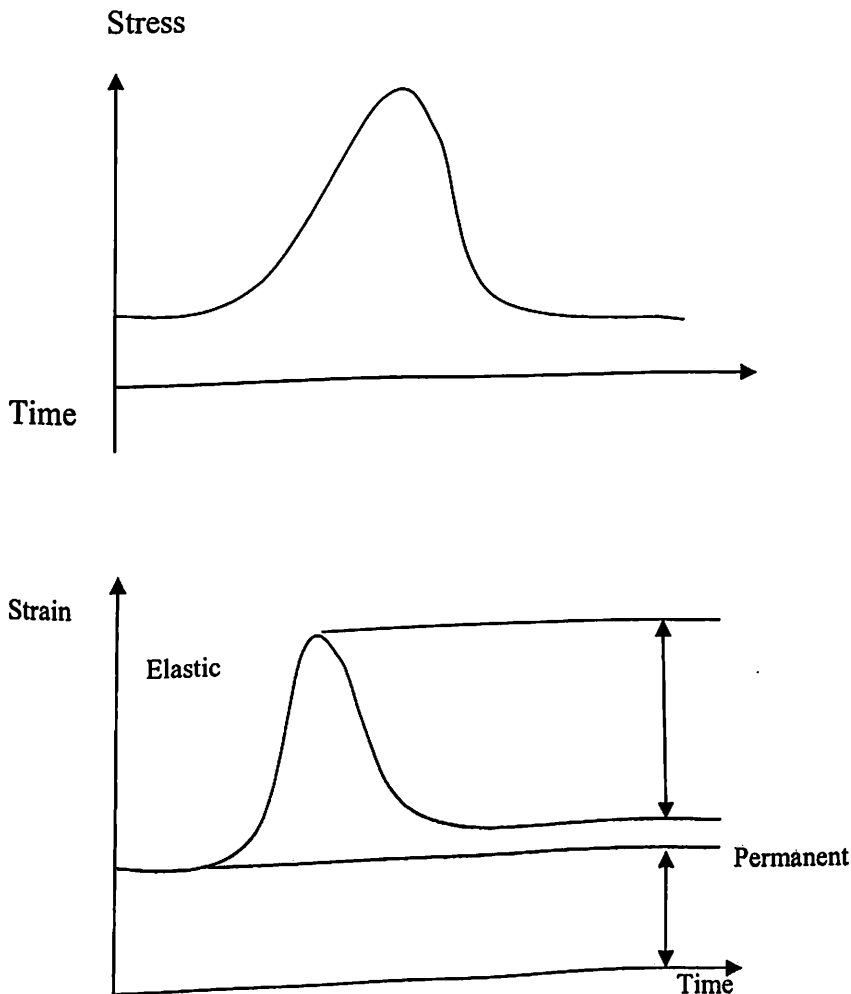


Figure 16 :Visco-elastic response to a moving wheel load

This is known as 'delayed elasticity'. Ultimately a permanent residual strain remains which, is irrecoverable and is directly caused by viscous behavior.

The response to a load pulse induced in an element of a bituminous material due to moving traffic loads is shown in figure 16. Here it is not possible to distinguish between the two components of elastic response, but the small permanent strain and larger elastic strain. Although the permanent strain is small for a single pulse load .when many millions of load applications are applied to a pavement, a large accumulation will develop and this is the

component which results in surface deformation. From the above it is clear why more deformation occurs at high ambient temperatures and where traffic is slow moving or stationary.

One of the prime roles of a bitumen modifier is to increase the resistance of the asphalt to permanent deformation at high road temperatures, without adversely affecting the properties of the bitumen or asphalt at other temperatures. This is achieved by either stiffening the bitumen so that the total viscoelastic response of the asphalt is reduced, with a corresponding reduction in permanent strain, or by increasing the elastic component of the bitumen, thereby reducing the viscous component, which again results in a reduction in permanent strain.

Increasing the stiffness of the bitumen is also likely to increase the dynamic stiffness of the asphalt, thus improving the load spreading ability of the material and increasing the structural strength and expected design life of the pavement; alternatively it may be possible to achieve the same structural strength but with a thinner layer. Increasing the elastic component of the bitumen will improve the flexibility of the asphalt which is important where high tensile strains are present.

6.2 The modification of bitumen

For many years researchers and development chemists have experimented with modified bitumens mainly for industrial use, adding asbestos, special fillers, mineral fibres and rubbers. In the last twenty years many researchers have looked at a wide spectrum of modifying materials for bitumens used in road construction.

For the modifier to be effective and for its use to be both practicable and economic, it must

- be readily available;
- resist degradation at asphalt mixing temperatures;
- blend with bitumen;
- improve resistance to flow at high road temperatures without making the bitumen too viscous at mixing and laying temperatures or too stiff or brittle at low road

temperatures;

- be cost effective;

The modifier when blended with bitumen should have the following characteristics:

- maintain its premium properties during storage, application and in service;

- be capable of being processed by conventional equipment;
- be physically and chemically stable during storage, application and in service;
- achieve a coating or spraying viscosity at normal application temperatures;

6.2.1 The modification of bitumen by the addition of sulphur

Sulphur is used in two types of asphalt paving processes and a number of proprietary products. Sulphur-extended asphalt utilizes a relatively small amount of sulphur as a diluent to the bitumen. The second process known as THERMOPAVE, uses high sulphur contents where the excess sulphur behaves as a mouldable filler, producing a very workable mix which can be laid by machine without roller compaction and when cool is very resistant to deformation.

A special category have also developed THERMOPATCH, which is a high sulphur content asphalt for repairing potholes, utility reinstatements, etc, in both bituminous and concrete pavements. It is free-flowing and is simply poured into the hole, the surface is leveled and, when cool, it is ready for trafficking. The amount of sulphur that will react with bitumen depends on the temperature and composition of the bitumen. Sulphur reacts predominantly with the naphthenic-aromatic fraction of bitumen, either by adding to the molecule, or by oxidizing it with the extraction of hydrogen as hydrogen sulphide. Between 119.3°C, the melting point of pure monoclinic sulphur, and 150°C, the reaction is mainly one of addition, producing an increase in the polar aromatic fraction and a relatively small change in the rheological properties of the bitumen. Above 150°C the competitive oxidation reaction increases sharply, producing an increase in asphaltenes and an effect on the properties of the bitumen similar to air blowing. The evolution of hydrogen sulphide at temperatures in excess of 150°C is clearly unacceptable; however, it has been shown that by careful control of temperature and by the use of purpose-built equipment the problem of fume emissions can be overcome.

Depending on the chemical constitution of the bitumen, approximately 15% to 18% of sulphur can be dispersed in bitumen and remain stable for a prolonged period. Increasing the sulphur content above this level results in a temporary suspension of the excess sulphur during mixing. When the asphalt is hot the excess sulphur makes the asphalt very workable because sulphur is a low viscosity liquid at temperatures between its melting point and about

160°C. As the asphalt cools, the excess sulphur partially fills and conforms to the shape of the voids in the compacted material, keying together aggregate particles, thereby increasing interparticular friction within the asphalt and imparting high mechanical strength to the mix.

In practice, the stiffening mechanism of the sulphur is not quite as simple as this, and changes in the behaviour and properties of the asphalt modified by sulphur are also time dependent. Initially the Marshall stability of asphalt mixes made with sulphur is usually slightly lower than when unmodified bitumen is used. However, after 7 to 21 days the Marshall stability increases to approximately twice that of the unmodified material. The most likely explanation for this behaviour is that crystallisation of the sulphur is retarded by some interaction with the bitumen.

The influence of sulphur content on the Marshall stability of a sand asphalt manufactured using a 200 pen bitumen is shown in figure 17. This shows the substantial increases in Marshall stability that can be achieved by the addition of sulphur.

6.2.2 The modification of bitumen by the addition of rubbers

Polybutadiene, polyisoprene, natural rubber, butyl rubber, chloroprene, random styrene-butadiene rubber, etc, have all been used with bitumen but their effect is mainly to increase viscosity in some instances the rubbers have been used in a vulcanized (cross-linked) state, e.g. reclaimed tyre crumb, but this is difficult to disperse in bitumen, requiring high temperatures and long digestion times and can result in a heterogeneous binder, with the rubber acting mainly as a flexible filler.

6.2.3 The modification of bitumen by the addition of organo-manganese compound

The use of organo-manganese compounds in bitumen is the subject of both a U.S. patent (No 4234346) and a UK patent (No 1600897) which indicate that paving materials of improved strength are obtained by adding to the bitumen a soluble organo-manganese compound, either alone, or in combination with organo-cobalt or organo-copper compounds. This product is better known under its brand name - CHEMCRETE. The use of manganese modified bitumens in asphalt and macadam is claimed to improve the temperature susceptibility of the

mixes, thereby improving their physical properties, i.e. Marshall Stability, resistance to permanent deformation and dynamic stiffness.

To enable the organo-manganese compound to be dispersed rapidly in bitumen the material is blended with a carrier. The modifiers in the range currently differ from each other with respect to the type and concentration of the organo-metallic compounds and the viscosity of the carrier oil used. Both aspects need to be considered to ensure the appropriate modifier is used for a particular application.

The mechanism put forward in the chemcrete patent is that certain ring structure compounds in bitumen, for example tetra hydro naphthalenes and similar structures, are readily auto-oxidised. It is believed that manganese promotes the formation of a diketone compound which then forms stable, chemically resistant complexes with the metal. These complexes tie together bitumen molecules which ultimately improve the temperature susceptibility of the bitumen and increase the strength of the bituminous mixture

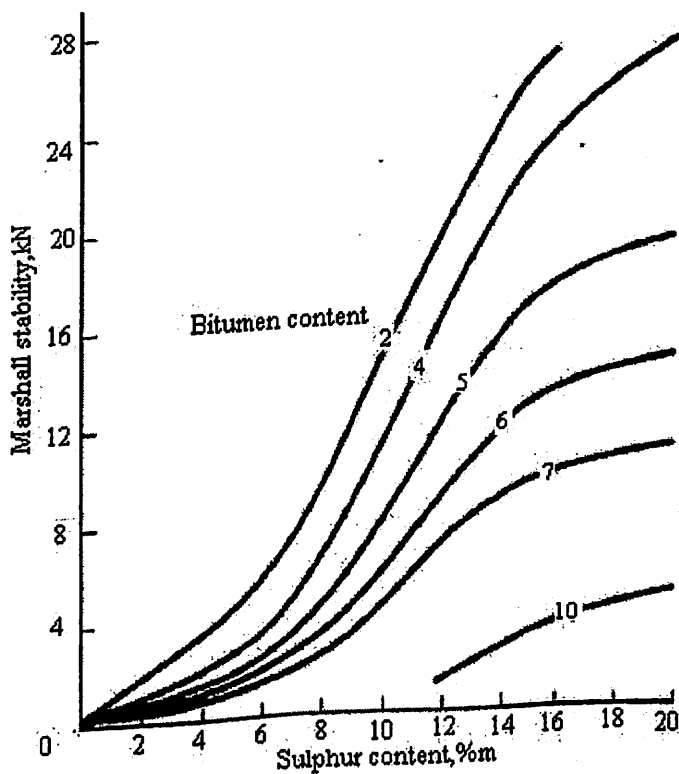


Figure 17: Effect of sulphur content on Marshall properties

The curing reaction is dependent on oxygen availability, bitumen film thickness and temperature.

Storage experiments carried out by CHEMCRETE have shown that a 100 pen bitumen containing 2%w of manganese modifier (UI-49) stored at 160°C for 28 days hardened from 127 pen to 100 pen. The Marshall stability and quotient measured on two sand asphalts, one manufactured using 100 pen bitumen containing CHEMCRETE, the other unmodified 50 pen bitumen. The initial Marshall properties of these two mixes are very similar; however, after 12 months the Marshall stability of the modified sand asphalt had increased by over 400%. During this 12 month period the Marshall flow increased by about 75%, resulting in an overall increase in Marshall quotient of over 200%. The increase in Marshall flow is believed to show that the gain in strength during curing is not due to embrittlement of the bitumen. Similar improvements were determined, using a laboratory wheel-tracking test, on cores cut from a road trial. Deformation rates at 45°C, immediately after laying, on modified and unmodified asphalt were very similar - 5 mm/h. However, after six months the deformation rate on the modified asphalt had dropped to less than 1 mm/h.

A large number of road trials covering a wide range of highway maintenance applications have been undertaken in the last five years. The use of organo-manganese modifiers in asphalts is currently being evaluated by the TRRL and it is understood that it is to be included in the Department of Transport specification in 1990

6.2.4 The modification of bitumen by the addition of thermoplastic polymers

Polyethylene, polypropylene, polyvinyl chloride, polystyrene and ethylene vinyl acetate (EVA) are the principal thermoplastic polymers which have been examined in modified road binders. As thermoplastics, they are characterised by softening on heating and hardening on cooling. Thermoplastic polymers, when mixed with bitumen, associate at ambient temperature, increasing the viscosity of the bitumen. Unfortunately they do not significantly increase the elasticity of the bitumen and when heated they can separate, which may give rise to a coarse dispersion on cooling. However, accepting these limitations, EVA at a concentration of 5% in 70 pen bitumen has become very popular.

EVA copolymers are thermoplastic materials with a random structure produced by the copolymerisation of ethylene and vinyl acetate. Copolymers with low vinyl acetate content possess properties similar to low density polyethylene. As the level of vinyl acetate increases so the copolymer properties change.

The properties of EVA copolymers are controlled by molecular weight and vinyl acetate content:

- **molecular weight:** the molecular weights of many polymers, are defined in terms of an alternative property; standard practice for EVAs is to measure melt flow index (MFI), a viscosity test that is inversely related to molecular weight; the higher the MFI, the lower the molecular weight and viscosity; this is analogous to the penetration test for bitumen – the higher the penetration the lower the average molecular weight and viscosity of the bitumen; Experiment 2 shows its effect after blending with Bitumen.
- **vinyl acetate content:** in order to appreciate the main effects of vinyl acetate on the properties of the modified binder it is useful to consider a simple illustration of its structure, as shown in figure 18; this shows how the regular polyethylene segments of the chain can pack closely together and form what are known as crystalline regions; it also shows how the bulky vinyl acetate groups disrupt this closely packed arrangement to give non-crystalline or amorphous rubbery regions; the crystalline regions are relatively stiff and give considerable reinforcing effect, whereas the amorphous regions are rubbery; the more vinyl acetate groups (or the higher the vinyl acetate content), the higher the proportion of rubbery regions, and conversely, the lower the proportion of crystalline regions. EVA modified bitumen stiffens rapidly as the EVA polymer crystallises. (This process occurs below the minimum rolling temperature). They are thermally stable at normal asphalt mixing temperatures. However, during static storage some separation may occur and it is therefore recommended that the blended product should be thoroughly circulated before use.

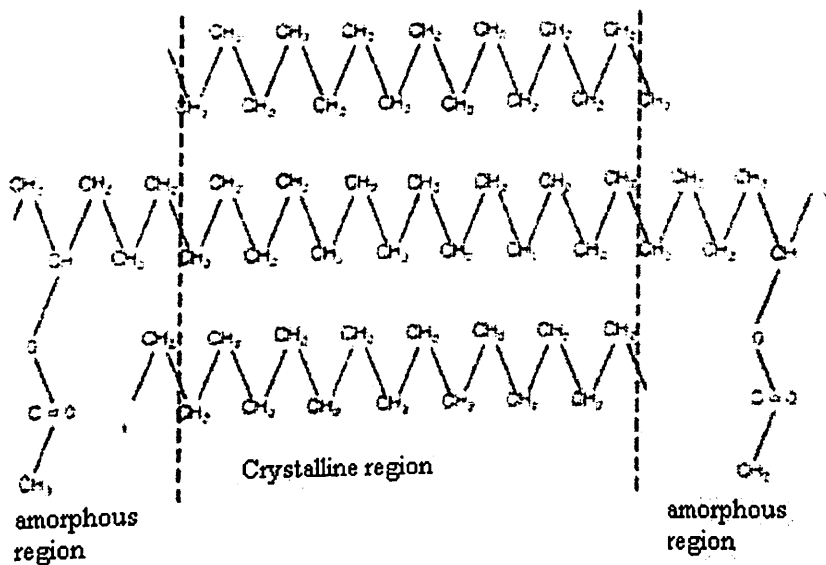


Figure 18 : Packing of the polyethylene in EVA

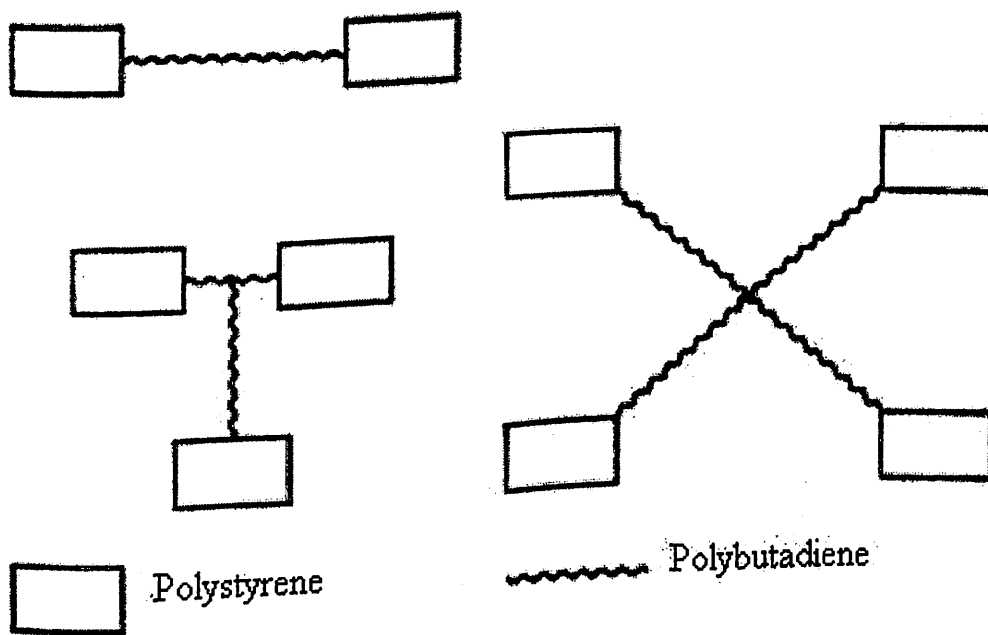


Figure 19 : Linear and branched thermoplastic rubber

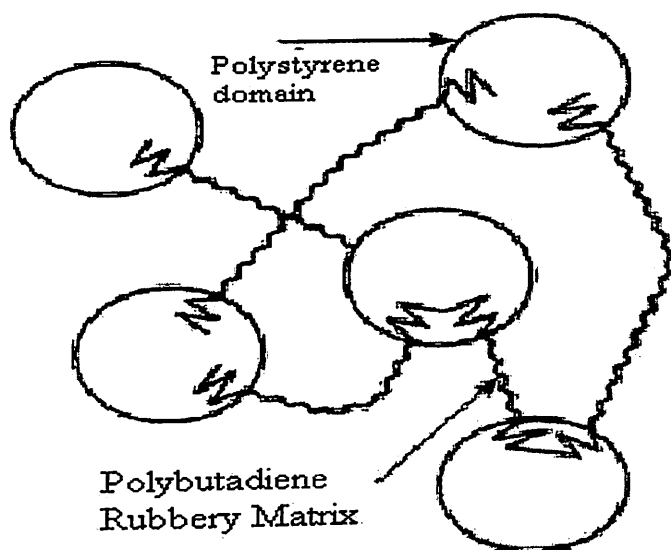


Figure 20 : Phase structure of thermoplastic rubber

6.2.5 The modification of bitumen by the addition of thermoplastic rubbers

Of the four main groups of thermoplastic elastomers - polyurethane, polyether-polyester copolymers, olefinic copolymers and styrenic block copolymers, it is the styrenic block copolymers which have proved to present the greatest potential when blended with bitumen. Styrenic block copolymers, commonly called thermoplastic rubbers (TR), may be produced by a sequential operation of successive polymerization of styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS). Alternatively, a di-block precursor can be produced by successive polymerization of styrene and mid-block monomer, followed by a reaction with a coupling agent.

Thus, not only linear copolymers but also multi-armed copolymers can be produced; these are often referred to as star-shaped, radial or branched copolymers as shown in figure 19. Thermoplastic rubbers derive their strength and elasticity from a physical cross-linking of the molecules into a three-dimensional network. This is achieved by the agglomeration of the polystyrene end-blocks into separate domains, as shown in figure 20, providing the physical cross-links for a three-dimensional polybutadiene or polyisoprene rubbery matrix. It is the polystyrene end-blocks which impart strength to the polymer and the mid-block which gives the material its exceptional elasticity.

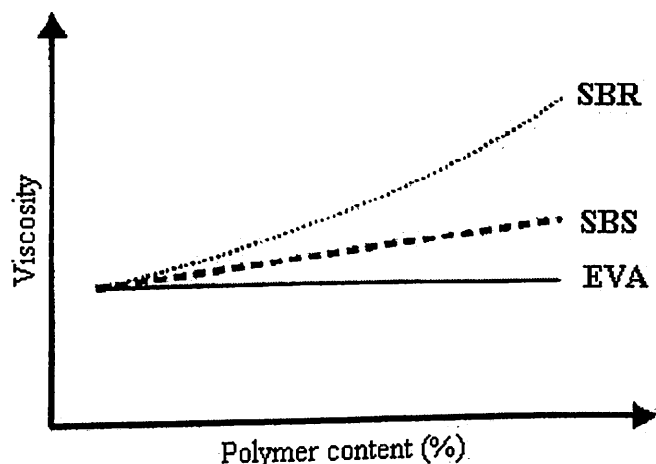


Figure 21: Typical Viscosity vs Polymer Content Relationship
(Courtesy : A.R.Thermosets Lab.)

At temperatures above the glass transition point of polystyrene (100°C) the polystyrene softens as the domains weaken and will even dissociate under stress, thus allowing easy processing. Upon cooling, the domains reassociate and the strength and elasticity is restored, ie the material is thermoplastic.

6.3 The influence of bitumen constitution on thermoplastic rubber/bitumen blends

As we know, bitumens are complex mixtures which can, to a limited extent, be subdivided into groups of molecules which have common structures:

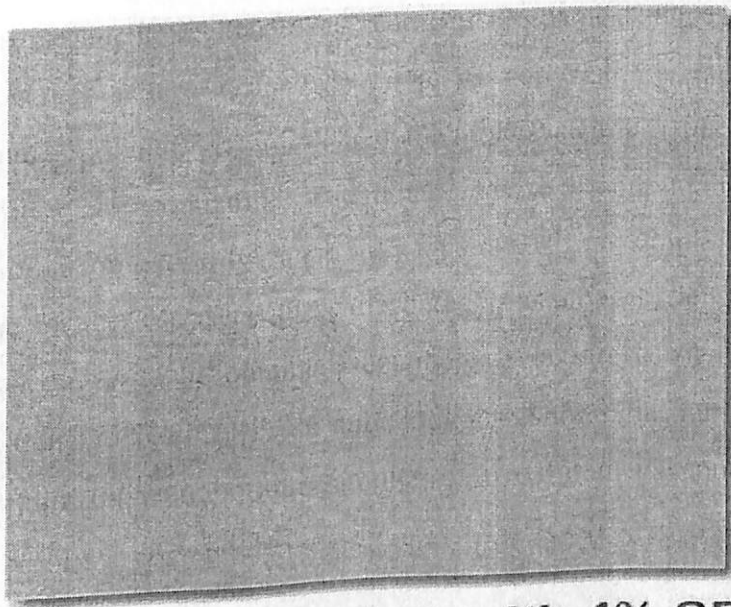
- saturates
- aromatics
- resins
- asphaltenes

The saturates and aromatics can be viewed as carriers for the polar aromatics, i.e. the resins and asphaltenes. The polar aromatics are responsible for the visco-elastic properties of the bitumen at ambient temperatures. This is due to association of the polar molecules which leads to large structures. in some cases even to three-dimensional networks, ie 'gel' type bitumen. The degree to which this association takes place depends on the temperature, molecular weight distribution the concentration of the polar aromatics and on the solvency

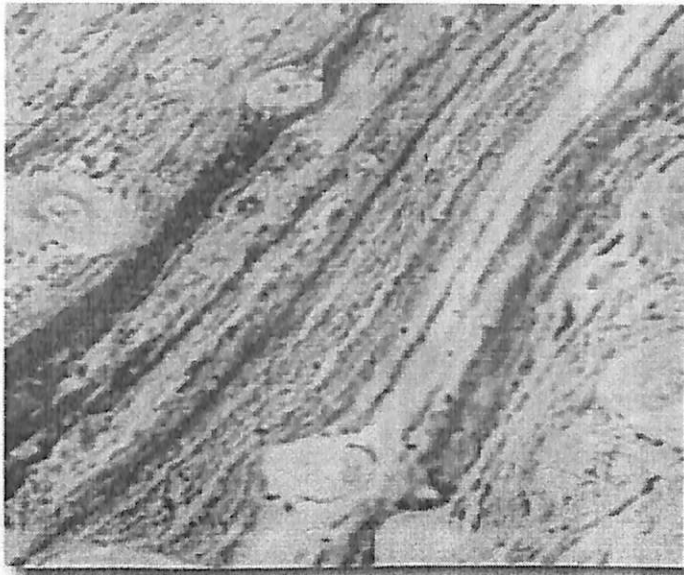
power of the saturates and aromatics in the maltene phase. If the concentration and molecular weight of the asphaltenes is relatively low, the result will be a 'sol' type bitumen.

The addition of thermoplastic rubbers, With a molecular weight similar to or higher than that of the asphaltenes disturbs the phase equilibrium. The polymer and the asphaltene 'compete' for the solvency power of the maltene phase and If insufficient maltenes are available, phase separation may occur . Figure 22 shows the microscopic structures of 'compatible' and 'incompatible' bitumen/polymer systems. The compatible system has a homogeneous 'sponge-like' structure whereas the Incompatible system has a coarse discontinuous structure.

Phase separation or incompatibility can be demonstrated by a simple hot storage test. The storage vessel used for the test, it has three discharge arms along Its length to enable the top, middle, and bottom thirds to be obtained separately. Tests are carried out on the top and bottom third and the middle third is discarded. Figure shows the numerical difference in softening point of the top and bottom samples of two bitumens containing 7% of SBS thermoplastic rubber after 1,3,5 and 7



Compatible system with 4% SBS



Incompatible system with 4% SBS

Figure 22: Compatible & Incompatible systems

days storage at 140°C. The results clearly show that the compatible system is extremely stable, whereas the incompatible system has separated dramatically. With virtually no polymer remaining in the bottom sample after 7 days storage. The implications of this in full-scale storage are obvious.

The main factors influencing storage stability are:

- the amount and molecular weight of the asphaltenes;
- the aromaticity of the maltene phase;
- the amount of polymer present;
- the molecular weight and structure of the polymer;
- the storage temperature.

6.3.1 Compatibility and Stability

A polymer may be incompatible, slightly compatible or compatible with bitumen.

• Incompatible polymers, when mixed with asphalts, result in heterogeneous mixtures without cohesion or ductility. The polymer affects the colloidal equilibrium of the asphalt and, therefore, the cohesion of the material.

- Slightly compatible polymers require special mechanical, thermal or chemical processes to successfully improve asphalts.
- Compatible materials yield physically stable blends, using conventional mixing techniques, and they may or may not improve the physical properties of the asphalt. A proper degree of compatibility between polymer and asphalt is necessary in order to avoid separation during storing, pumping and application of the asphalts and to achieve the expected properties in the pavement. Poor storage stability will render the polymer modified asphalt unsuitable for use in paving binder applications, roofing applications, and other industrial specialty products. In order to find out if phase separation or incompatibility is present, several approaches are accepted: phase compatibility, rheological changes and softening point variation. For this test, PMB is poured into a metal toothpaste tube and left in an oven for three days at 160°C. Samples are then taken from the bottom portion of the blend and the top portion of the blend, and softening points between these two samples are compared. The difference between the softening point of the top portion and the softening point of the bottom portion shall not differ by more than 4°C. Any higher difference would suggest substantial phase separation (absence of storage stability). The same samples are also examined using fluorescence microscopy to compare their microstructures. For true stability, the top portion of the blend should have the same continuous phase as the bottom portion

6.4 The manufacture of thermoplastic rubber/bitumen blends

The quality of the polymer dispersion achieved is influenced by a number of factors, but is primarily dependent on the shear rate applied by the mixer. When the polymer is added to the hot bitumen, the bitumen immediately starts to penetrate into the polymer particles, causing the styrene domains of the polymer to become solvated and swollen. Once this has occurred the level of shear exerted on the swollen particles is critical if a satisfactory dispersion is to be achieved within a realistic blending time. Thus, medium or preferably high shear mixers are required to adequately disperse thermoplastic rubbers in bitumen.

4.1 Thermosetting binders

Thermosetting polymers are produced by blending two liquid components, one containing a resin

and the other a hardener, which react chemically to form a strong three dimensional structure.

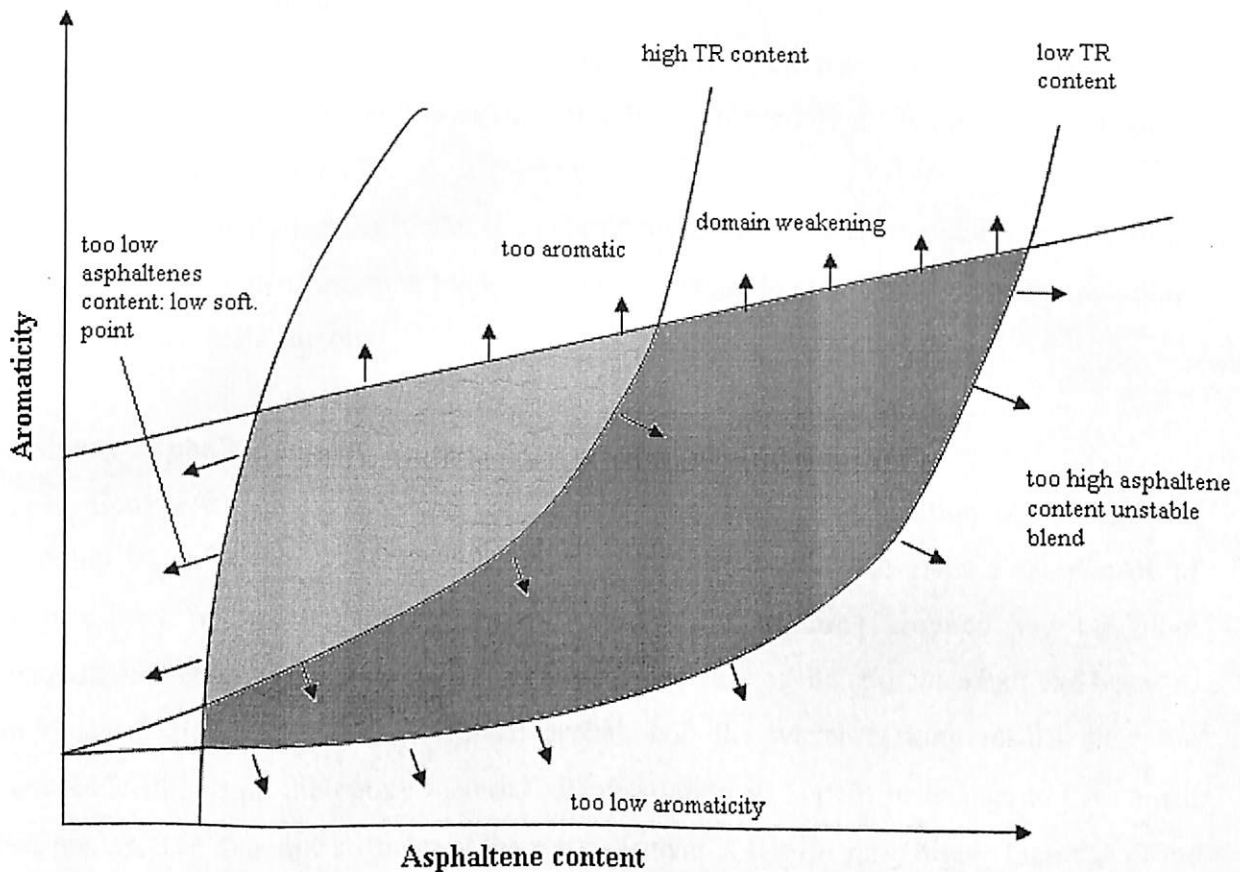


Figure 23: Influence of bitumen constitution on bitumen/thermoplastic rubber blends

. Two component epoxy resins blended with bitumen display the properties of modified thermosetting resins rather than those of bitumen. The remarkable family of two-component thermosetting resins was developed around thirty years ago and found wide application as surface coatings and adhesives.

The principal differences between bitumen (a thermoplastic) and thermosetting binders are as follows:

- when the two components in a thermosetting binder are mixed the usable life of the binder is limited; the amount of time available is strongly dependent on temperature: the higher the temperature the shorter the usable life;
- after a thermoset product is applied it continues to cure and increase in strength, of

organo-manganese compounds; the rate of curing on the road is dependent on the ambient temperature;

- as temperature increases, bitumen softens and flows; thermosetting binders are much less temperature susceptible and are virtually unaffected by the temperature changes experienced on a road;
- the cured thermosetting binder is an elastic material and does not exhibit viscous flow;
- when cured, thermosetting binders are very resistant to attack by chemicals. Including solvents, fuels and oils

6.5 Epoxy Asphalt

Epoxy Asphalt, which most clearly demonstrates the combination of strength and flexibility which can be achieved using thermosetting binders. Table gives a comparison of the properties of two hot rolled asphalt mixes, one containing bitumen and the other containing the epoxy asphalt binder. The Marshall stability of the epoxy asphalt can be up to ten times greater than the conventional asphalt and the wheel-tracking results show no measurable rutting on the epoxy material. demonstrating its superb resistance to permanent deformation. The dynamic stiffness of the epoxy asphalt is significantly higher than that of the conventional material, particularly at high ambient temperatures. However flexural fatigue tests using asphalt bonded to a steel plate (simulating flexing of an orthotropic bridge deck) showed that in this test the fatigue life of the epoxy asphalt was at least an order of magnitude greater than that of the conventional asphalt.

Table 6: Comparison between epoxy asphalt and conventional asphalt

Test	Epoxy Asphalt	Conventional Asphalt
Marshall stability kN	45	7.5
Wheel- tracking rate at 45°C	0	3.2

References: 1.Shell Bitumen Handbook ,chap 10, page 149-167

2.Lee,D.Y. Modification of asphalt and paving mixtures, Ind.Eng.Chem.Prod. Res.Develop. vol 14,pp 171-177

Chapter 7

7.0 EXPERIMENTAL WORK : Some experimental work was done in the bitumen laboratory of IIP ,dehradun and A.R. Thermosets Kanpur . Work is based on the modification of bitumen.

Experiment No. 1

7.1 OBJECTIVE: The objective of this study is to 'modification of bitumen using different polymers'.

The whole work is divided into three parts.

- Experimental procedure of various tests used for characterization of different samples.
- Observation table
- Interpretation of data.

List of the facility used in the study are:

- Penetrometer.
- Softening Point Apparatus
- Ductilometer
- Rolling Thin Film Oven Test (RTFOT) Apparatus

7.2 Procedure:

7.2.1) By using Styrene-Butadiene-Styrene (SBS)

Homogenization of bitumen and the polymer was carried out in a glass assembly using 200 gm of bitumen sample to establish process variables like: homogenization temperature and duration to achieve the desired grade of PMB. Glass assembly consists of a wide mouth round bottom flask (500-ml capacity) with provision of measuring inside temperature through a thermo well slantly fixed in flask to measure operating temperature with the help of an iron – constantan thermocouple. The heating to flask is provided through a heating mantle (1/2 litre capacity). The heat input to the RB flask is controlled through an automatic pyrometer controller in order to maintain the flask at the desired

temperature. Homogenization of bitumen and polymer is achieved using a stirrer is set maximum for complete homogenization. It may be noted that basically the entire operation is carried out batch wise. About 1%, i.e., 2gm of SBS was added into the sample and when temperature of flask reached to 160°C then time counting was started. The temperature was maintained at 160°C±2°C for 3 hours.

7.2.2 By using Crumb Rubber (CRMB)

Same glass assembly was used find about 1% i.e. 2gm of crumb when temperature of the flask reached 180°C and it was maintained throughout for 3 hours.

Table 7: Feedstock Analysis

S.No.	CHARACTERISTICS	FEEDSTOCK	
		FEEDSTOCK-A	FEEDSTOCK-B
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	74	115
2.	Softening Point °C (R&B) ,min.	44	39
3.	Ductility at 27°C, cm.	90	*

*this indicates that ductility of the feedstock cannot be determined because of softness of feedstock (high pen)

Table 8: Experimental work with FEEDSTOCK B
(Modification with SBS)

S.No.	CHARACTERISTICS	PMB S1
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	25
2.	Softening Point °C (R&B) ,Min.	52.6
3.	Ductility at 27 °C, Cm.	80.5
4.	Frass Breaking Point, °C, Max.	-
5.	Flash Point by °C, Min.	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	29.41
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2
8.	Viscosity at 150 °C, Poise	2.01
Thin Film Oven Test (TFOT), on Residue		
9.	Loss in weight,% Max.	<1
10.	Increase in Softening Point, °C, Max.	13.6
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	48
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	24

**Table 9: Experimental work with FEEDSTOCK B
(Modification with CRUMB RUBBER)**

S.No.	CHARACTERISTICS	CRMB S2
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	28
2.	Softening Point °C (R&B) ,Min.	50
3.	Ductility at 27 °C, Cm.	*
4.	Frass Breaking Point, °C, Max.	-
5.	Flash Point by °C, Min.	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	47
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2
8.	Viscosity at 150 °C, Poise	*
Thin Film Oven Test (TFOT), on Residue		
9.	Loss in weight,% Max.	<1
10.	Increase in Softening Point, °C, Max.	12
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	53.57
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	24.2

*Not required

**Table 10 : Experimental work with FEEDSTOCK A
(Modification with SBS)**

S.No.	CHARACTERISTICS	PMB S3
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	14
2.	Softening Point °C (R&B) ,Min.	57.4
3.	Ductility at 27 °C, Cm.	33
4.	Frass Breaking Point, °C, Max.	-
5.	Flash Point by °C, Min.	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	30
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2
8.	Viscosity at 150 °C, Poise	2.79
Thin Film Oven Test (TFOT), on Residue		
9.	Loss in weight,% Max.	<1
10.	Increase in Softening Point, °C, Max.	14.2
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	28.57
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	68

Table 11: Experimental work with FEEDSTOCK A
(Modification with CRUMB RUBBER)

S.No.	CHARACTERISTICS	CRMB S4
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	8
2.	Softening Point °C (R&B) ,Min.	67
3.	Ductility at 27 °C, Cm.	*
4.	Frass Breaking Point, °C, Max.	-
5.	Flash Point by °C, Min.	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	**
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2
8.	Viscosity at 150 °C, Poise	**
Thin Film Oven Test (TFOT), on Residue		
9.	Loss in weight,% Max.	<1
10.	Increase in Softening Point, °C, Max.	8
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	60
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	**

**Could not be determined as the sample was brittle i.e. on Elongation get cracked

*No

Table 12: Comparative study of Modifier in FEEDSTOCK B

S.No.	CHARACTERISTICS	PMB (SBS) S1	CRMB S2
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	25	28
2.	Softening Point °C (R&B) ,Min.	52.6	50
3.	Ductility at 27 °C, Cm.	80.5	*
4.	Frass Breaking Point, °C, Max.	-	-
5.	Flash Point by °C, Min.	>220	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	29.41	34.31
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2	2
8.	Viscosity at 150 °C, Poise	2.01	*
Thin Film Oven Test (TFOT), on Residue			
9.	Loss in weight,% Max.	<1	<1
10.	Increase in Softening Point, °C, Max.	13.6	12
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	48	53.57
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	24	24.2

Table 13: Comparative study of Modifier in FEEDSTOCK A

S.No.	CHARACTERISTICS	PMB S3	CRMB S4
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	14	8
2.	Softening Point °C (R&B) ,Min.	57.4	67
3.	Ductility at 27 °C, Cm.	33	*
4.	Frass Breaking Point, °C, Max.	-	-
5.	Flash Point by °C, Min.	>220	>220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	30	**
7.	Separation , Difference in Softening Point, R&B, °C, Max.	2	2
8.	Viscosity at 150 °C, Poise	2.79	*
Thin Film Oven Test (TFOT), on Residue			
9.	Loss in weight,% Max.	<1	<1
10.	Increase in Softening Point, °C, Max.	14.2	11.6
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	28.57	60
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	68	**

*Not required

**Could not be determined as the sample was brittle i.e. on Elongation get cracked

Table 14: Requirement of POLYMER MODIFIED BINDERS (PMB)**Under IRC:SP:53-2002**

S.No.	CHARACTERISTICS	GRADE AND REQUIREMENTS		
		PMB120	PMB70	PMB40
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	90 to 150	50 to 90	30 to 50
2.	Softening Point °C (R&B) ,Min.	50	55	60
3.	Ductility at 27 °C, Cm.	+75	+60	+50
4.	Frass Breaking Point, °C, Max.	-24	-18	-12
5.	Flash Point by °C, Min.	220	220	220
6.	Elastic Recovery of Half Thread in Ductilometer 15 °C,% Min.	75	75	75
7.	Separation , Difference in Softening Point, R&B, °C, Max.	3	3	3
8.	Viscosity at 150 °C, Poise	1-3	2-6	3-9
Thin Film Oven Test (TFOT), on Residue (IS:9382-1992)				
9.	Loss in weight,% Max.	1.0	1.0	1.0
10.	Increase in Softening Point, °C, Max.	7	6	5
11.	Reduction in Penetration of Residue ,at 25 °C, % Min.	35	35	35
12.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	50	50	50

Table 15: Requirement of CRUMB RUBBER MODIFIED BINDERS (CRMB)**Under IRC:SP:53-2002**

S.No.	CHARACTERISTICS	GRADE AND REQUIREMENTS		
		CRMB120	CRMB70	CRMB40
1.	Penetration at 25°C, 0.1mm,100gm, 5 sec	<70	<60	<50
2.	Softening Point °C (R&B) ,Min.	50	55	60
3.	Flash Point by °C, Min.	220	220	220
4.	Elastic Recovery of Half Thread in Ductilometer at 15 °C, % Min.	50	50	50
5.	Separation , Difference in Softening Point, R&B, °C, Max.	4	4	4
Thin Film Oven Test (TFOT), on Residue (IS:9382-1992)				
6.	Increase in Softening Point, °C, Max.	7	6	5
7.	Penetration at 25 °C, 1 mm, 100gm, 5 sec, Minimum % of Original	60	60	60
8.	Elastic Recovery of Half Thread in Ductilometer at 25 °C, % Min.	35	35	35

7.3 Results and Discussion

- From experimental study and work it is quite clear that the feed stock (MARKED A & B) has softening point 44°C & 39°C respectively with their penetration at 25°C , 74 and 115 respectively.
- The ductility of feed stock A at 27°C is +90 whereas the ductility of feedstock B at 27°C is not possible to determine because of its high penetration. Thus we are having two feed stocks for making bitumen, one is of low Pen (74) and other is of high Pen (115). (As shown in table -8)

When feed stock-B is treated with 1% SBS (elastomer), softening point was found to be 52.6 and Pen 25. This indicates that there is tremendous decrease in penetration which results decrease inelastic recovery and found to be very poor i.e. 29.41 (as shown in table -9)

- When feed stock-B is treated with crumb rubber (1%), softening point was found to be 50 and Pen 28. This indicates that there is tremendous decrease in penetration which results decrease in elastic recovery and found to be marginally poor i.e. 47. (as shown in table 10)
- Experimental data shows that on the basis of softening point crumb rubber falls under CRMB 50 grade. For this grade penetration should exist between 60-70 whereas found to be 28 which is extremely poor. Also SBS modified bitumen on the basis of softening point falls under PMB120 but on penetration basis the grade of bitumen does not satisfy the specification as penetration was found to be 25 which is extremely poor whereas it should lie between 150-90 (as shown in table 15). Also experimental data shows that both finished product PMB S1 and CRMB S2 have extremely poor elastic recovery of half thread at 15°C (as shown in table 13).
- From table 12 it is quite clear that when Feed stock A is treated with 1% crumb rubber under specified conditions (180°C vigorous stirring) the softening point was found to be 67 which falls under CRMB40 grade. Also the elastic recovery of thread at 15°C could not be determined because under this condition the finished product become brittle i.e. extremely hard which on elongation at 15°C gets cracked this may be due to extreme decrease in penetration (as shown in table 12).

- When feed stock A is treated with 1% SBS under specified conditions (160°C vigorous stirring) the softening point was found to be 57.4 which falls under PMB70 grade. Penetration comes out to be 14 which does not meet the specification. Ductility is found to be 33 which is far less than specification (+60). Recovery does not meet the specification as it is far below i.e. 30 from the specification (+60). Viscosity is in the desired range. After RTFOT the reduction in penetration meets the specification and elastic recovery of half thread Ductilometer at 25°C also is according to the specifications (as shown in table 11).
- SBS modified bitumen falls under PMB70 and crumb modified falls under CRMB 60. The penetration of SBS modified bitumen comes out to be 14 but it does not meet at all the required specification while nothing can said about crumb modified bitumen as it requires penetration <60 . Ductility of SBS modified bitumen is poor and in case of crumb rubber modified bitumen it is not required. Elastic recovery of SBS modified sample was poor while crumb modified sample get cracked as it was brittle but after RTFOT reduction in penetration meets the specification for both the samples. Elastic recovery of half thread was up to the mark in SBS modified bitumen but in crumb rubber modified bitumen it is not required. Increase in softening point shows deviation in both the cases.
- From whole of the experimental study it may be pointed out that feedstock B is much better for the modification of bitumen with the use of elastomer and crumb rubber because with feed stock A these modifiers gave many deviations in various characteristics from the specification. Even deviation occurs with feed stock B also but not like feed stock A. Also elastomer (SBS) gave much better results as compared to crumb rubber because its softening point is towards higher side.
- In this practice we have seen that by taking 1% of polymer/Crumb Rubber product is going to be very hard and giving very low penetration value, so to reach exactly to specifications we have to take modifier in some less quantity like 0.85%, 0.9% or the feed stock should be have high penetration value.

Experiment No. 2:

Objective : To observe the effect of Thermoplastic Polymer – Ethylene Vinyl Acetate (EVA) in the modification of Bitumen.

Procedure : Take the bitumen of known Penetration value (70) and EVA of different grade. Mix them thoroughly by homogenizer at asphalt mixing temperature 160°C. There is a wide range of EVA copolymers available which are specified by MFI and vinyl acetate content. For example EVA with an MFI of 150 and a vinyl acetate content of 19 is the 150/19 grade. From the wide range available the 150/19 and to a lesser extent the 45/33 grades are the most popular, usually blended in 70 pen bitumen. EVA copolymers are easily dispersed in, and have good compatibility with bitumen.

Result & Discussion: After doing the testing of the Modified bitumen sample and Binder sample (for marshall test) we obtained the following results:

Table 16: Effect of EVA grade 150/19 and 45/33 on Bitumen

Bitumen	Penetration At 25 °C,dmm	Softening point °C	Marshall Stability, kN
70 pen	69	49	6.2
70 pen +5%EVA 150/19	50	66	7.8
70 pen +5%EVA 45/33	56	58	8.0

These results shows that penetration value is decreasing highly for EVA 150/19 than Eva 45/33 but 45/33 gives more stability than 150/19. Softening Point of bitumen is increasing. Hence this bitumen can work at high severe condition (i.e. higher temperature, Heavy duty load) with good load bearing capacity. EVA tends to improve asphalt workability because of its susceptibility to shear and because it uses a slightly softer base bitumen.

The higher the MFI, the lower the molecular weight and viscosity; this is analogous to the penetration test for bitumen – the higher the penetration the lower the average molecular weight and viscosity of the bitumen. the more vinyl acetate groups (or the higher the vinyl acetate content), the higher the proportion of rubbery regions, and conversely, the lower the proportion of crystalline regions. EVA modified bitumen stiffens rapidly as the EVA polymer crystallizes.

If the optimal performance of EVA modified bitumens is to be achieved in practice it is essential that they are specified and costed on a rational basis and applied accepting that they have limitations. If these are acknowledged, then EVA modified bitumen will make a significant contribution to improving the cost-effectiveness of roads

Experiment No.3

Objective: To observe the effect of different polymer/ rubbers on softening point at different concentrations.

Procedure: Mix the bitumen with Styrene-Butadiene-Styrene , Ethylene Vinyl Acetate, Styrene-Butadiene Rubber modifiers at different concentration i.e. 1%, 2%,4%, 5%,6% by blending in homogenizer .After that check their Softening Point and Plot the graph.

Results: SBR shows a little effect on concentration changes, but SBS gives sufficient deviation in softening point ,while EVA give intermediate values. Due the presence of higher content of styrene in SBS, its become harder than others.

Table 17 : Polymer Content and Softening Point of different modified Bitumen

Polymer Content,(%)	1	2	4	5	6
Softening Point./SBS	50	53	59	63	69
Softening Point/EVA	50	52	56	58	61
Softening Point /SBR	50	51	51	52	52

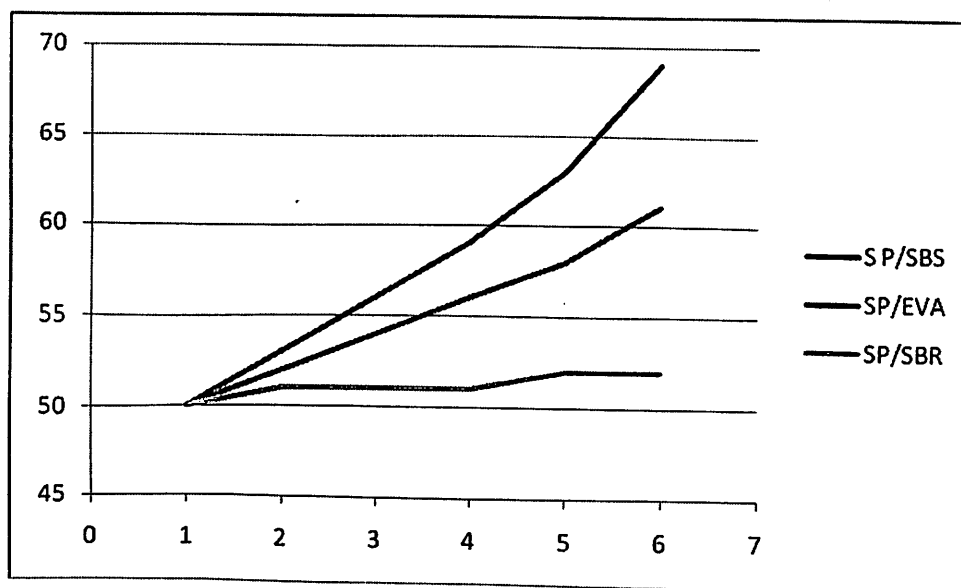


Figure 24 : Effect of polymer content on softening point for diff. Modifiers.

Vinyl acetate group produces amorphous (rubbery region) but ethylene content present in its chain gives crystalline region which is responsible for some hardness, hence shows higher softening point than SBR. SBR is mainly rubbery product which does not increase the softening point of bitumen on increasing its concentration

References: 1. Laboratory manuals of IIP Dehradun , & A.R.Thermosets.

2. Specifications given by IRC & BS.