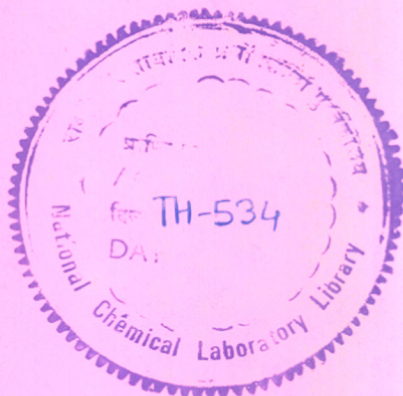


THERMOMECHANICAL BEHAVIOUR OF MODIFIED ASPHALTS

A THESIS
SUBMITTED TO THE
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FOR THE DEGREE OF
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(IN CHEMISTRY)

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Certified that the work incorporated in the thesis "Thermomechanical Behaviour of Modified Asphalts" submitted by Shri Johnson Mathew was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.



(Dr. V. M. Nadkarni)
Research Guide

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A handwritten signature in black ink, appearing to read 'Johnson Mathew', with a horizontal line underneath.

[Johnson Mathew]

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INTRODUCTION

1. INTRODUCTION

1.1 General Introduction

Asphalt is a dark brown to black carbonaceous material. Asphalt is represented as asphaltene miscelles in a hydrocarbon solvent consisting of saturated and unsaturated paraffins and aromatic structures. Asphalt occurs naturally as rock, lake or native asphalt and is also obtained as residue in the refining of crude oil. The native asphalts vary in their asphalt content and characteristics depending on the source as illustrated in Table 1.

The asphalt may be suitable for use as found or it may need further processing. It has been used traditionally in road laying and roofing. Petroleum asphalt has been obtained as distillate residuals ever since the refining of petroleum started in the early twentieth century. At present it accounts for more than 90% of the asphalt produced. The petroleum asphalt consists of hydrocarbon derivatives with only traces of inorganic materials. Its characteristics depend on the source of petroleum crude and also in the variations in the manufacturing process for a particular crude oil. By terminating the crude distillation at different cut off points (temperature), asphalts of different softening point and penetration index can be obtained as shown in Figure 1 (2).

The different types of petroleum may be categorized into three groups on the basis of their asphalt contents;

- (a) Asphaltic petroleum carry 90-100 percent of asphaltic bodies.
- (b) Semi asphaltic petroleum carry 50-70 percent of asphaltic bodies.

- (c) Non asphaltic petroleum do not contain any asphaltic bodies but may generate them during the distillation process.

1.2 Chemical Composition and Structure of Asphalt

Asphalt is a complex mixture of a large number of hydrocarbons. The structure of asphalt varies with the source. Even for a particular source there may be a wide variation in the features and molecular weight. Experimental evidence shows that a typical asphalt molecule consists of fused aromatic rings with hanging aliphatic chains exhibiting different degrees of olefinic unsaturation. The schematic representation of an asphalt micelle is shown in Figure 2 (3). The constituents present in asphalt may be classified into four major groups based on their solubility and physical characteristics. These include carbenes, carboids, asphaltenes, and petrolenes (maltenes). These constituents vary in their molecular structure and chemical composition in terms of the ratio of carbon to hydrogen. The relative contents of these constituents would also vary with the type of asphalt.

Carbenes are dark brown substances which are soluble in carbon disulfide, but insoluble in carbontetrachloride. In a single source of asphalt the concentration of carbenes increases with thermal ageing or oxidation. Certain native asphalts contain a large percentage of carbenes. Petroleum asphalts do not show carbenes unless the asphalt is overheated or overblown. They occur to a maximum extent of two weight percent in thermally degraded native asphalts.

Carboids are dark coloured substances which are soluble in carbontetrachloride and insoluble in carbon disulfide. They are infusible substances having a fixed percentage of carbon (25-30%) and a small percentage of oxygen (less than 3%).

Asphaltenes and petroleues are the major constituents of asphalt; and in certain types of asphalt these are the only constituents. Asphaltenes are dark brown to black coloured friable solids which are insoluble in petroleum ether (60-80 grade) but are soluble in chloroform and carbondisulfide. The asphaltene fraction has the greatest influence on the viscosity of asphalt. It has no definite melting point and on heating it decomposes to a carbonaceous residue. Its specific gravity is greater than one. The carbon to hydrogen ratio is the greatest in asphaltenes in the range of 1 : 1.16. The consistent C : H ratio in asphaltene fraction in different asphalts indicates structural similarity in all the petroleum asphaltenes. It is proposed that asphaltenes are formed by the addition of oxygen and sulfur to petroleum resins (4,5,6) and by intermolecular changes that occur on thermal ageing in air. A schematic representation of asphaltene micelle is shown in Figure 3 based on NMR and analytical studies (7). The asphaltenes derived from natural asphalt have a high percentage of oxygen and sulfur (7-13%) (8,9). Asphaltenes impart hardness to asphalt. Hence greater the percentage of asphaltenes, greater is the hardness of asphalt. The molecular weight of asphaltene has been shown to be of the order of around 3×10^5 by ultracentrifugation methods (10,11,12). Other techniques such as osmotic pressure measurements (13), molecular film method (14), cryoscopy (15,16,17) and light absorption coefficient studies have indicated the molecular weights of asphaltenes to be 8×10^4 , $8-14 \times 10^4$, $6-60 \times 10^2$, $1-4 \times 10^3$ respectively. The different methods of molecular weight determination have their intrinsic bias. The methods based on weight average are

influenced by the presence of large molecular weight species in trace amounts, while those based on number average are affected by low molecular weight species. The extensive scatter in the molecular weight data gathered represents a broad molecular weight distribution in the asphaltene fraction ranging from 3×10^2 to 3×10^5 . Thus asphaltenes themselves are a complex mixture of fused polynuclear aromatic rings with pendant alkylchains.

Petrolenes (Maltenes) are the dark oily fraction of asphalt soluble in petroleum ether. The C : H ratio in maltenes is 1 : 1.52. Their molecular weight in different samples falls in the range of 200 to 500. They have a specific gravity less than one. It is composed of saturated and unsaturated hydrocarbons containing cyclic compounds with a small percentage of sulfur, nitrogen and oxygen. As a general rule, lower the softening point of asphalt, the greater is the percentage of its oily constituents, maltenes.

1.3 Flow and Deformation Behaviour of Asphalt

Asphalt is an amorphous solid under normal conditions of temperature and pressure. The temperature dependence of the viscosity of asphalt is shown in Figure 4 (18). The asphalt flux obtained from the refinery bottoms is a thermoplastic which softens in the range of 30° to 45°C as determined by the softening point measurement. The suitability of asphalt for a particular end-use is dependent on its mechanical properties such as tensile strength, compressive strength, impact strength, hardness and its processability in terms of flow. Most asphalt display viscoelastic properties on deformation ^{in the solid state}. For a given asphalt the ratio of elastic to the permanent part of

the deformation depends on the stress, time of loading and temperature. At very low strains and short time of loading the deformation is elastic. At high strains and long loading times the viscous deformation predominates. At small extent of deformation, the relation between the stress and strain is linear. However, at high values of elongation and long loading times, deviations from linearity may occur in certain cases. The viscosity of hydrocarbons is related by the Walther equation given below:

$$\log \log (100 \eta_{\infty}) = a - m \log T \quad [1]$$

where η_{∞} is the limiting viscosity, ^{in poise} at low shear rates, T is the absolute temperature, a and m are constants showing the intercept level and slope. Thus the constant m signifies the susceptibility of asphalt viscosity to temperature. At low temperature levels (60°C and lower) or high shear rates which are typical of asphalt service conditions after incorporation in a roof or pavement, semisolid and solid asphalts display an increasing elastic component as shown in Figure 5 (19).

1.4 Asphalt Modification Processes

A number of processes are available for modifying the visco-elastic behaviour of asphalt, so that higher useful temperatures can be obtained for a given grade of asphalt. These include air blowing of asphalt, physical blending with chemical additives and fillers or reactive compounding with reactive monomers such as maleic anhydride, cashew nut shell liquid, etc. The modifications lead to improvement in either the low or the high temperature properties.

1.4.1 Air blowing

Air blowing is a process in which asphalt is converted to a harder product by air contact at 200°-275°C. During air blowing, dehydrogenation and polymerisation of the asphaltenes are involved. Oxygen is not retained in the asphalt product except in a very minor quantity. The reaction is exothermic with a heat of reaction of 61 to 72 kcal/gm mole. The oxygen in the air combines with the hydrogen in the asphalt to evolve water vapour leaving unsaturation for crosslinking. An NMR study on the oxidation of asphalt indicates that the amount of aromatic carbon structure in asphalt increases with oxidation with a corresponding increase in the asphalt^{ene} fraction (3). A wide variety of industrial products are made from air blown asphalt such as laminates, pipe line coatings (20), waterproofing (21) and joint fillers.

1.4.2 Sulfurisation of asphalt

This reaction is closely related to the reaction of oxygen with asphalt. The asphalt sulfurization was found to be endothermic with the heat of the reaction in the range of 8 to 12 kcal/gm mole. Polymerisation in the asphalt-sulfur reaction takes place by both sulfide and carbon linkages. The reaction of asphalt and sulfur was found to take place in two different ways. At higher temperature (240°C) ^{sulfur} dehydrogenated asphalt, whereas at lower temperature it combined with asphalt. The reactive part of the asphalt was found to be the aromatic - naphthene fraction. The product was asphaltene when dehydrogenated and polysulfide when sulfur combined with asphalt.

The changes in the properties of asphalt reacted at 240°C were attributed to an increase in the asphaltene content. The sulfurization of asphalt at 140°C leads to the incorporation of sulfur resulting in a more ductile material. The major use of sulfurised asphalt is as an electrical insulator.

1.4.3 Asphalt/Polymer blends

Asphalt-ethylene co-polymer compositions have been reported in patent literature. These compositions are made up of 5-95% by weight of an aromatic base petroleum asphalt and 5-95% by weight of a co-polymer of ethylene. The ethylene co-polymer is obtained by co-polymerising ethylene with an alkyl ester (containing 1-8 carbon atoms) made from either methyl methacrylic acid or acrylic acid.

Ethylene vinylacetate co-polymers have also been used in asphaltic paving compounds. An elastic asphalt mixture with good cohesion and utility as a pavement for metal bridges consists of 75% asphalt, 20% ethylene - vinyl acetate co-polymer and 5% terpene resin.

Asphalts compounds displaying improved fluidity and workability are prepared by adding 0.5 to 60 weight percent of thermoplastic block co-polymer rubber S-B-S (S = vinyl aromatic block polymer), B = conjugated diene block polymer). This asphaltic compound is useful in paving waterproofing, rustproofing, roofing, pipe coating and automobile undercoating.

1.5 Scope of the Present Investigation

The objective of the present investigation was to improve simultaneously the high and the low temperature performance of asphalt.

Asphalt was polymerised oxidatively and thermally with maleic anhydride (MAH) and cashew nut shell liquid (CNSL). The reactions were optimised to increase the melt viscosity at high temperature and decrease the brittle temperature so as to improve the low temperature crack resistance. An additional objective was to increase the mechanical properties. Fillers were incorporated into the modified asphalts. The fillers used were alumina in the presence of cashew nut shell liquid, and mica in the presence of maleic anhydride. Viscosity, penetration index, softening point and dynamic mechanical characterization of the samples were carried out. The modified asphalts were characterized ^{for their chemical structure} to evaluate the chemical reactions that occur during the modification of asphalt. The virgin and the modified asphalts were fractionated into two distinctive fractions based on solubility considerations. The composition of the fractions, the I-R absorption spectra and elemental analysis of the fractions were determined.

EXPERIMENTAL

2. EXPERIMENTAL

2.1 Materials

2.1.1 Asphalt

The asphalt used for the modification studies was obtained from M/s. Bharat Petroleum Corporation Ltd., Bombay. It was the distillation bottoms obtained from the refining of crude oil. It had the following specifications:

Grade 80/100

Specific gravity at 27°C	:	0.98
Softening point	:	45 ± 2°C
Flash point	:	175°C

2.1.2 Maleic anhydride

Empirical formula : $C_4H_2O_3$



It was procured from M/s. Loba-Chemie Bombay. It had a purity greater than 99% and a melting point of 53°C. It was used as received.

2.1.3 Cashew nut shell liquid

The crude cashew nut shell liquid was the product of M/s. Shakti Private Ltd with the following specifications:

Viscosity at 25°C	:	120 c.p.s
Iodine value	:	316
Hydroxyl value	:	180-194
Carboxyl value	:	8.6-10.9

Polymerisation time : 2 minutes and 27 seconds

2.1.4 Petroleum ether (60-80 grade)

Petroleum ether (60-80 grade) was obtained from Mak Chemical Industries, Bombay. It was dried and distilled before use.

2.1.5 Carbontetrachloride

Molecular weight	:	154
Boiling point	:	77°C
Density	:	1.6 g/cc
Refractive index	:	1.46

It was procured from Loba Chemical Industries, Bombay.

2.1.6 Glycerol

Glycerol was purchased from Mak Chemical Industries, Bombay. It was used as received.

2.1.7 S.B.S Elastomer

The S.B.S. block co-polymer used was of grade solprene-411 supplied by Phillips Petroleum Company having a softening point of 175-180°C.

2.2 CNSL Characterization

2.2.1 Polymerisation time

The polymerisation time of CNSL was determined as per the I.S.I. 840-1964. Five grams of CNSL were taken in a test tube and heated

to $205^{\circ} \pm 5^{\circ}\text{C}$ to remove traces of water. It was cooled to room temperature. 0.5 ml of 25% (v/v) solution of concentrated H_2SO_4 in dimethyl sulfate was added to it and the contents were thoroughly mixed. The test tube was maintained in an oil bath at 176°C and stirred slowly. The time taken by the material to transform into a stiff rubbery mass was noted as the polymerisation time.

2.2.2 Hydroxyl value determination

The hydroxyl value denotes the quantity of potassium hydroxide in milligrams needed to neutralize the acetic acid which combines by acetylation with 1 gm of fat, oil, fatty alcohol or fatty acid. It is a measure of the proportion of the free hydroxyl groups in the sample. The determination was done as per the following procedure (22).

The acetylating agent was prepared as follows: 25 ml of dry acetic anhydride was taken in a 100 ml volumetric flask and the volume was made up to the mark using dry and distilled pyridine. It was mixed well and stored in a brown coloured bottle. Into a 250 ml erlenmeyer flask labelled 'one', 1.5 gm sample was taken and 50 ml of acetylating agent was added to it. The contents were shaken well.

In another erlenmeyer flask labelled 'two', an equal amount of acetylating agent was taken for blank value determination. In a third erlenmeyer flask 1.1 gm of sample was taken for acid value determination. To it 10 ml of pyridine (neutralized) was added and titrated with 0.5 N ethanolic KOH to get a faint pink colour. The first and second erlenmeyer flasks were kept on a steam bath with a reflux condenser and warmed for 1 hr. After cooling the flasks and the

condensor, it was washed with neutralized ethanol. The flasks were then titrated with 0.5 N standardised ethanolic KOH solution using phenolphthalin as an indicator to get a light pink end point.

$$\text{Hydroxyl value} = \frac{(56.1) N (V_2 - V_1)}{W} + A \quad [2]$$

- N = Normality of ethanolic KOH solution
 V_2 = Volume of KOH solution used for blank test in ml
 V_1 = Volume of KOH solution used for the sample in ml
 W = Sample weight in gms
 A = Acid value

2.2.3 Acid value

Acid value denotes the milligrams of KOH needed to neutralize the free acids in one gram of fat or oil (22).

The solvent was prepared by mixing 125 ml of toluene with 125 ml of isopropyl alcohol. This solvent was neutralized using 0.1 N KOH solution using phenolphthalin indicator. The neutralized solvent had a faint but definite pink coloration. 5 gms of the sample whose acid value was to be determined was taken in a 250 ml erlenmyer flask. It was dissolved by warming in 125 ml of the neutralized solvent. This was then titrated against 0.1 N KOH solution using phenolphthalin indicator. The pink colour attained on titration matched with the pink colour of the solvent and this was taken as the end point.

$$\text{Acid value} = \frac{(56.1) A \times N}{W} \quad [3]$$

A	=	Volume of KOH used on ml
N	=	Exact normality of KOH solution
W	=	Sample weight in grams

2.2.4 Iodine value determination

Iodine value denotes the weight in grams of halogen calculated as iodine absorbed by 100 gms of the sample under specified conditions. It is an approximate measure of the number of olefinic or acetylinic bonds in the substance. The iodine value was determined by the Wijs method (22).

Wijs solution was prepared by dissolving 19 gms of iodine monochloride in one litre of a mixture of 700 ml acetic acid and 300 ml carbon tetrachloride. This solution was stored in a dark place.

0.5 gms of the sample was weighed in a glass thimble. This was taken in a 500 ml stoppered conical flask. To it 10 ml of CCl_4 and 25 ml of Wijs solution were added by pipet. It was shaken well to dissolve the contents and then placed in a dark place for 1/2 hr.

After half hour, 15 ml of 10% KI solution and 100 ml water were added to it. This was titrated against 0.1 N sodium thiosulfate solution using 1% starch as an indicator. The end point was yellow to colourless. In a similar manner a blank reading was obtained without using the sample under test.

$$\text{Iodine value} = \frac{(12.69) N (B-A)}{W} \quad [4]$$

N	=	Normality of the thiosulphate solution
B	=	Volume of thiosulphate solution for blank in ml

- A = Volume of the thiosulfate solution used for sample
in ml
- W = Weight of sample in gms

2.3 Preparation of Modified Asphalts

The chemical modification of asphalt was carried out in a mild steel reactor shown in Figure 6. It had a flanged lid with five ports for thermometer, stirrer, charging reactants, compressed air inlet, and exhaust. The three litre capacity vessel was heated by external heating elements. It had a valve at the bottom to drain the products. The reactor temperature and the stirrer speed were controllable.

Asphalt was chemically modified by reacting with maleic anhydride and cashew nut shell liquid. The reactions were conducted isothermally at various predetermined temperatures. The virgin asphalt flux was heated to the required temperature under constant stirring. After the reaction temperature was attained it was stirred for 10 minutes and a predetermined amount of the modifier (either maleic anhydride or cashew nut shell liquid) was charged into the reactor through the charging port. The compressed air (24.7 psi) was blown continuously for only those experiments which required air blowing. A number of parameters were varied in order to study the optimum conditions for the modification reaction and to study their effects on viscoelastic properties of asphalt. The effect of the following parameters were investigated.

- * The reaction temperature and time
- * The amount of modifier used (percent based on weight of asphalt)
- * Pressure of compressed air

2.3.1 Modification with maleic anhydride

The modification reactions with maleic anhydride were conducted at 125°, 150° and 175°C using 5%, 10% and 15% maleic anhydride (w/w with respect to asphalt). The reactions were run for 2,4,6, and 8 hrs. Asphalt was air blown using 10% maleic anhydride (w/w) with respect to asphalt at 175°C for 6 hrs under an air pressure of 24.7 psi. In all eleven experiments were conducted.

2.3.2 Modification with cashew nut shell liquid

Asphalt was modified with cashew nut shell liquid (10% w/w) in two different ways at 175°C for a period of 6 hrs. In the first experiment compressed air (24.7 psi) was blown and in the second experiment compressed air (24.7 psi) and Co-napthanate (0.1% w/w of asphalt) was used.

2.3.3 Filler modifications

In a few experiments the asphalt was modified with maleic anhydride in the presence of mica in 10/50 weight percent ratio. Here air (24.7 psi) was blown throughout the experiment. In all two experiments were conducted.

2.3.4 Modification with styrene-butadiene-styrene block copolymer and maleic anhydride

Asphalt was modified with 5 weight percent S.B.S. block copolymer. The block copolymer was in pellet form. The softening point was 175°-180°C. The experimentation was essentially a melt

blending. In another experiment asphalt was modified with 10 (w/w) percent maleic anhydride in the presence of S.B.S. block co-polymer at 5 (w/w) percent.

The details of the modification experiments by various methods are presented in Tables 2 and 3.

2.4 Physical Characterization of Modified Asphalts

2.4.1 Softening point determination

The softening point was determined as per the I.S.I. test procedure 334 for testing tar and bituminous materials. The ring and ball apparatus used for this work is shown in Figure 7. It consists of the following apparatus.

Steel balls, brass rings, ballguide, support, thermometer, 500 ml beaker, heating fluid.

Test procedure : The asphalt whose softening point has to be determined is fluidized by heating well above the softening point. It is then poured into the rings placed on a flat metal surface. The sample is allowed to solidify by cooling to room temperature and then mounted on to the holes. Two steel balls of diameter 19.5 mm and weight 3.5 gm are placed with the help of forceps above the asphalt sample in the rings. The set-up is then mounted inside the beaker filled with deaerated distilled water maintained at 5°C. The water is heated at a constant rate of 1°C/min. The temperature at which the ball penetrates through the asphalt sample and touches the bottom plate is noted as the softening point temperature.

2.4.2 Penetration index determination

The penetration index was determined as per the I.S.I. test

procedure 334 for testing tar and bituminous materials. The penetration index apparatus is shown in Figure 8. It consists of a metal container (diameter 70 mm, internal depth 45 mm), needle, waterbath, penetration apparatus, thermometer and stop watch.

Test procedure: The asphalt sample was initially homogenised above its softening point of 45°C. It was then cooled to room temperature and poured into a flat stainless steel container. The 50 mm long needle having a tip of diameter 0.15 mm was placed on top of the asphalt sample. The needle was released for a period of three minutes. The distance the needle travelled for three minutes at 60°C was noted as the penetration index.

2.4.3 Viscosity measurement

The viscosity of the asphalt samples was determined on the Ferranti Shirley viscometer (cone and plate model). It consists of a measuring unit and a control unit shown in Figure 9 and 10.

Test procedure: The smallest cone having a cone constant 62.6591 and diameter 2 cm was used to measure the viscosity.

In a typical analysis this cone was attached to the motor. Approximately five grams of sample were placed on the heating plate. The heating fluid (oil) was circulated till the sample attained the desired temperature. A rough contact between the plate and the cone was made by rotating the adjustment jack. The fine contact was then made with the micrometer screw. The cone was then set into motion at specific speeds. The corresponding readings were noted. Each

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speed correspond to a specific shear stress.

2.4.4 Viscoelastic behaviour

The data on the solid state viscoelastic properties of the samples were generated for my work on the Rheometrics dynamic spectrometer R.D.S.-7700 by the courtesy of Dr. R. D. Orwoll, Rheometrics, N.J.

2.5 Chemical Characterisation

2.5.1 Extraction of asphalt samples

The asphalt was weighed accurately and transferred into a Soxhlet apparatus. It was extracted for 24 hrs with petroleum ether. The asphaltene fraction was left in the Soxhlet, while a solution of the maltenes in petroleum ether was obtained in the round bottom flask used for the Soxhlet extraction. Petroleum ether was then evaporated to get the maltenes. The results of the fractionation are presented in Table 4.

2.5.2 Molecular weight determination by vapour pressure osmometry

The number average molecular weight (\bar{M}_n) of asphalt samples as well as maltenes and asphaltenes were determined by a Knauer vapour pressure osmometer (Model No. 0600). The measurement chamber of a vapour pressure osmometer is shown in Figure 11. The experimentation consists initially of establishing the instrument constant K, for the solvent used at the temperature of measurement with the help of a pure compound of known molecular weight as a standard. In the present investigation toluene was used as a solvent. The temperature

of measurement was 45°C and benzil (molecular weight 210) was used as the standard. Mathematically the measurement can be shown by the expression

$$\Delta r/KC = \frac{1}{\overline{Mn}} + A_2C \quad [5]$$

where Δr = instrument reading as a function of concentration

C = Concentration in moles/lit

A_2 = Second areial coefficient

The instrument constant is established by taking the instrument reading (Δr) for three different concentrations of benzil and by plotting Δr versus concentration. The intercept of this plot gives $(\Delta r)_{C=0}$. This is related to the molecular weight by the following mathematical expression

$$(\Delta r)_{C=0} = K/\overline{Mn} \quad [6]$$

Knowing $(\Delta r)_{C=0}$ and molecular weight K can be evaluated for a particular solvent at a particular temperature. The molecular weight of the polymer can be established in a similar way. Instrument readings are taken for different concentrations. (Δr) is plotted against concentration to establish (Δr) for a particular polymer. Knowing this and the instrument constant, \overline{Mn} can be calculated.

For a typical sample (asphaltene fraction of cashew nut shell liquid air blown sample) the V.P.O. data obtained is given in Table 5. The molecular weight of the asphaltene fraction was found to be 3568. The molecular weights of other samples were determined in a similar manner.

2.5.3 Infrared Spectroscopy

Infrared spectroscopy can be used to evaluate the structural changes that occur during the course of a chemical reaction. The absorption frequency of a functional group such as $C=O$ group will be altered by the micro environment and hence by the structural features in the close proximity to it. During chemical reactions the microenvironment is altered. This can serve as a pointer to the nature of the chemical changes taking place. In our investigation asphalt was modified by maleic anhydride. A comparison of the infrared spectra of virgin asphalt blended with maleic anhydride and chemically modified asphalt would reveal the mode of reaction between asphalt and maleic anhydride.

RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

Asphalt based materials are used extensively as binders, sealants and waterproof coatings in diverse applications because of their low cost, inherent cohesive nature, weather-resistant properties and ease of processing in the molten state. In a number of these applications, such as in road construction, in coatings on railwagon undercarriage, the materials are exposed to a wide range of temperature and load conditions. The temperature of the surface coated or paved with asphalt could reach 60°C on a hot summer day and could drop well below 0°C in winter in certain climatic zones. The material has also to sustain the stresses generated by the thermal expansion and contraction. A combination of high temperature and low temperature performance is therefore required from end use considerations. The critical properties include high softening point, good tracking and flow resistance at elevated temperature (60-70°C), high elastic modulus and cohesive strength at use temperatures, coupled with good impact strength and crack resistance at low temperature. A low melt viscosity at the application temperature (120°-200°C) is also desirable for ease of spreading.

The asphalt flux as obtained from the refinery bottoms is a thermoplastic with softening point in the range of 30°-45°C and little cohesive strength at elevated temperature thus limiting its usefulness. However the thermomechanical properties can be improved by choice of base stocks and by processing. One of the most widely used modification of asphalt is air blowing. This process consists of blowing air into asphalt at temperatures upto 230°C, to harden the asphalt

by polymerisation of the asphaltenes. As a result of further fusion of the condensed aromatic rings in the blowing process the softening point and the cohesive strength at elevated temperatures are improved.

However, the low temperature impact and crack resistance are not improved. The low temperature performance of asphalt can be improved by physical blending with rubber crumbs (23,24,25,26) or with elastomers such as block co-polymers of styrene and butadiene (27,28,29, 30,31). Although the property modifications achieved by rubber incorporation have been found to be specific to the interactions between the particular grades of asphalt and rubber (32), generally this modification method does not lead to improvement in the high temperature performance. In order to achieve a balanced improvement in both the low and high temperature properties of asphalt chemical modification of asphalt via reactions with vinyl monomers has been found to be effective. Maleic anhydride has been identified as a useful modifier for improving the strength and toughness of asphalt (33). Grosmanin et al (34) have also reported asphalt modification with acrylic acid and maleic anhydride via the Diels-Alder reaction.

The objectives of the present work were to investigate the thermomechanical properties of the different modified asphalts and to indicate how the performance of asphalt might be affected by these properties. The modified asphalts investigated include chemical modification by maleic anhydride, physical blend with styrene-butadiene-styrene rubber, air blowing, and use of inorganic fillers. The effective use of cashew nut shell liquid (CNSL), an agro based raw material, as chemical modifier for asphalt to improve the low

and high temperature performance has also been demonstrated.

3.1 Flow behaviour

All the modified asphalts except the rubber-modified asphalt exhibited non-Newtonian flow behaviour at 120°C as compared to the Newtonian nature of the starting asphalt flux. The viscosity versus shear rate curves (logarithmic scale) of selected samples are shown in Figures 12 to 17. The shear thinning behaviour can be represented in the form of a power law as

$$\eta = k\dot{\gamma}^{n-1} \quad [7]$$

$$\log \eta = (n-1) \log \dot{\gamma} + \log k \quad [8]$$

The non-Newtonian flow index can be determined from the plots of $\log \eta$ vs $\log \dot{\gamma}$. For a comparative analysis of the modified asphalts the viscosity at 120°C and 150 sec⁻¹ was used. The values of $\eta_{120/150}$, the non-Newtonian flow index and the softening point penetration index and viscosity of the various samples are reported in Table 6. The main process parameters influencing the extent of modification are the temperature and reaction time. Concerning the amount of maleic anhydride 10% modification appears to be optimum and the extent of modification at this amount can be further improved by longer reaction time as shown by the 8 hr sample (MAH-9).

Modification of asphalt by addition of S.B.S. (sample SBS-1) increases the viscosity and yet the viscous behaviour is Newtonian Asphalt modified by maleic anhydride (MAH-5, MAH-6, MAH-8, MAH-9) or CNSL air blown (CNSL-1, CNSL-2) give products exhibiting similar non-Newtonian characteristics with $0.65 < n < 0.68$. Addition of mica

decreases the power law index considerably and also increases the viscosity at $\dot{\gamma} = 150 \text{ sec}^{-1}$ and temperature of 120°C .

3.2 Viscoelastic Behaviour

The viscoelastic properties of a material represent the response of the material to applied load over a range of temperatures and deformation rates. Perfect elastic materials store all the energy as potential energy when they are deformed. On the other hand, all the energy used in the deformation of viscous fluids is dissipated as heat. Polymeric materials manifest intermediate behaviour and are thus 'viscoelastic' in nature.

The viscoelastic spectrum of a material is represented by the variation of storage and loss moduli with temperature at a fixed frequency. The spectrum is rate dependent and is shifted to higher temperature with increasing frequency. The visco-elastic data of asphalt were collected over a range of frequencies (1, 10, 100 rad/s) corresponding to the range of deformation rates encountered in the end use and over a temperature range of -60 to 80°C .

The viscoelastic parameters of relevance to the performance characteristics of asphalts include the loss modulus peak temperature, peak value of G'' , the zero shear storage modulus $G'0$ value of G' at 60°C and temperature at which G' is equal to 10^6 dynes/cm^2 . These are reported in Table 7 for the modified asphalts. Typical viscoelastic spectra for the asphalt flux, blown asphalt (AB-1), SBS blend and asphalts chemically modified with maleic anhydride (MAH-9) and cashew nut shell liquid (CNSL-1) are shown in Figures 18 to 22.

The temperature of occurrence, absolute value and width of the loss modulus peak, G'' are pertinent to low temperature impact and crack resistance. The loss modulus peak signifies mechanisms at the molecular level available for dissipating energy thereby relieving stresses. Therefore material with a higher and broader loss modulus peak occurring at a temperature below the lowest end use temperature is preferred for improving resistance to cracking. Crack generation is the result of excessive energy build up in the material beyond its elastic limit (capacity to store the work as potential energy). Generation and propagation of cracks serve as mechanisms for relieving the stresses. In the case of viscoelastic materials above the relaxation peak temperature, mechanisms associated with molecular motions are available for dissipating energy and therefore the material is more resistant to cracking. From the viscoelastic characterization results it can be seen that although the G'' peak temperature is dependent on frequency the peak value of G'' does not vary significantly with the rate of deformation (over 1 to 100 rad/sec). The modified asphalts MAH-9, SBS-1, MAH-12, and CNSL-1 exhibit significant reduction in the G'' peak temperature relative to the control whereas no significant shift in the peak temperature is observed with the air blown asphalt (AB-1). All the methods of modification except SBS blend namely air blowing chemical modification with MAH and CNSL, increase the peak value of the loss modulus from about 5×10^8 dyne/cm² to $9-10 \times 10^8$ dyne/cm². Thus the chemical modification by MAH or CNSL seems to be the most effective way for improvement in low temperature crack resistance.

Concerning the optimization of the conditions of chemical modification by MAH with reference to samples MAH-4, 5, 6, 8 and 9 the reaction time appears to have greater effect on lowering the peak temperature than the amount of MAH and a reaction time of 8 hr or more is recommended at 175°C.

The zero shear modulus, $G'0$, obtained by extrapolation of the G' curve to the low temperature plateau represents the intrinsic modulus of the material. The chemical modification with CNSL and air blowing showed considerable improvement in $G'0$ from 4×10^9 dyne/cm² for the control to 9×10^9 dyne/cm². Chemical modification with maleic anhydride increased the $G'0$ of the parent asphalt by about 75%, but blending with SBS did not have any effect on $G'0$.

The values of the storage modulus at 60°C and the temperature corresponding to a G' value of 10^6 dyne/cm² are significant for assessing the tracking resistance and cohesive strength of the asphalts at elevated temperatures. The reference value of 10^6 dyne/cm² has been chosen for G' because it represents atmospheric pressure. The $G'E_G$ temperature should be higher than the maximum exposure temperature in the end use. Assuming that the maximum use temperature in coating and paving applications is about 60°C, the G' value at 60°C would have an indication of the cohesive strength of the material at elevated temperature. Both these parameters, namely $G'60$ and $G'E_G$ temperature show considerable dependence on frequency. The values at a frequency of 100 rad/sec would be relevant to the use of asphalt in construction of roads for heavy traffic. Whereas the parameter values at 1 rad/sec would be pertinent for coating applications. Referring to the results

in Table 7, blending with S.B.S. did not significantly improve the high temperature properties (sample SBS-1). However, blending of SBS with simultaneous chemical modification by maleic anhydride (sample MAH-12) significantly improved the high temperature cohesive strength. The improvement in G'_{60} and $G'E_6$ temperature as a result of air blowing (AB-1), maleic anhydride modification (MAH-6, MAH-9) and CNSL modification (CNSL-1) are comparable.

The most dramatic improvement in the high temperature properties was obtained by maleic anhydride modification with air blowing (MAH-11) and by reaction incorporation of 50% mica (by weight) in the maleic anhydride modified asphalt (MAH-10) although at the cost of low temperature flexibility.

It was also found that the temperature corresponding to $G'E_6$ can be related to the softening point of the material as shown in Figure 23. There exists a straight line fit between $G'E_6$ temperature and softening point at any frequency of interest.

In the present case the co-relation has been shown for frequencies of 1, 10, and 100 radians/sec. This provides a method for determining the softening point or the $G'E_6$ temperature when only one of the parameters is known. In Table 6 the softening points marked with + are determined by using the following co-relation between softening point and $G'E_6$ temperature at 10 radians/sec frequency.

$$\text{Softening point} = 0.745 T + 22.55 \quad [9]$$

T is the $G'E_6$ temperature at a frequency of 10 radians/sec. The equation [9] has a co-relation coefficient of 0.98 and is therefore

a fairly accurate method for estimating the softening point.

In summary chemical modification with either maleic anhydride or cashew nut shell liquid improved both the low and high temperature properties of the asphalt flux. The viscosity enhancement is greater with CNSL modification than with MAH indicating greater extent of polymerisation. The CNSL experiment required blowing of air for affecting the chemical reaction whereas the MAH modification does not require air blowing. However air blowing in the presence of (MAH-11) or absence (AB-1) of maleic anhydride improved only the high temperature mechanical behaviour. Blending with SBS improved the low temperature flexibility without enhancing the softening point and the cohesive strength at elevated temperature.

The addition of mineral fillers improved the mechanical properties of the modified asphalts. However, in the case of mica incorporated in MAH modified asphalt (MAH-10) the modulus improved was accompanied by a reduction in the low temperature flexibility. Contrary to this observation the addition of 20% alumina to the CNSL modified asphalt (CNSL-2) enhanced the modulus of the composite without a significant loss in the low temperature crack resistance. This may be attributed to the very fine particle size of the alumina relative to the mica grade filler.

The effective property modification with CNSL is quite encouraging, although further optimization of the reaction conditions needs to be done. CNSL is considerably less expensive than maleic anhydride, and therefore it would be most cost effective modifier. The chemistry and uses of CNSL have been reviewed by Ghatge and Maldar (35). Crude

cashew nut shell liquid extracted with low boiling petroleum solvents contains about 9% anacardic acid (I) and 10% cardanol (II) whose structures are illustrated in Figure 24. Commercial CNSL is supplied after heat treatment either during the extraction of oil or at a later stage. On heating, anacardic acid is decarboxylated to cardanol (III). Therefore, refined CNSL mostly contains a mixture of (II), (III) and small amount of polymerized CNSL. The aliphatic side chains usually consists of mixtures of $C_{15}H_{29}$, $C_{15}H_{27}$ and $C_{15}H_{25}$ namely one, two and three double bonds in a linear chain as below:

Saturated	5.4%
Monoolefin	48.5%
Diolefin	16.8%
Triolefin	29.3%

In the air blowing process, polymerization of asphaltenes takes place by further condensation of the aromatic fused ring structures, thereby increasing the brittleness. However if the clusters of fused aromatic rings can be linked through a flexible unit based on a vinyl monomer or an unsaturated oil like CNSL, the degree of polymerization can be improved without any adverse effect on the low temperature flexibility. This hypothesis would then explain the improvement in both the low temperature relaxation behaviour and the high temperature cohesive strength of asphalts modified with maleic anhydride and CNSL. The greater extent of viscosity enhancement with CNSL modification relative to the MAH modification may be attributed to the longer chain length of the unsaturated linking moiety in CNSL.

3.3 Chemical Structure Characterization

3.3.1 Fractionation

Virgin asphalt was separated into maltenes and asphaltenes by the method of selective solubility. Modification of asphalt increases the asphaltene fraction while the maltene content decreases. Asphaltenes and maltenes are empirically differentiated by their respective physical properties. Asphaltenes are friable solids while maltenes are oils at room temperature. The increase in the viscosity of modified asphalt is due to an increase in the asphaltene content. Cashew nut shell liquid or maleic anhydride might be coupling maltenes to maltenes or maltenes to asphaltenes thus increasing the asphaltene fraction.

3.3.2 Microanalysis

Asphaltenes and maltenes differ in their elemental composition. The carbon to hydrogen ratio in asphaltenes falls in the range 1:1.10 to 1:1.45. Asphaltenes have greater aromatic character than maltenes. Interesting observations emerge when maltene and asphaltene in the modified asphalts are compared to the virgin asphalt. The asphaltene of modified asphalt attain greater maltene like elemental composition. The ratio of carbon to hydrogen shifts from 1:1.16 in virgin asphalt to 1:1.45 in asphalt modified with 10 wt% MAH at 175°C for 8 hrs. Simultaneously the asphaltene content increases while the maltene content decreases. These observations point towards the conversions of maltenes to asphaltenes during the chemical modification. The physical and solubility characteristics of the modified maltenes are similar to asphaltenes while the elemental composition is invariant. This is probably due to coupling of maltene with

maltene or maltene with asphaltene. The extent to which this occurs is only partial. The asphaltene fraction increases from 22.6 to 42.5 weight percent. Under the most ideal conditions of reaction with 10 wt% MAH at 175°C for 6 hrs in the presence of air. Results of the elemental analysis of some specified samples are shown in Table 8.

3.3.3 Molecular weight

The molecular weights of virgin and modified asphalts as well as maltene and asphaltene fractions were determined by V.P.O. These are presented in Table 9. It is noted that the number average molecular weight of asphalt samples remains unaffected by the modification reactions. However, the molecular weight of the maltene in modified asphalt samples decreases while the molecular weight of the asphaltene increases. The microanalysis has revealed that the H/C ratio of the asphaltene increases. This could occur most probably by the conversion of maltene into asphaltenes by the modification reaction. The absence of a notable increase in \bar{M}_n of asphalt is an indication of the general nature of the modification reaction. If the modification were due to polymerization type reaction the \bar{M}_n of the modified ^{asphalt} should have been greater than that of the virgin asphalt. This is not observed. The molecular weight of asphaltene increases from 2468 in virgin to a maximum of 3970 in asphalt modified by maleic anhydride at 175°C for 6 hrs by air blowing. The typical calculations for obtaining molecular weight are shown in Table 5 and Figure 25. Here maleic anhydride is providing a bridge between maltene and asphaltene or between maltene molecules as a result

of the modification. Maleic anhydride can take part in both polyaddition and polycondensation reactions. It provides a bridge between two maltene or asphaltene molecules. The modification primarily involves oligomerization of maltene to form asphaltene moieties. To a lesser extent the reaction involves coupling of asphaltene with maltenes. The exact nature of the transformation can only however be quantitatively established by exhaustive fractionation of the modified asphalts into a large number of fractions. critically evaluating their molecular weights.

3.3.4 I-R Spectroscopic analysis

The melt viscosity measurement and number average molecular weight determination of the parent and modified asphalts show that the constitution of asphalt changes on heating with maleic anhydride. It is highly probable that chemical reactions occur between maleic anhydride and asphalt constituents. The virgin asphalt (control), Asphalt + MAH 10% (175°C/6 hrs) (MAH-5), Asphalt + MAH 10% (175°C/6 hr) (MAH-11), and asphalt air blown at 175°C/6 hr (AB-1) and its fractionated samples (asphaltenes and maltenes) were characterized by I-R spectroscopy. The I-R of maleic anhydride was taken as the reference. In order to find the nature of the chemical linkages modified asphalts, an I-R spectrum of a physical mixture of 10% MAH with the virgin asphalt was also taken. This is referred to as the synthetic mixture.

Absorption on the I-R region is related to the functional groups present in the organic compounds. On chemical modification these functional groups either disappear or show a slight shift in the absorption frequencies. Thus qualitative interpretations of the

nature of the reaction occurring in the chemical modification can be arrived at by comparing the absorption frequencies with those established for the various model compounds. In a highly complex system, the absorptions related to the various constituents are observable only above a critical concentration. This is generally around five weight percent. In the present investigation maleic anhydride concentration is ten weight percent. It was thus presumed that absorption in the infra-red region could indicate the chemical nature of the reaction occurring between asphalt and maleic anhydride.

The chemical reaction between maleic anhydride and asphalt can be ideally followed by observing the changes in the absorption frequencies of the maleic anhydride moiety. The prominent absorption frequencies for a number of model compounds of interest to the present investigation such as maleic anhydride, maleic acid, fumaric acid, succinic anhydride, succinic acid, diethyl succinate and diethyl fumarate are presented in Table 10. Maleic anhydride can react with asphalt either through the anhydride group or by the addition across $-\text{CH} = \text{CH}-$. Also maleic anhydride on hydrolysis or on esterification is converted to maleic acid, maleate, and these compounds undergo cis-trans isomerism above a critical temperature (138°C) to fumaric acid or fumarates. During the course of the reaction of maleic anhydride with asphalt (at 175°C) it is possible to observe the formation of derivatives of any one of the model compounds.

The I-R spectra of maleic anhydride in nujol is presented in Figure 26. The absorption frequencies of interest are those corresponding to $\text{C}=\text{O}$ and $\text{CH} = \text{CH}$ (cis) groups. If the modification proceeds

through the opening of the cyclic anhydride then the C=O absorption doublet at 1848 and 1790 cm^{-1} will become as singlet and will be shifted by 72 cm^{-1} to 1718 cm^{-1} . If the reaction proceeds by opening of the $\text{CH}=\text{CH}$ (cis) then the absorption at 690 cm^{-1} will disappear.

Similarly if the $\text{CH}=\text{CH}$ (cis) is converted into $\text{CH}=\text{CH}$ (trans) by cis-trans isomerism then the absorption will shift to 970 cm^{-1} as in fumaric acid.

The I-R spectra of the parent asphalt, its asphaltene and maltene do not absorb in the C=O as well as $\text{CH}=\text{CH}$ (cis) frequency ranges. These samples absorb in the frequency ranges corresponding to $\text{C}=\text{C}$ (trans). Hence the reaction across the anhydride group can be interpreted, while there is some uncertainty about the disappearance of $\text{CH}=\text{CH}$ (cis) absorption as this group could disappear either through polymerization or by the conversion into $\text{CH}=\text{CH}$ (trans) which is not detectable (asphalt absorbs in this range).

A synthetic mixture of asphalt with ten weight percent maleic anhydride was prepared at room temperature by physical blending. The absorption spectra of this blend is presented in Figure 27. The spectra reveals the absorption arising from the parent asphalt as well as from maleic anhydride. No reaction has occurred on blending. Absorption of the anhydride group and the $\text{CH}=\text{CH}$ (cis) are noted. Hence the modification by maleic anhydride is amenable by I-R analysis.

The I-R spectra of asphalt air blown (AB-1) at 175°C is shown in Figure 27. A comparison of this spectra with that of parent asphalt maltene and asphaltene shows the generation of keto groups (1690 cm^{-1}) in small amounts due to the oxidation of olefinic side

chains in the maltene fraction of the parent asphalt.

The infra-red absorption spectra of the maltene fraction in parent as well as the modified asphalts are presented in Figure 28. The keto group formation on modification is noted indicating the incorporation of maleic anhydride in the maltene fraction. This is however marginal and could be due to olefinic side chain oxidation during the modification reaction. The molecular weight determination show that the molecular weight of the maltenes do not change on modification. Thus the absorption in $\text{C}=\text{O}$ frequency range is primarily due to the side chain oxidation and not due to incorporation of maleic anhydride. On extraction with acetone the intensity of this absorption decreases considerably. Unreacted maleic anhydride, hydrolysed maleic anhydride as well as fumarates are present in the maltene fraction at the end of the modification reaction. The prominent absorption frequencies are noted in Table 12.

The asphaltene in parent sample does not absorb in the $\text{C}=\text{O}$ region while the asphaltenes in the modified samples show pronounced absorption in this region, Figure 29, Table 13. The absorptions are around 1720 cm^{-1} which correspond to the formation of esters. No absorption is seen around 690 cm^{-1} corresponding to $\text{C}=\text{C}$ unsaturation in maleic anhydride.

It can be concluded from the I-R analysis that during the modification of asphalt with maleic anhydride chemical reactions positively occur between asphalt and maleic anhydride through the anhydride group of maleic anhydride. The disappearance of $\text{CH}=\text{CH}$ (cis) could

be either due to chain growth polymerization across this bond or due to isomerization across this bond into CH = CH trans. Since maltenes have olefinic side chains which also show absorption in this range (970 cm^{-1}) it is difficult to say with certainty whether the absorption in this range arises from an isomerization of maleic anhydride.

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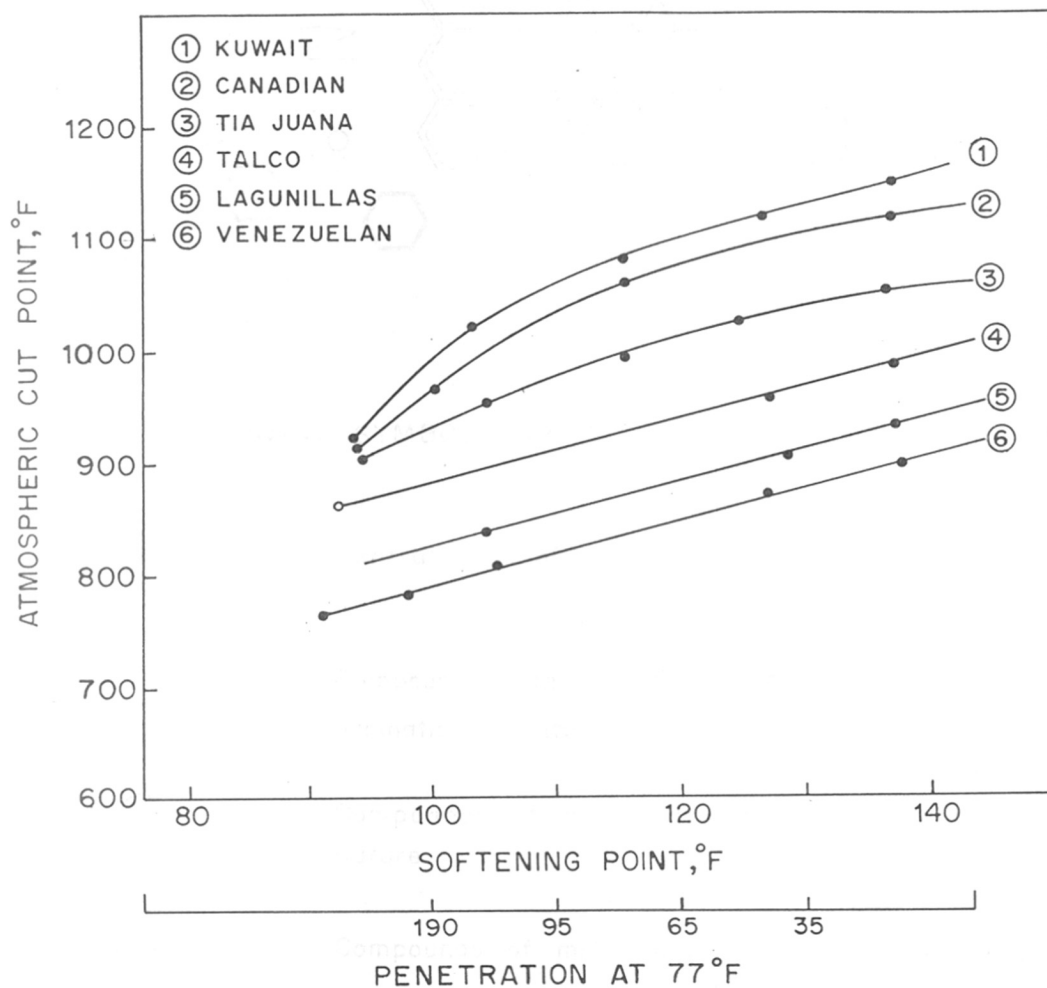
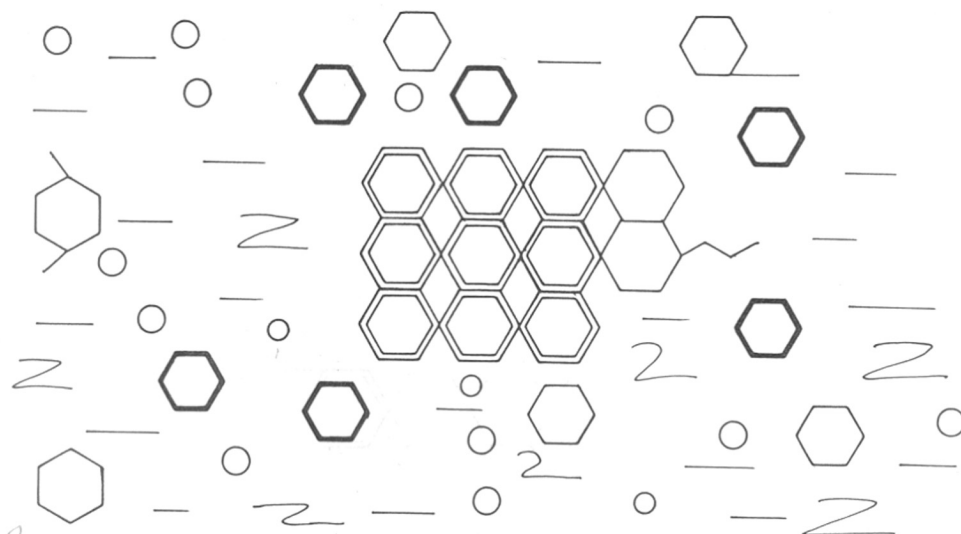


FIG.1: ASPHALT RESIDUE FROM VARIOUS CRUDES AS AFFECTED BY THE CUT POINT (2)



THE FOLLOWING SYMBOLS APPLY



Central part of asphaltene



Compounds with high molecular weight predominantly aromatic in nature



Compounds of mixed aromatic and naphthenic nature



Compounds of mixed naphthenic-aliphatic nature



Compounds of predominantly aliphatic nature

FIG. 2 SCHEMATIC REPRESENTATION OF ASPHALT MICELLE (3)

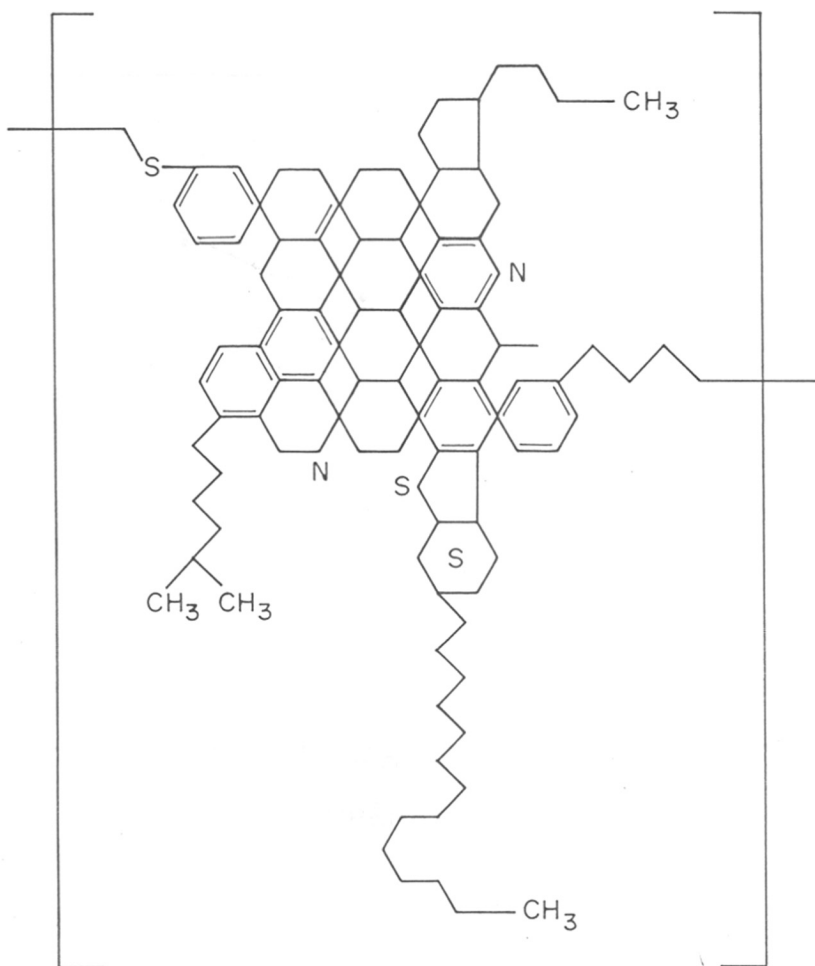


FIG. 3: HYPOTHETICAL STRUCTURE OF A PETROLEUM ASPHALTENE (7)

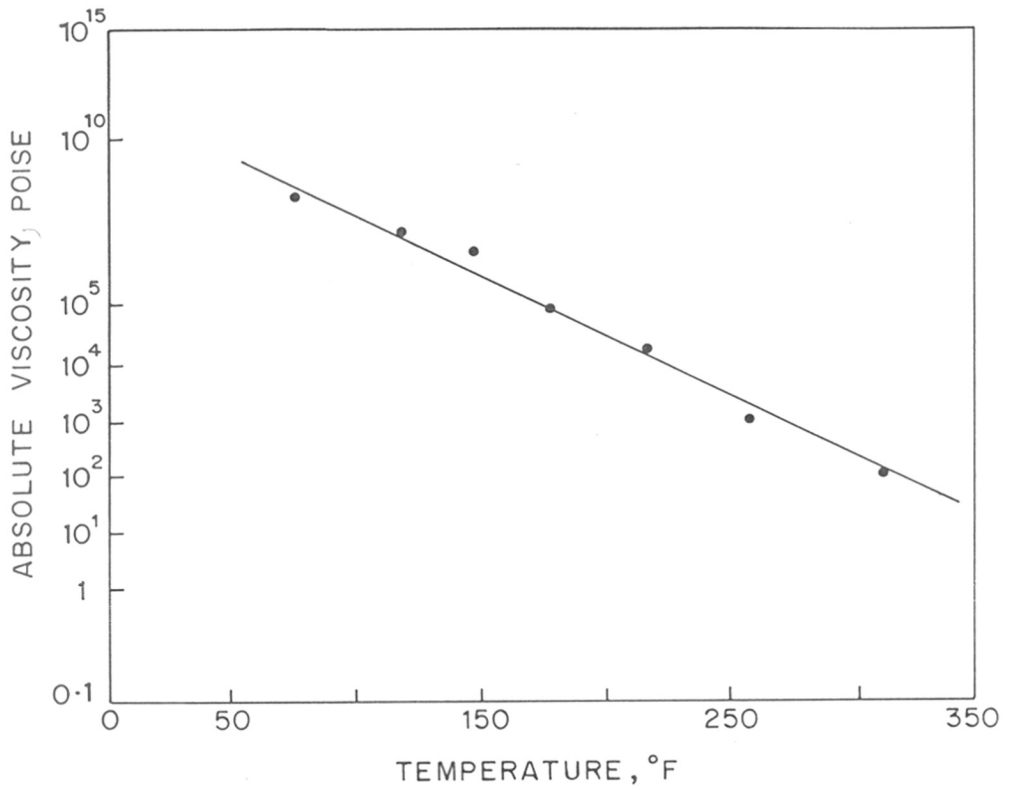


FIG.4: STANDARD VISCOSITY VERSUS TEMPERATURE CHART FOR ASPHALT OF ANY GRADE (18)

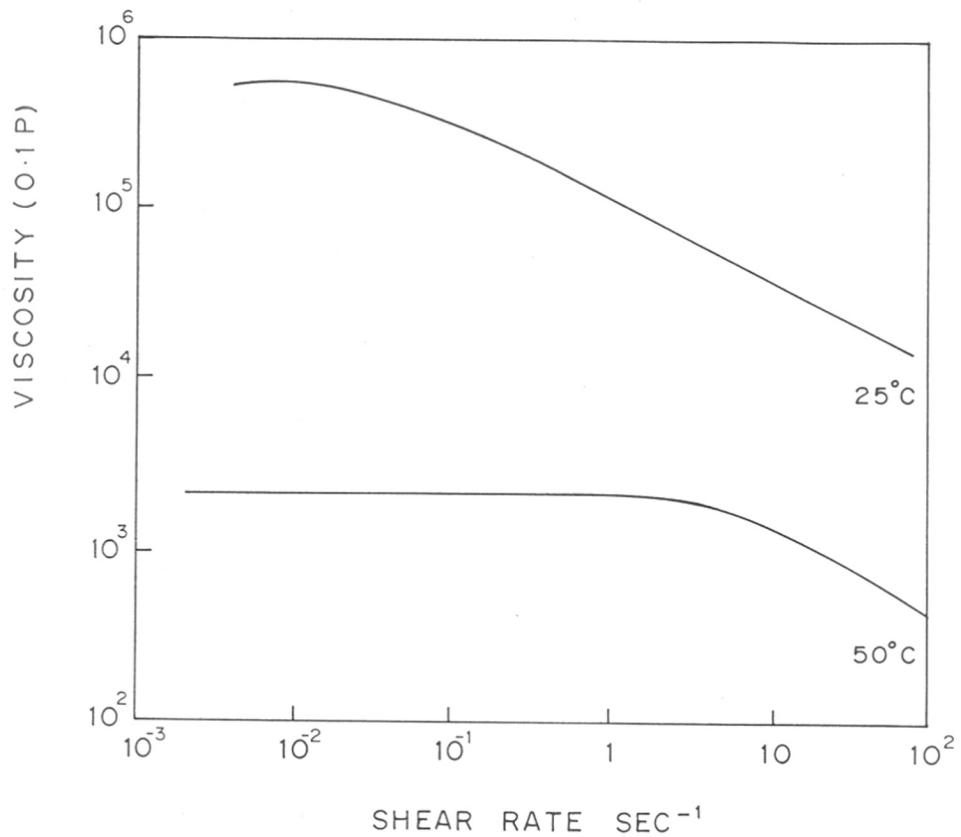
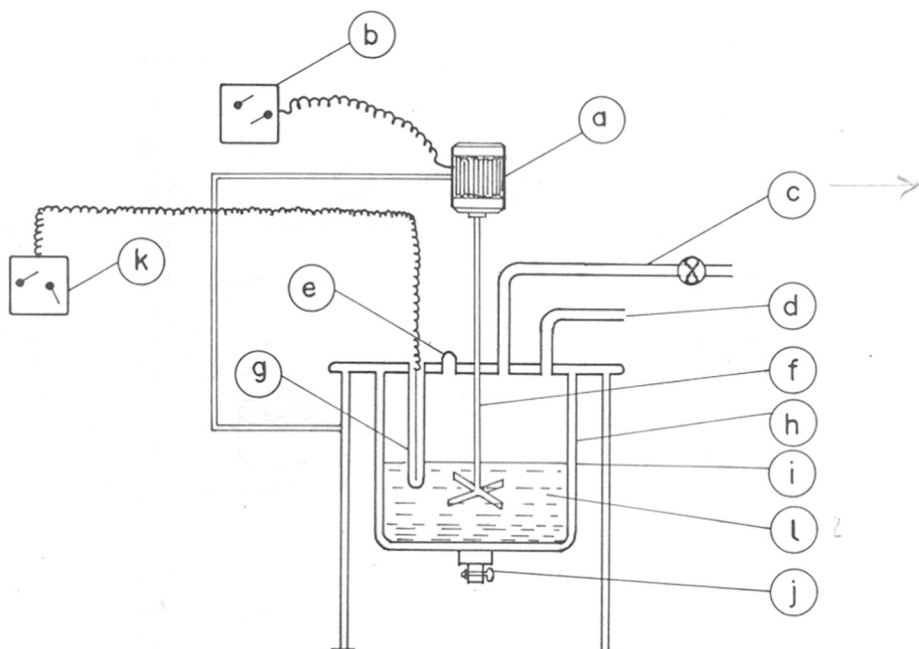
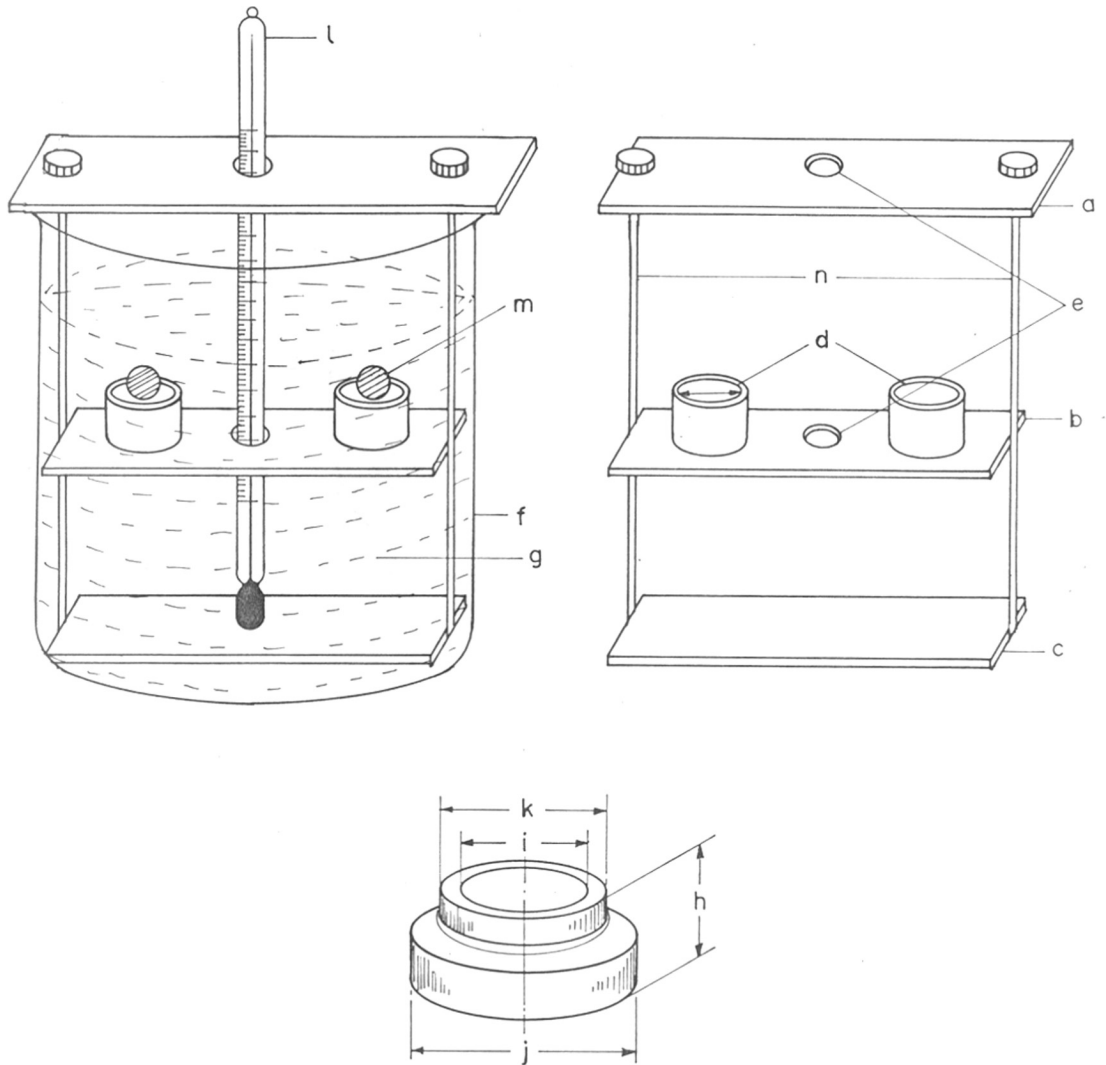


FIG. 5 ASPHALT VISCOSITY AND SHEAR RATE (19)



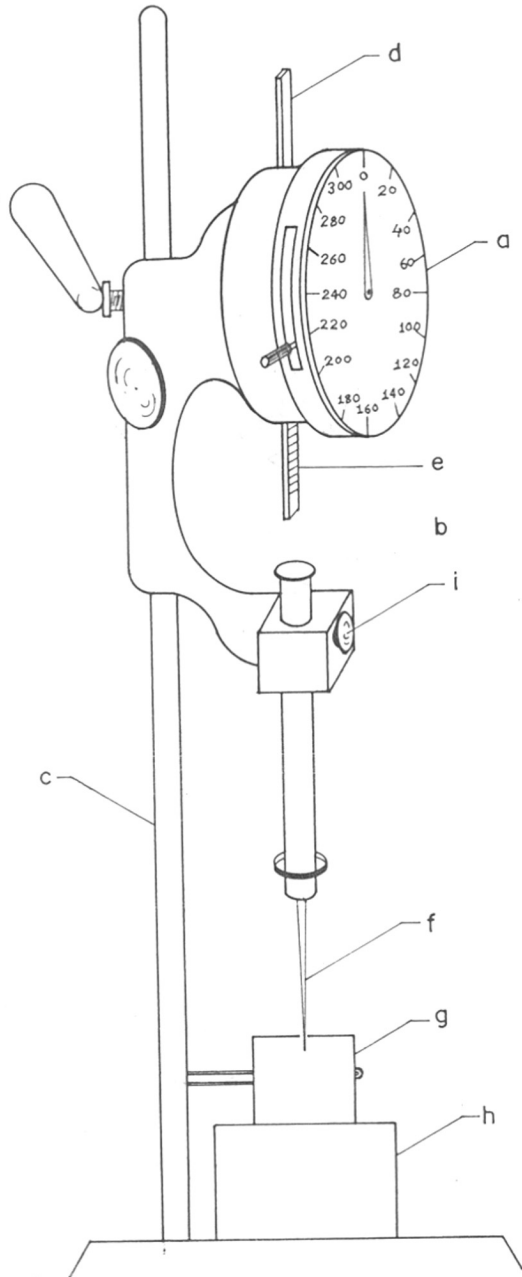
- (a) Motor
- (b) Speed controller
- (c) Compressed air line (with valve)
- (d) Exhaust pipe
- (e) Reactant addition inlet
- (f) Stirrer
- (g) Thermocouple
- (h) Asbestos coated heating arrangement for reactor
- (i) Mild steel reactor
- (j) Discharge valve
- (k) Temperature controller
- (l) Asphalt

FIG. 6 REACTOR ASSEMBLY USED FOR CHEMICAL MODIFICATION OF ASPHALT



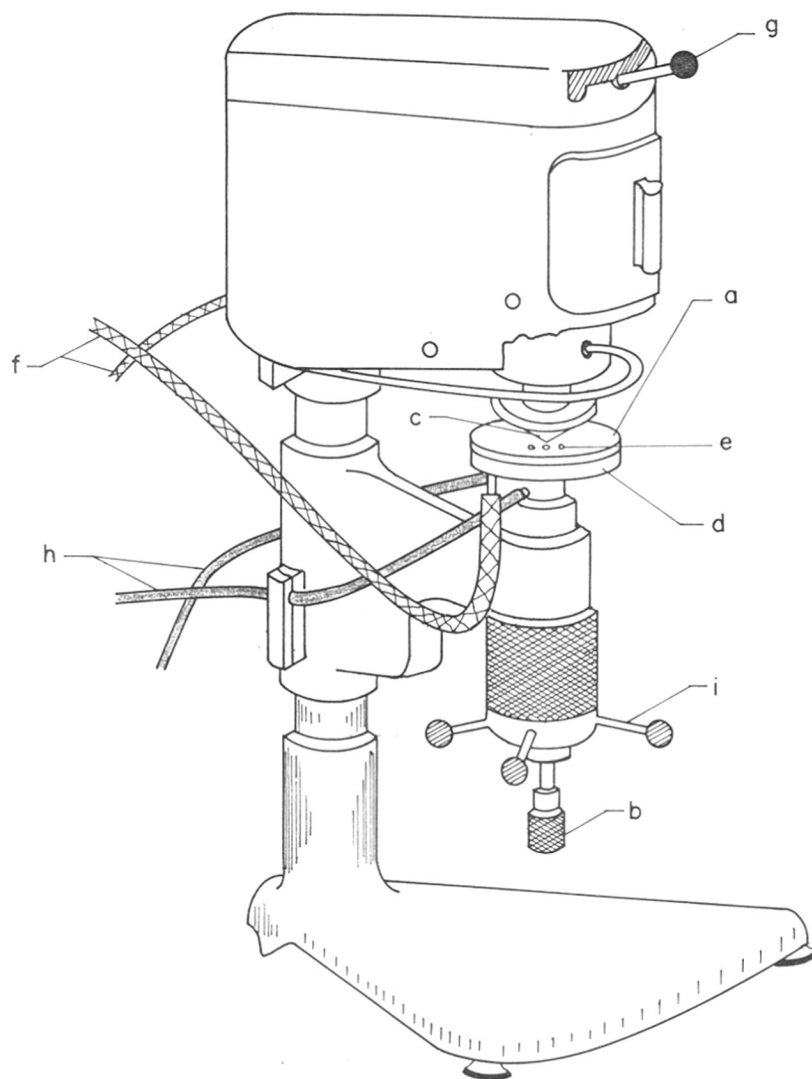
- | | |
|----------------------------------|--|
| a) Upper plate | h) Height of ring 6.4 ± 0.1 mm |
| b) Middle plate | i) Inner dia. 15.9 ± 0.1 mm (bottom part) |
| c) Bottom plate | j) Outer dia. 20.6 ± 0.1 mm |
| d) 2 Circular holes of 19.5 dia. | k) Inner tapered dia 17.5 ± 0.1 at the top |
| e) 2 Holes on plates a & b | l) Thermometer range $0^{\circ} - 200^{\circ}\text{C}$ |
| f) 500ml Beaker | m) Steel balls 2 no's |
| g) Heating fluid | n) Guide bar |

FIG. 7: SOFTENING POINT APPARATUS



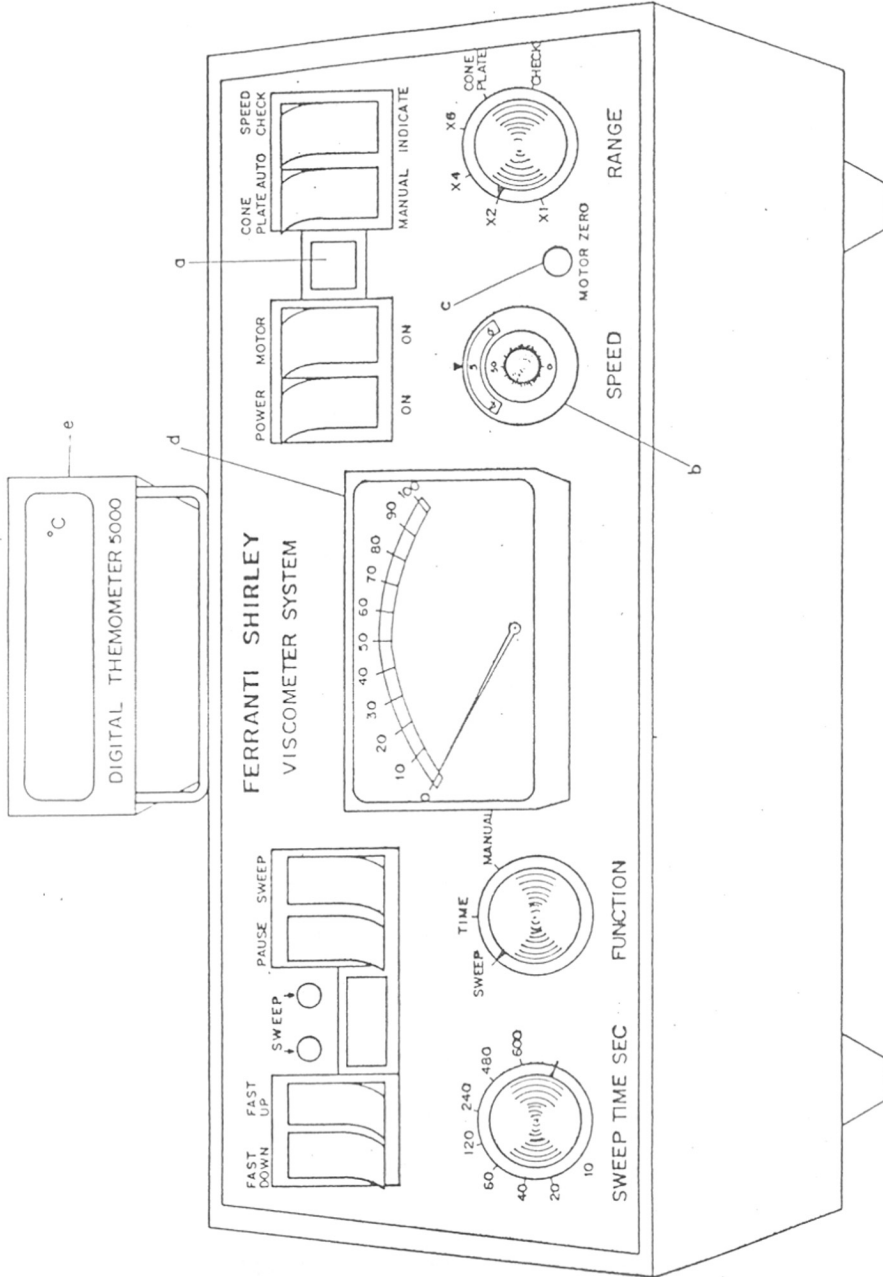
- a) Dial
- b) Rod
- c) Stand
- d) Pin
- e) Rod
- f) Penetration index needle
- g) Stainless steel container
- h) Thermostat
- i) Knob of the needle

FIG. 8: PENETRATION INDEX APPARATUS



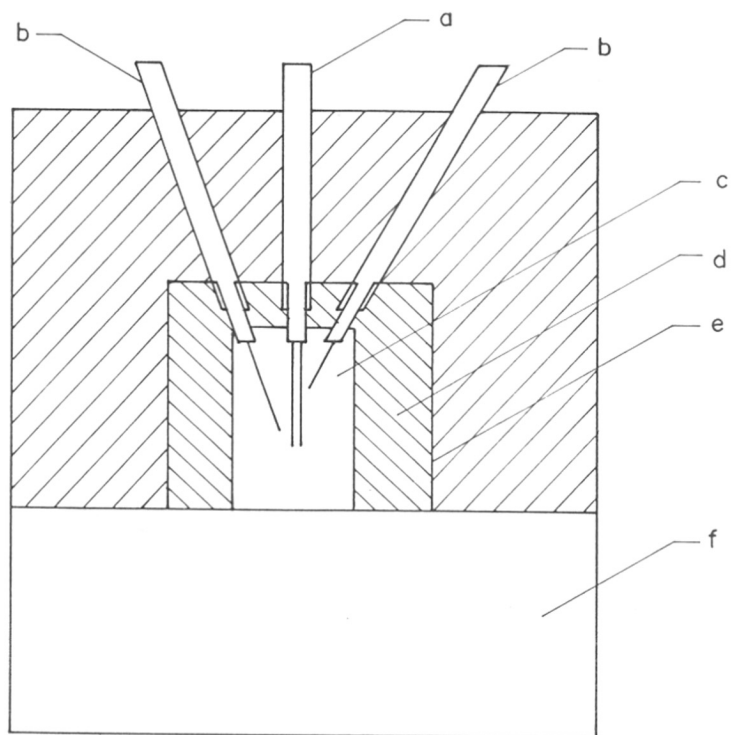
- | | |
|---------------------|-----------------------------|
| a) Stationary plate | f) Heating coil |
| b) Micrometer screw | g) Gear unit |
| c) Cone | h) Heating and cooling coil |
| d) Cooling jacket | i) Adjustment jack |
| e) Thermocouples | |

FIG. 9 FERRANTI SHIRLEY MEASURING UNIT



a) Lamp , b) Potentiometer knob , c) Sensitizer , d) Analog indicator , e) Temperature display unit.

FIG. 10 FERRANTI SHIRLEY CONTROL UNIT



- a) Thermistor
- b) Syringe guide
- c) Aluminium block
- d) Chamber
- e) Solvent cup and wick
- f) Foam

FIG. 11. MEASUREMENT CHAMBER OF A VAPOUR PRESSURE OSMOMETER

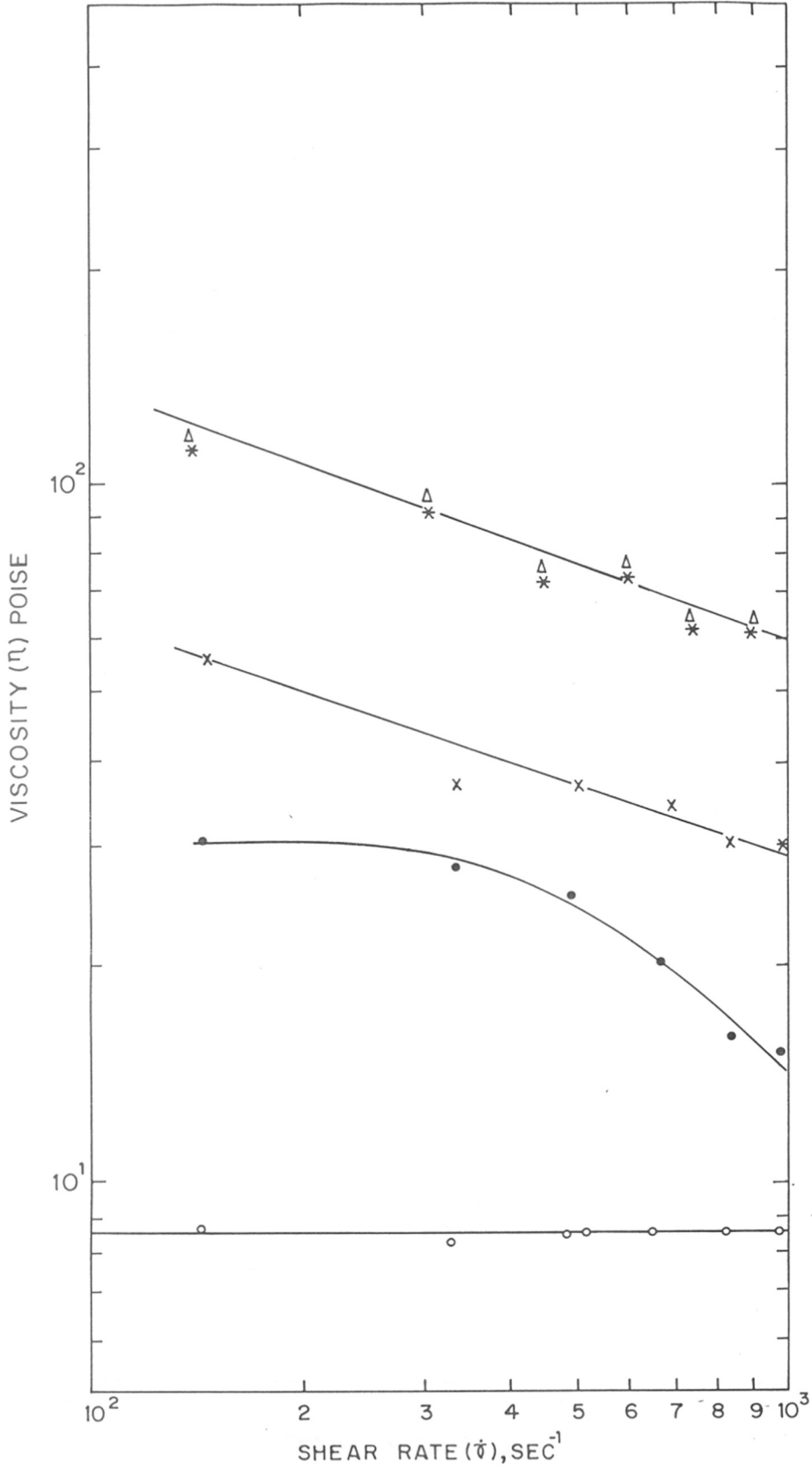


FIG.12: VISCOSITY VERSUS SHEAR RATE CURVE FOR MAH-7(●); MAH-8(x); MAH-9(*); MAH-5(Δ) AND (○) REPRESENTS CONTROL ASPHALT

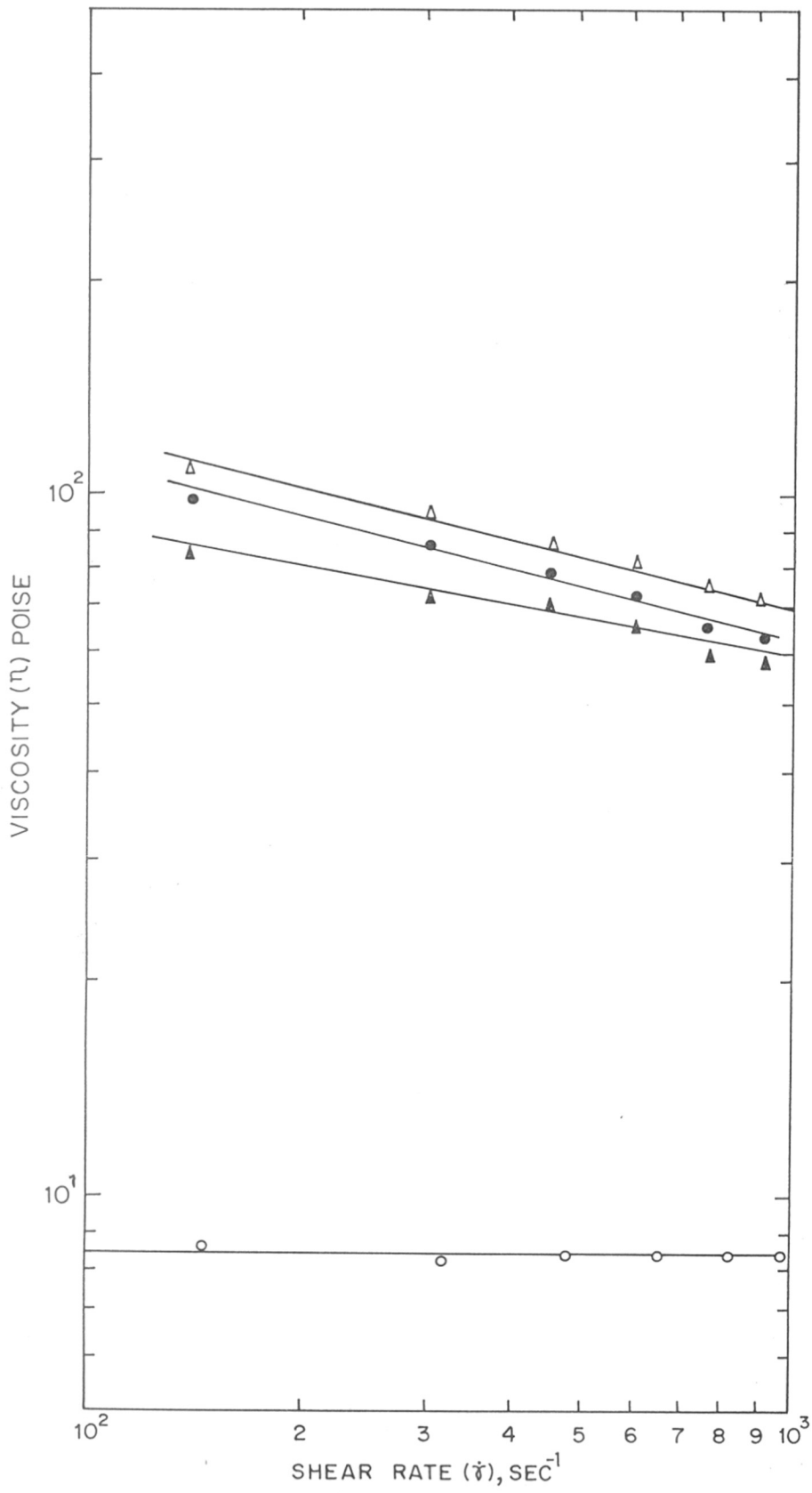


FIG.13 : VISCOSITY VERSUS SHEAR RATE CURVE FOR MAH-1 (\blacktriangle); MAH-2 (\bullet); MAH-3 (Δ) AND (\circ) REPRESENTS CONTROL ASPHALT

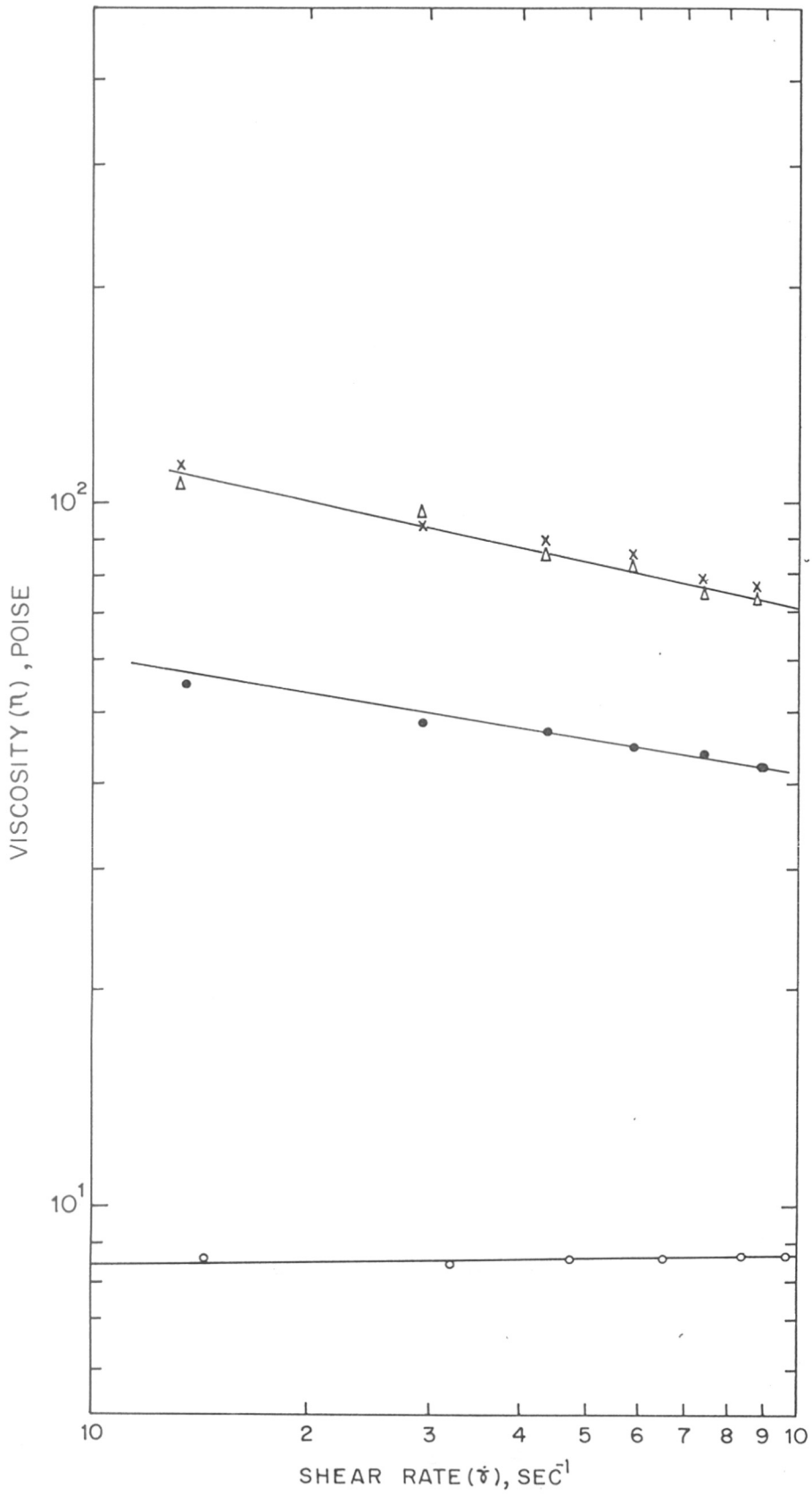


FIG.14: VISCOSITY VERSUS SHEAR RATE CURVE FOR MAH-4 (●); MAH-5 (Δ); MAH-6 (x) AND (○) REPRESENTS CONTROL ASPHALT

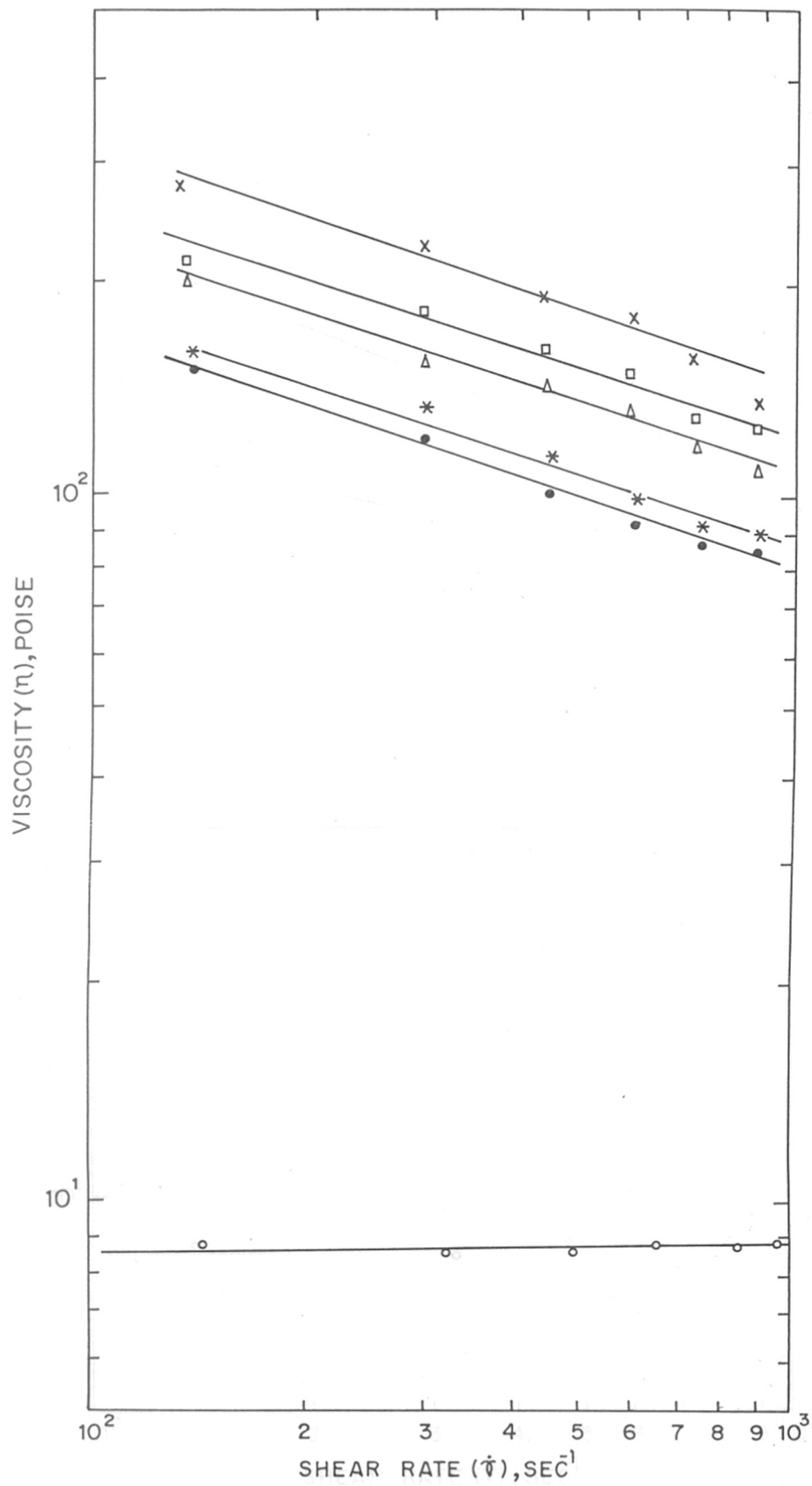


FIG.15: VISCOSITY VERSUS SHEAR RATE CURVE FOR AB-1 (●); MAH-11(*) ; CNSL-1 (Δ); CNSL-2 (x); CNSL-3 (□) AND (○) REPRESENTS CONTROL ASPHALT

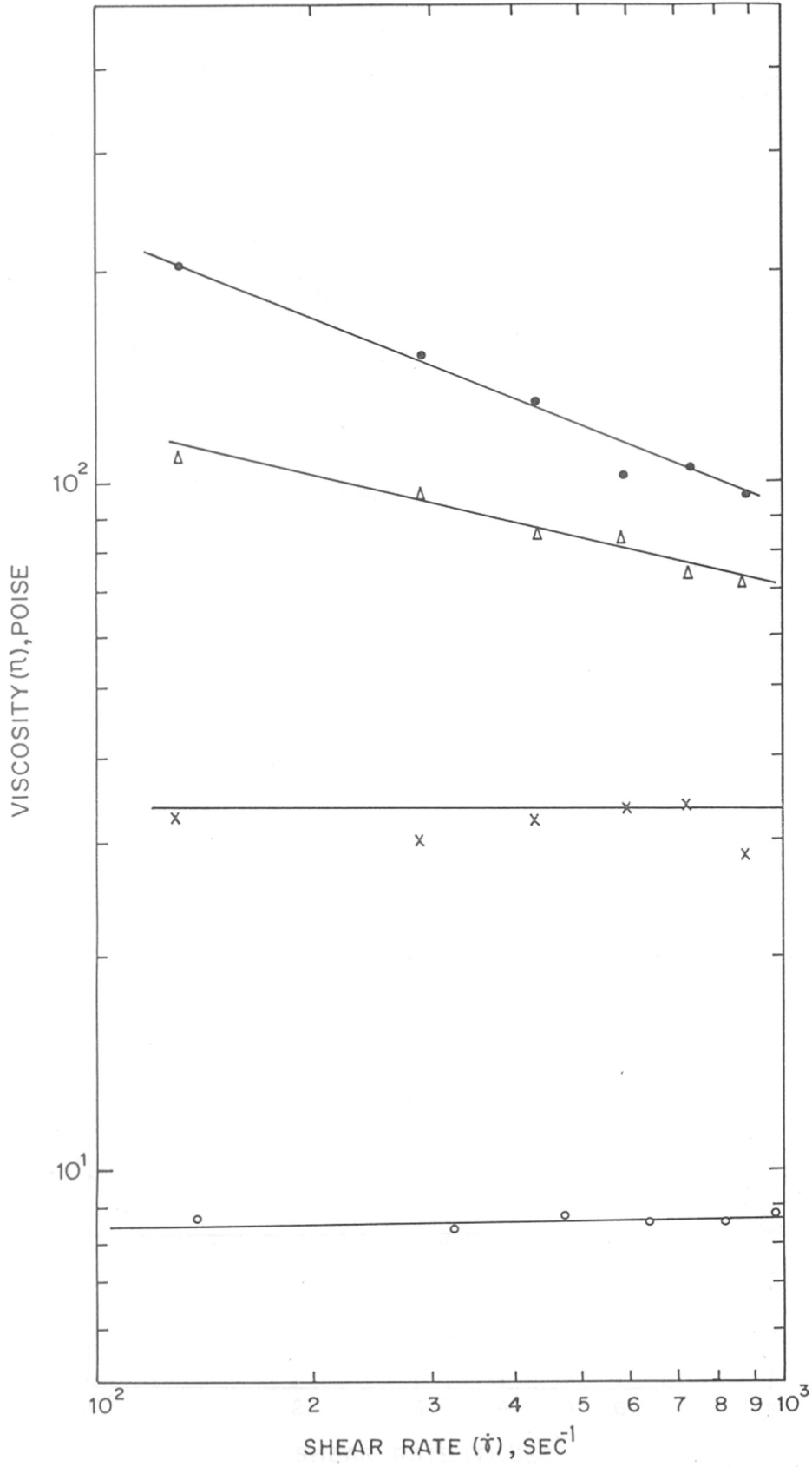


FIG.16: VISCOSITY VERSUS SHEAR RATE CURVE FOR SBS-1(x); MAH-5(Δ); MAH-12(\bullet) AND (\circ) REPRESENTS CONTROL ASPHALT

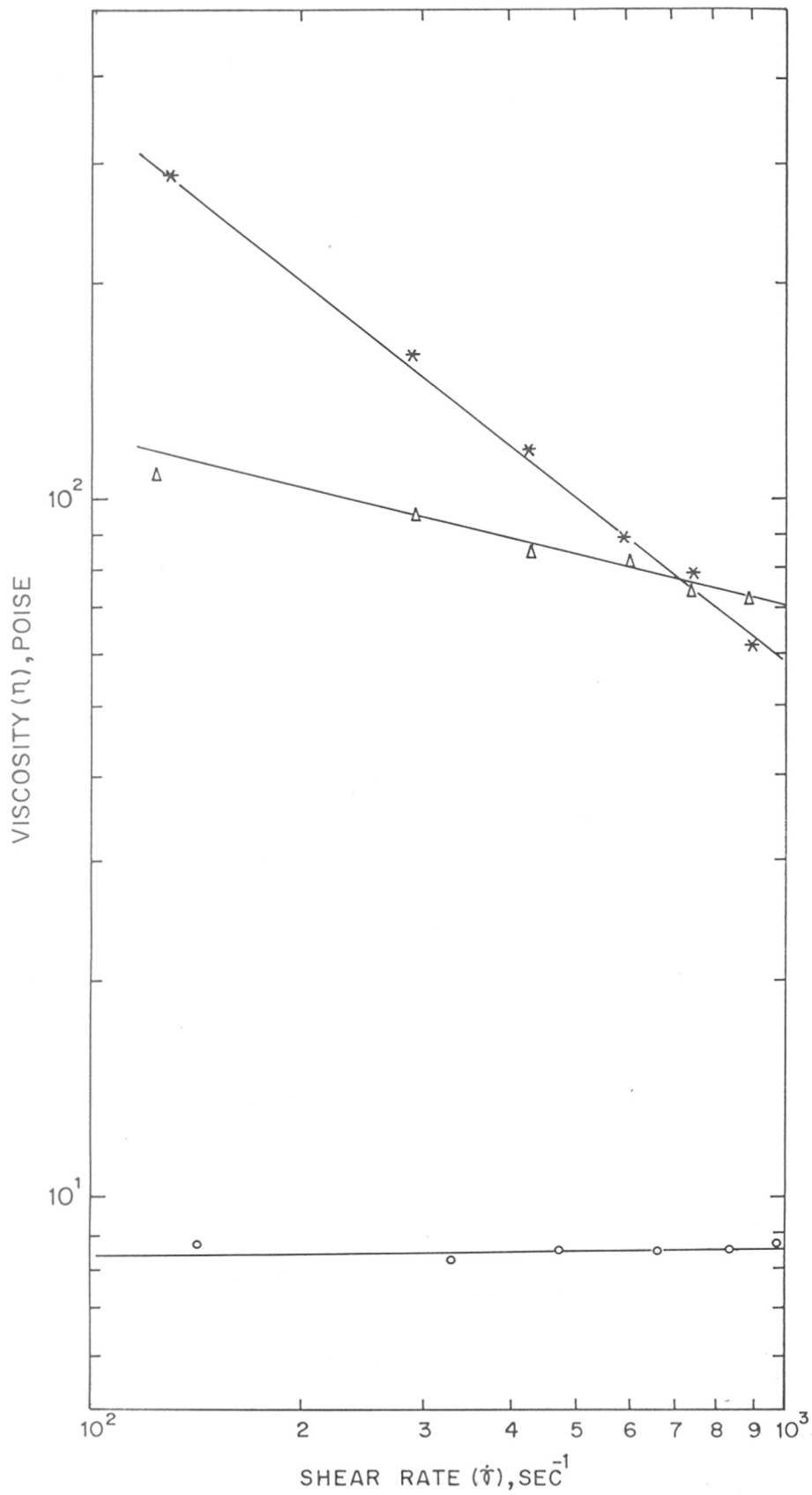


FIG.17 : VISCOSITY VERSUS SHEAR RATE CURVE FOR MAH-10(*);
MAH-5(Δ), AND (\circ) REPRESENTS CONTROL ASPHALT

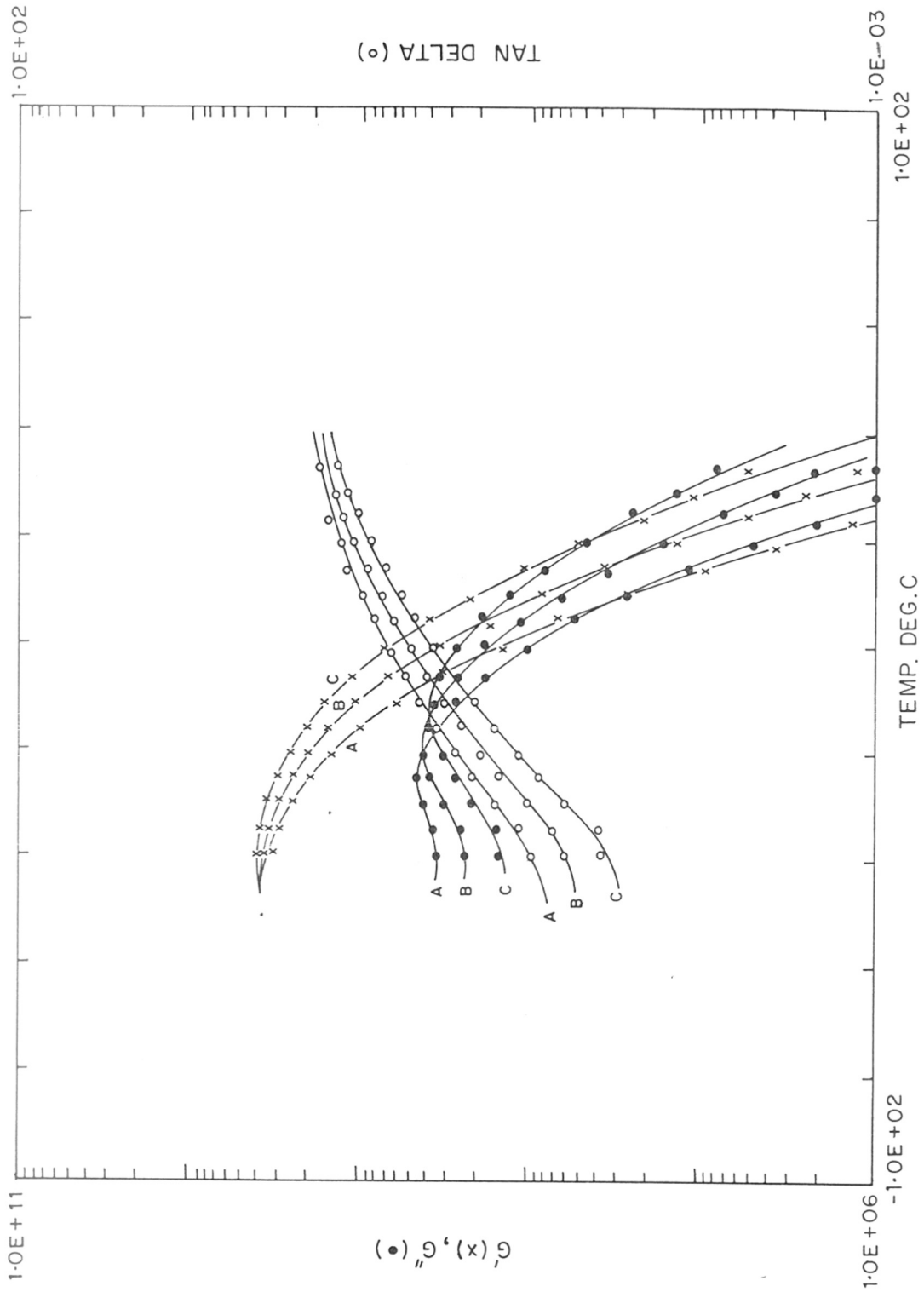


FIG.18 : VISCOELASTIC PROPERTIES OF PARENT ASPHALT AT A(1),B(10) AND C(100) rad/s

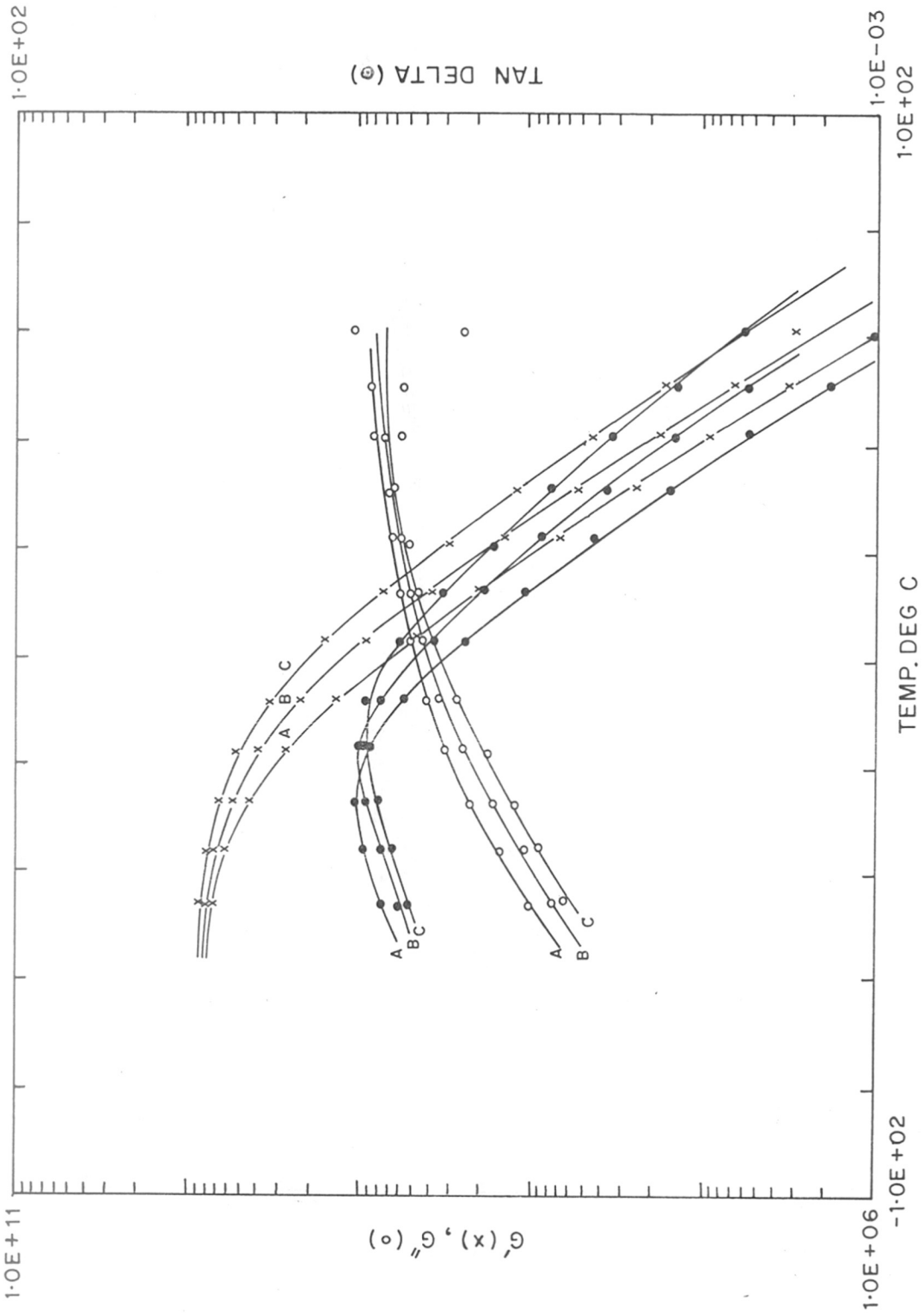


FIG.19: VISCOELASTIC PROPERTIES OF AB-1 AT A(1); B(10) AND C(100) rad/s

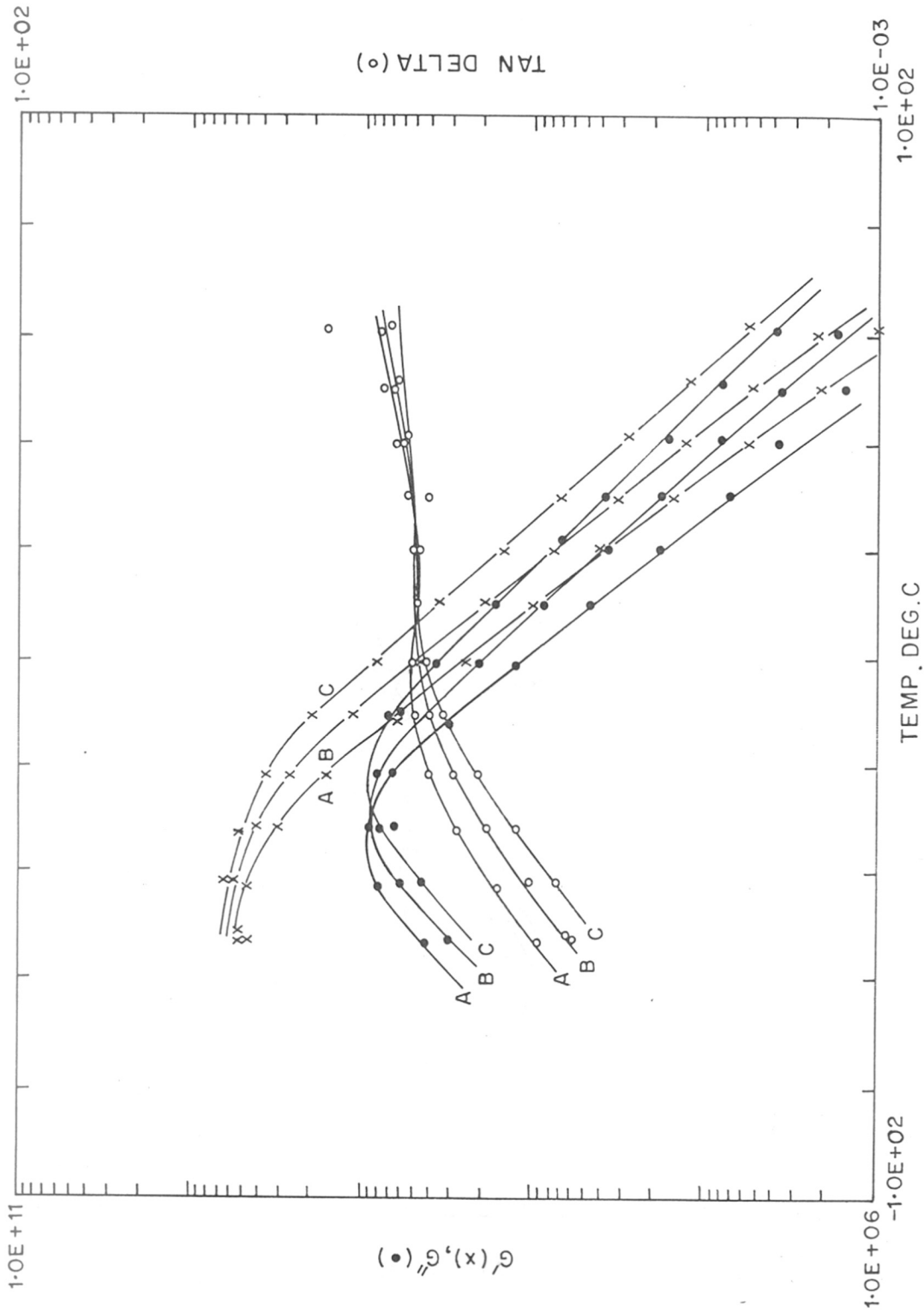


FIG.20: VISCOELASTIC PROPERTIES OF MAH-9 AT A (1); B (10) AND C (100) rad/s

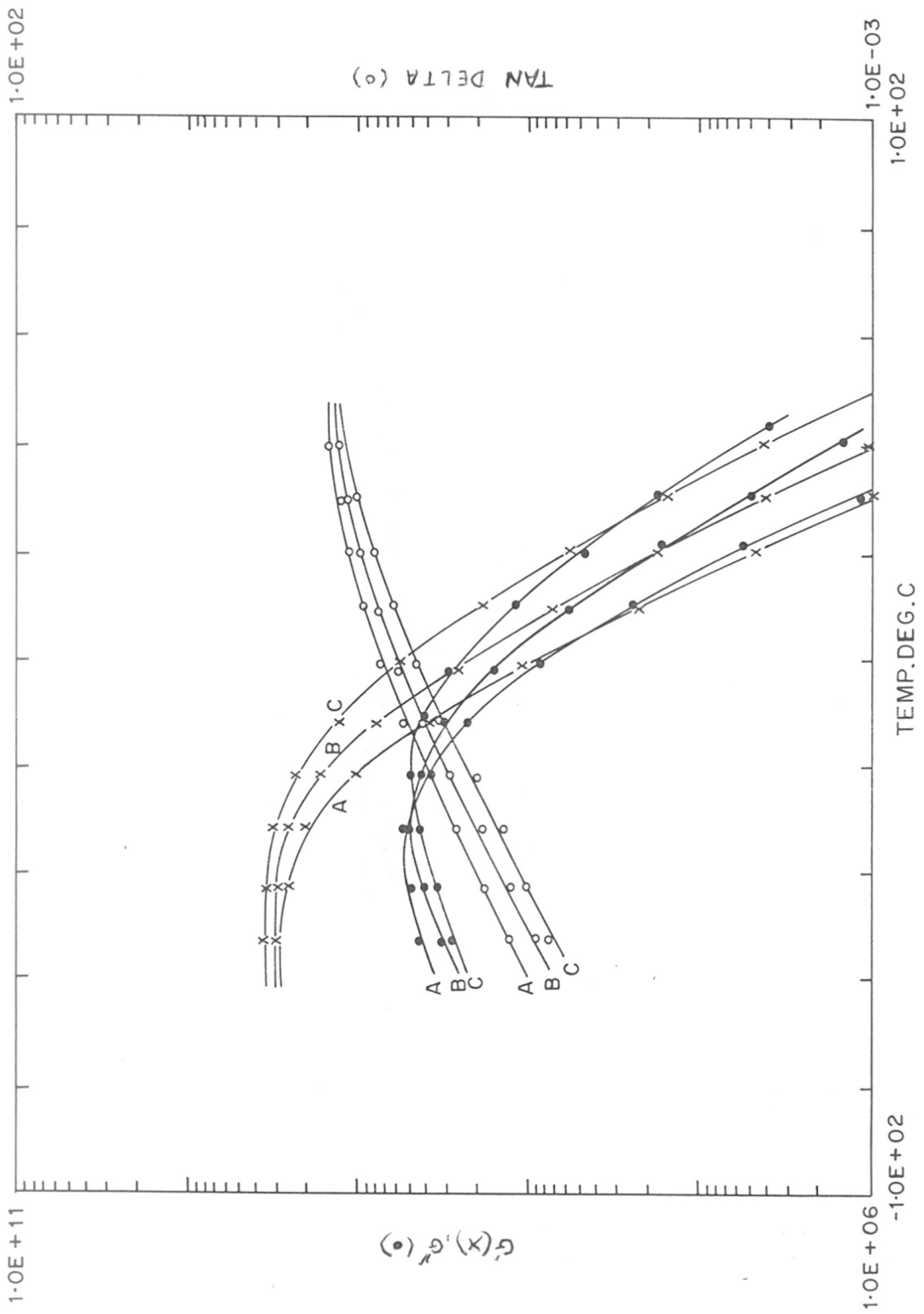


FIG.21: VISCOELASTIC PROPERTIES OF SBS-1 AT A(1) ; B(10) AND C(100) rad/s

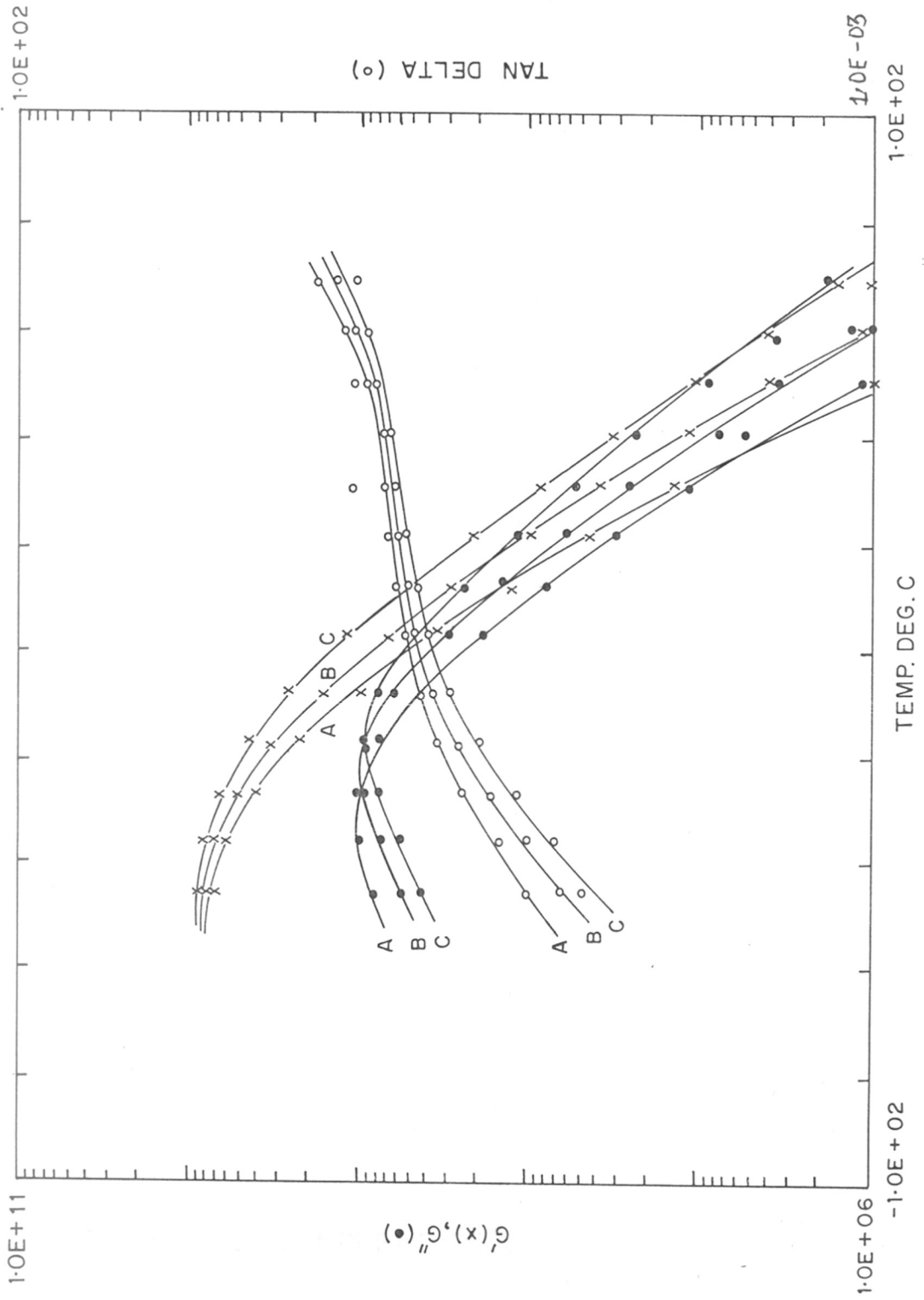


FIG.22: VISCOELASTIC PROPERTIES OF CNSL-1 AT A(1) ; B(10) AND C(100) rad/s

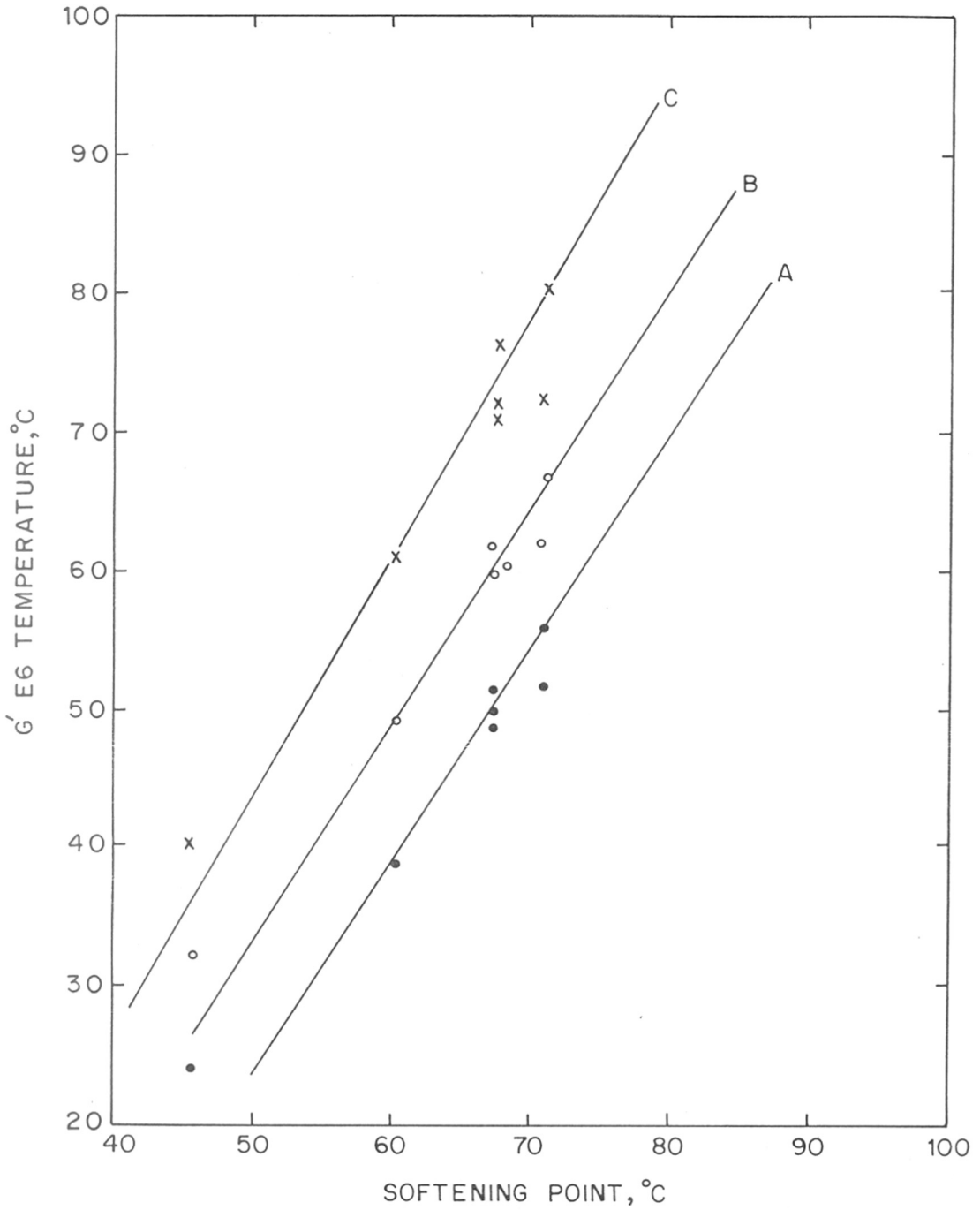
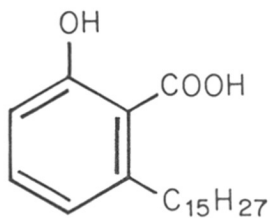
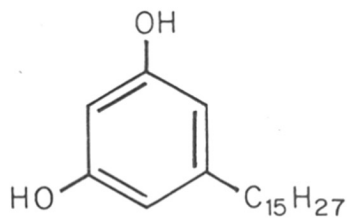


FIG.23: G' E6 TEMPERATURE °C VERSUS SOFTENING POINT °C

I ANACARDIC ACID



II CARDOL



III CARDANOL

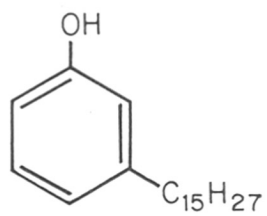


FIG.24: DIFFERENT COMPONENTS IN CNSL

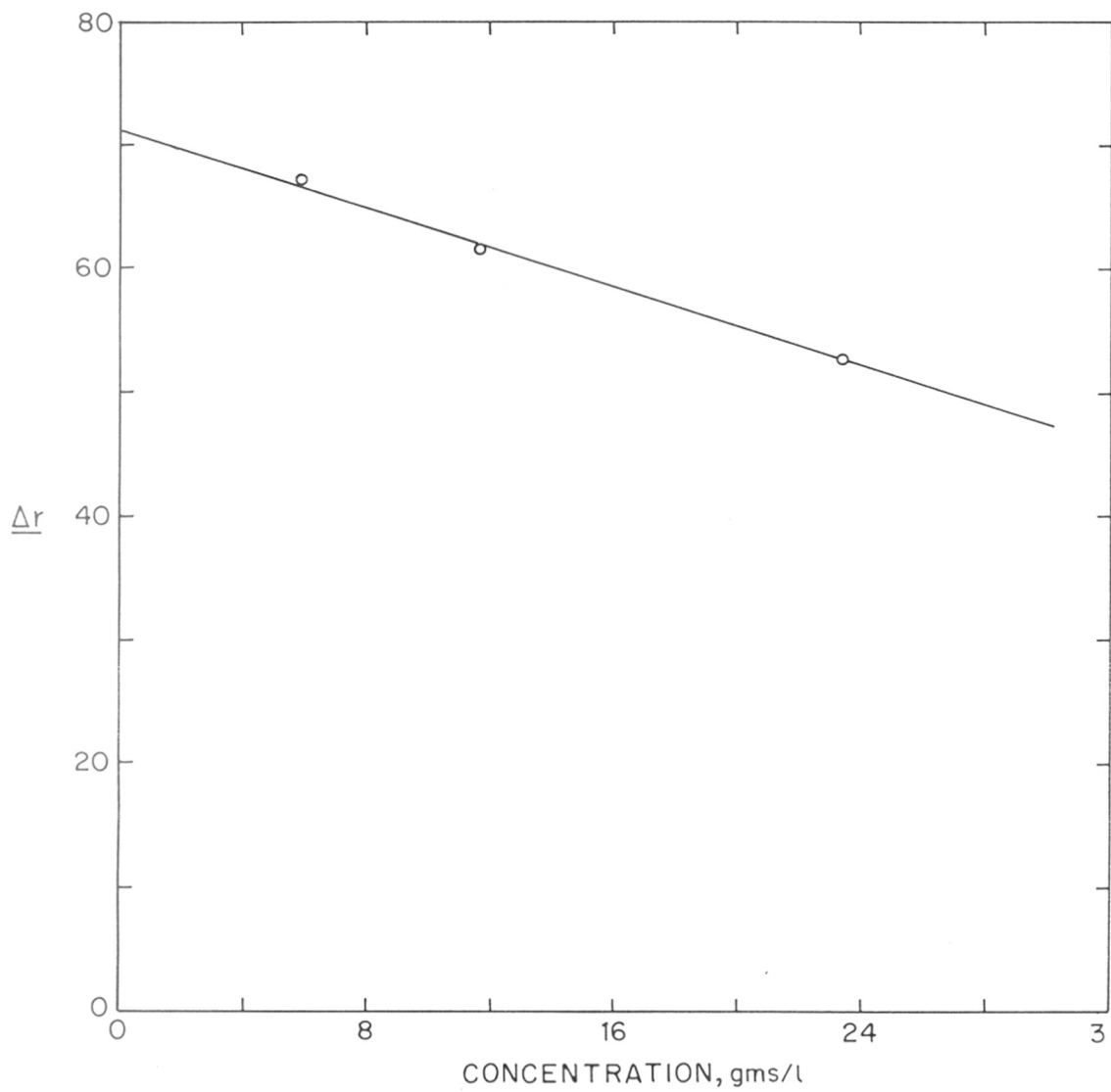


FIG.25: Δr VERSUS CONCENTRATION (gms/lit)

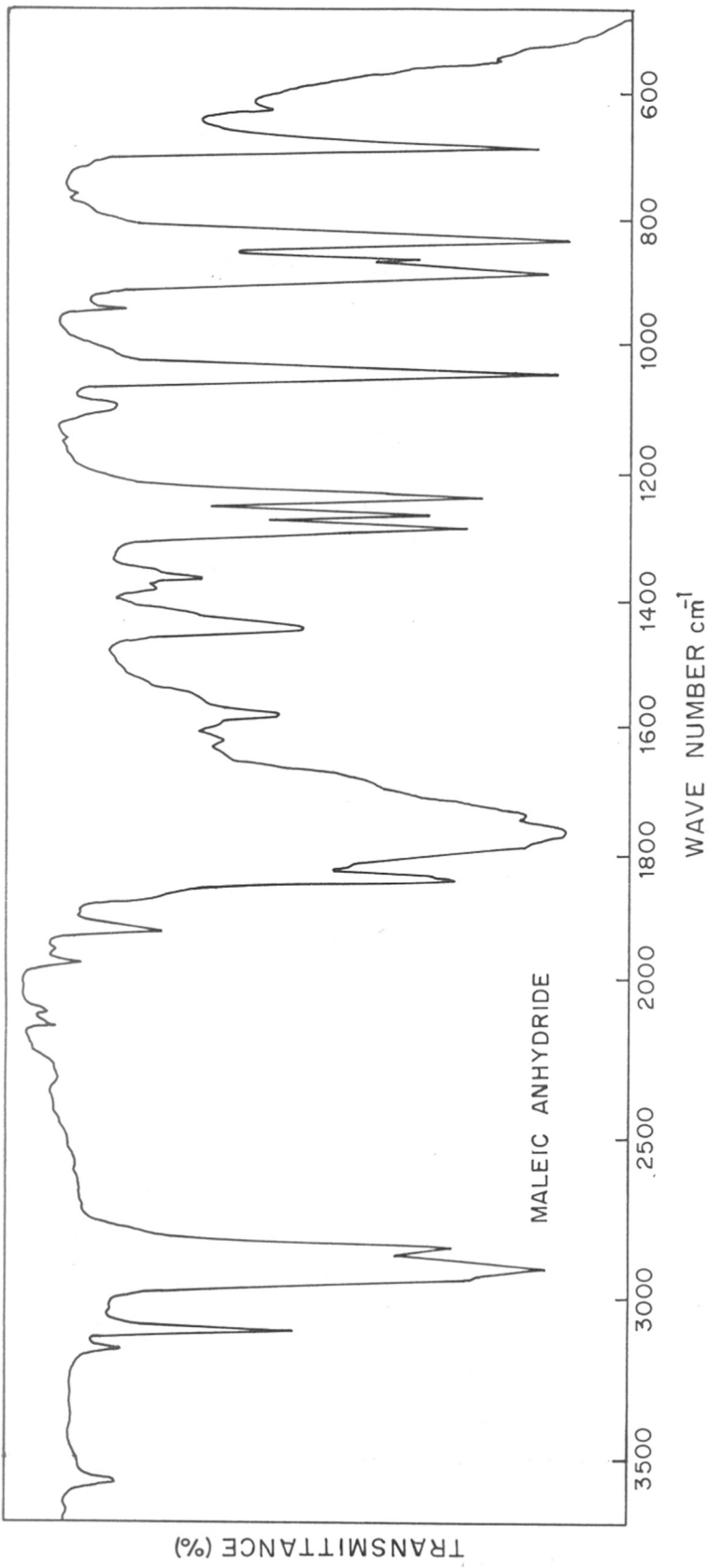


FIG.26

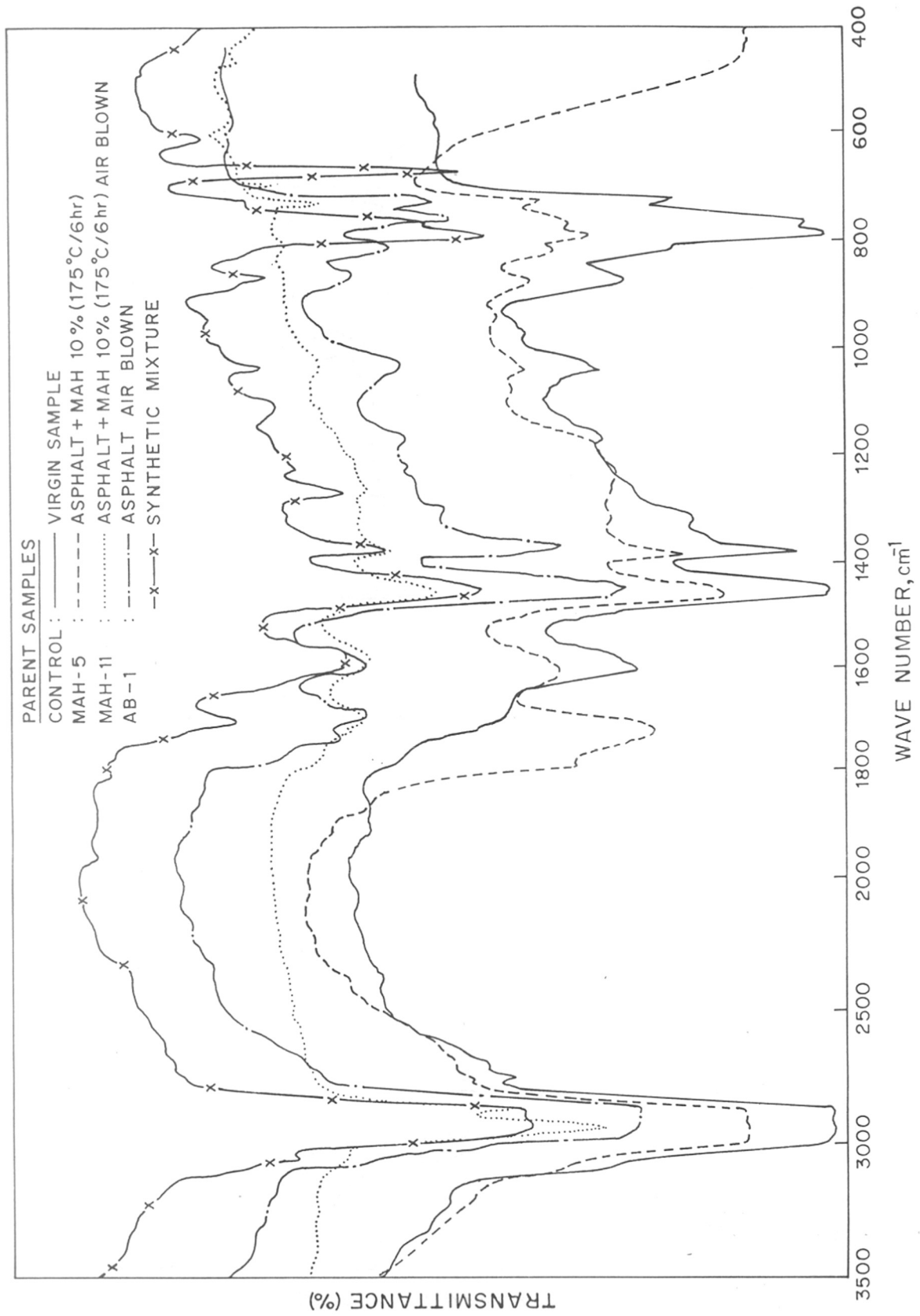


FIG.27

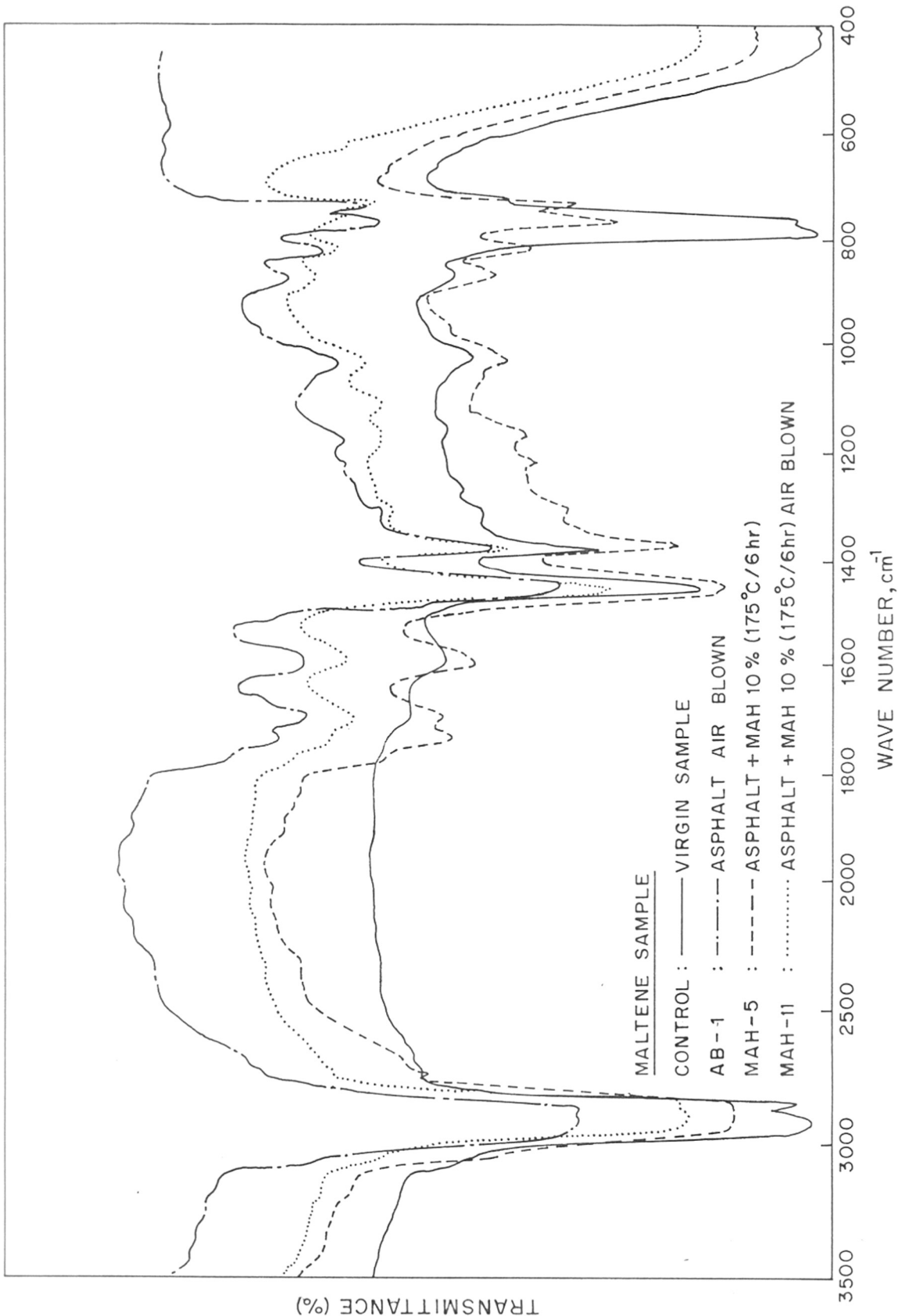


FIG. 28

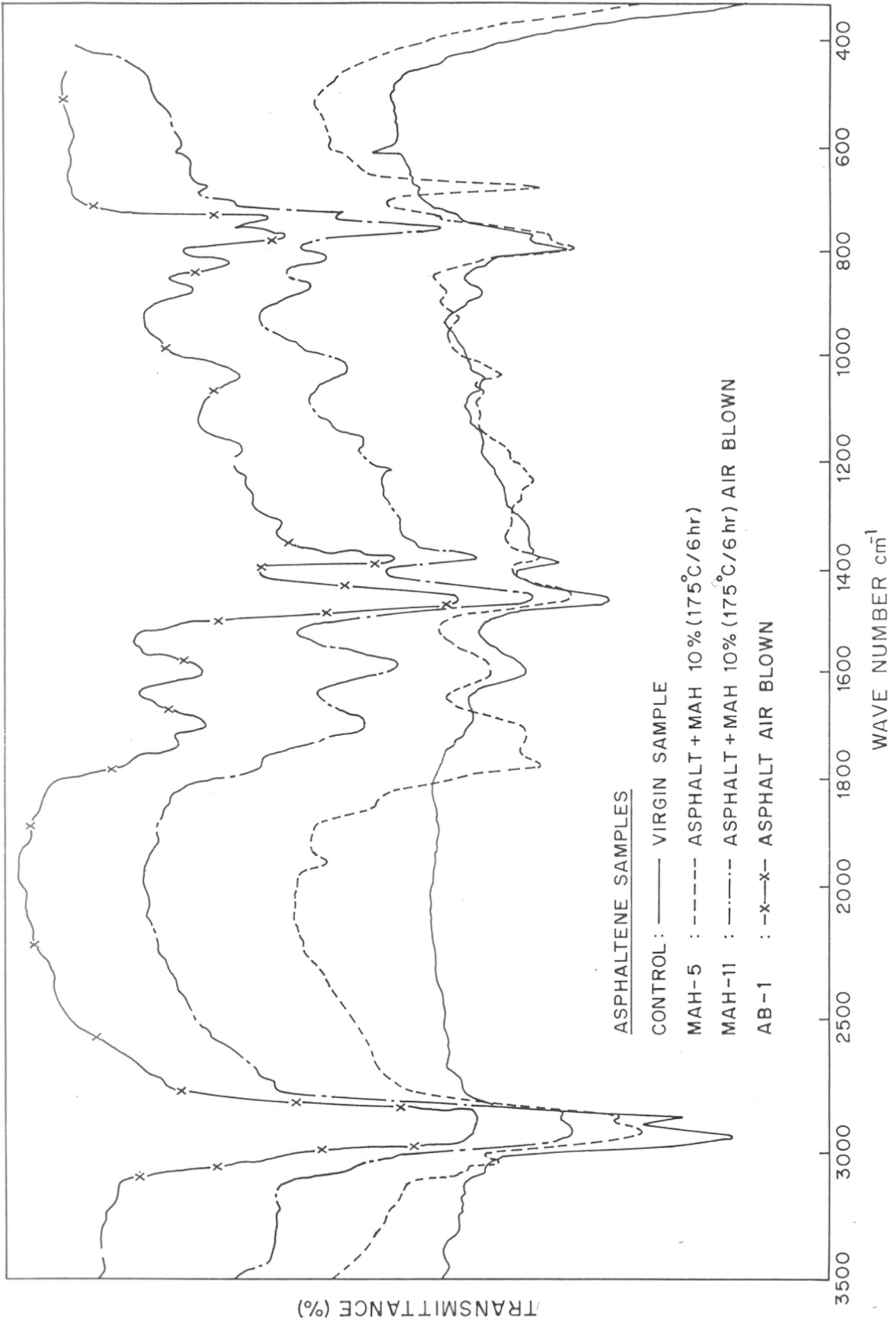


FIG.29

Table 1

Data Illustrating Typical Composition and Properties of Native Asphalts (22)

S.No.	Property	Kentucky	Oklahoma	Alabama	Texas	Sicily	Germany
1	Type of mineral	Sand to sandstone	Sand	Oolitic limestone	Lime stone	Mainly limestone	Lime-stone
2	Bitumen content (wt %)	7-9	12.5	4.5	10-20	8-9	4.7-9.5
3	Softening point* mm	Too soft	Over 360	15-25	4	Too soft	Soft

* Determined by ring and ball method.
Penetration of 100 gm at 25°C for 5 seconds

Table 2Optimization of Conditions of Modification with Maleic Anhydride

No.	Sample code	Amount of modifier %	Temperature °C	Reaction time hrs
1	MAH-1	10	125	6
2	MAH-2	10	150	6
3	MAH-3	10	175	6
4	MAH-4	5	175	6
5	MAH-5	10	175	6
6	MAH-6	15	175	6
7	MAH-7	10	175	2
8	MAH-8	10	175	4
9	MAH-9	10	175	8

Table 3

Details of Various Methods of Asphalt Modification
Reaction Temperature = 175°C Reaction Time = 6 hrs

No.	Sample code	Modifier	Amount of ^a modifier %	Air blowing
1	Control	-	-	-
2	AB-1	-	-	Yes
3	MAH-11	MAH	10	Yes
4	MAH-10	Mica/MAH	50/10	-
5	MAH-12	SBS/MAH	5/10	-
6	SBS-1	SBS	5	-
7	CNSL-1	CNSL	10	Yes
8	CNSL-2	Alumina/CNSL	20/10	Yes
9	CNSL-3	CNSL with catalyst	10	Yes

a = Weight percentage based on asphalt

Table 4

Fractionation of Asphalt Samples in Petroleum Ether 60-80

Sr.No.	Sample code	Sample	Weight percentage maltenes	Weight percentage asphaltene
1	Control	Virgin asphalt	77.4	22.6
2	MAH-5	Maleic anhydride 10% 175°C/6 hr	64.2	35.8
3	MAH-9	Maleic anhydride 10% 175°C/8 hr	62.9	37.10
4	AB-1	Asphalt air blown 175°C/6 hr (air blown)	60.8	39.2
5	CNSL-1	CNSL 10% 175°C/6 hr (air blown)	60.4	39.60
6	MAH-11	Maleic anhydride 10% 175°C/6 hr (air blown)	57.5	42.50

Table 5

V.P.O. Data for a Typical Asphaltene Sample of CNSL-1

No.	Solvent	Thermostat setting temperature °C	Instrument setting	Instrument constant K obtained by benzil
1	Toluene	45°C	Zero	51.8

$$\text{I. Molarity of solution} = \frac{\text{Molarity of benzil} \times \text{Intercept}}{\text{Reading for benzil}}$$

$$\text{II. Molecular weight} = \frac{\text{Wt of sample in 1000 ml}}{\text{Molarity of solution}}$$

Sample code	Concentration gms/lit	Average reading of asphaltene	Intercept	Molarity of solution	Molecular weight
CNSL-1	16.947	62.4	71	0.009398	3568

Table 6

Viscosity Softening Point and Penetration Index Data on
Modified Asphalts

Sr. No.	Sample code	Viscosity ^a poise	Flow index n	Softening point °C	Penetration ^b index at 60°C for 3 min.
1	Control	8.6	1.00	45.5	*
2	MAH-1	80.6	0.813	58	30.2
3	MAH-2	94.0	0.760	65.5	258
4	MAH-3	107	0.782	67.5	128
5	MAH-4	40.7	0.80	60.5	270
6	MAH-5	107	0.655	67.5	126
7	MAH-6	107	0.655	71	124
8	MAH-7	30.3	--	66	236
9	MAH-8	57.6	0.667	67	210
10	MAH-9	107	0.655	71	119
11	MAH-10	294	0.214	87 ⁺	68
12	MAH-11	163	0.727	90 ⁺	25
13	MAH-12	200.6	0.585	80 ⁺	96
14	AB-1	120	0.667	78 ⁺	102
15	SBS-1	28	1.00	59 ⁺	*
16	CNSL-1	200.5	0.678	77 ⁺	115
17	CNSL-2	263.0	0.677	88 ⁺	59

a = At 120°C and 150 sec⁻¹

b = Depth travelled in mm at 60°C for 3 minutes

* = Needle completely penetrates through the sample

+ = Values determined through equation [9]

Table 7
Dynamic Mechanical Properties of Modified Asphalts

Sample code	G'' Peak Temp (°C)		G'₀, dynes/cm² (1, 10, 100 rad/sec)	G'', dynes/cm² (1, 10, 100 rad/sec) Peak value	G'₆₀°C, dynes/cm²		G'E₆ Temp °C		
	1 r/s	10 r/s			1 r/s	10 r/s	1 r/s	10 r/s	
Control	-25	-18	4 x 10 ⁹	5 x 10 ⁸	10 ⁶	10 ⁶	24	32	40
MAH-4	-34	-26	5 to 6 x 10 ⁹	6.5-7 x 10 ⁸	10 ⁶	10 ⁶	39	49	61
MAH-5	-37	-27	5 x 10 ⁹	7 x 10 ⁸	10 ⁶	10 ⁶	49	60	71
MAH-6	-34.5	-26	5.5 to 6 x 10 ⁹	6.7-7.5 x 10 ⁸	10 ⁶	1.2 x 10 ⁶	52	62	72
MAH-8	-34	-25	4.5 x 10 ⁹	6-7 x 10 ⁸	10 ⁶	1.1 x 10 ⁶	54	62	76
MAH-5	-37	-27	5 x 10 ⁹	7 x 10 ⁸	10 ⁶	10 ⁶	49	60	71
MAH-9	-37	-31.5	6-7 x 10 ⁹	10 x 10 ⁸	10 ⁶	2 x 10 ⁶	56	67	80
SBS-1	-34	-27	3.5 x 10 ⁹	5-6 x 10 ⁸	10 ⁶	10 ⁶	30	40	49
MAH-12	-37	-27	7-8 x 10 ⁹	9-10 x 10 ⁸	10 ⁶	1.7 x 10 ⁶	56	66	77
MAH-11	-25	-19	7 x 10 ⁹	9-10 x 10 ⁸	2.3 x 10 ⁶	5 x 10 ⁶	70	80	90
AB-1	-26	-19	9 x 10 ⁹	10 x 10 ⁸	10 ⁶	2 x 10 ⁶	60	67	75
MAH-10	-27	-19	20 x 10 ⁹	25-30 x 10 ⁸	2 x 10 ⁶	7 x 10 ⁶	65	78	87
CNSL-1	-31	-22	9 x 10 ⁹	10 x 10 ⁸	10 ⁶	10 ⁶	50	61	73
CNSL-2	-31.5	22	11 x 10 ⁹	13 x 10 ⁸	13 x 10 ⁶	5 x 10 ⁶	65	75	88

Table 8

Elemental Analysis

S.No.	Sample Code	Sample	Carbon %	Hydrogen %	Oxygen %	H/C
1	Control	Virgin asphalt	82.46	10.17	7.37	1.47
2	MAH-5	Maleic anhydride 10% 175°C/6 hr	83.04	10.6	6.36	1.52
3	MAH-9	Maleic anhydride 10% 175°C/8 hr	83.53	10.78	5.69	1.54
4	AB-1	Asphalt 175°C/6 hr (air blown)	83.78	10.6	5.62	1.51
5	CNSL-1	CNSL 10% 175°C/6 hr (air blown)	84.68	10.36	4.96	1.41
6	MAH-11	Maleic anhydride 10% 175°C/6 hr (air blown)	84.2	10.36	5.44	1.47
7	-	Asphaltene of control	82.89	8.09	9.02	1.16
8	-	Asphaltene of MAH-5	83.62	8.36	8.02	1.20
9	-	Asphaltene of MAH-9	81.38	9.92	8.70	1.45
10	-	Asphaltene of AB-1	82.60	9.80	7.60	1.42
11	-	Asphaltene of CNSL-1	82.11	9.18	8.71	1.33
12	-	Asphaltene of MAH-11	82.76	9.36	7.88	1.35
13	-	Maltene of control	83.82	10.73	5.45	1.52
14	-	Maltene of MAH-5	84.04	10.90	5.06	1.54
15	-	Maltene of MAH-9	83.96	10.89	5.15	1.54
16	-	Maltene of AB-1	83.96	11.90	4.14	1.70
17	-	Maltene of CNSL-1	83.06	12.37	4.57	1.80
18	-	Maltene of MAH-11	83.68	12.56	3.76	1.87

Table 9

Molecular Weight of Different Modified Asphalts

Sr. No.	Sample code	Name	Molecular weight
1	Control	Virgin asphalt	1005
		Maltene of control	857
		Asphaltene of control	2468
2	MAH-5	Asphalt + 10% MAH 175°C/6 hrs	1009
		Maltene of MAH-5	752
		Asphaltene of MAH-5	2616
3	MAH-11	Asphalt + 10% MAH 175°C/6 hr air blown	1008
		Maltene of MAH-11	650
		Asphaltene of MAH-11	3970
4	CNSL-1	Asphalt + 10% CNSL at 175°C/ 6 hr air blown	1074
		Maltene of CNSL-1	737
		Asphaltene of CNSL-1	3568

I-R Interpretation of Model Compounds

Sr. No.	Name of the sample	Frequency -1 cm	Assignment
1	Maleic anhydride	a) 1848 & 1790	a) c=O stretching vibration
		b) 690	b) C-H in C = C (cis)
2	Maleic acid	a) 1705	a) c=O stretching vibrations
		b) 690	b) C-H in C = C (cis)
3	Fumaric acid	a) 1680	a) c=O stretching vibrations
		b) 970-960	b) C-H in C = C (trans)
4	Succinic anhydride	a) 1865 & 1782	a) c=O stretching vibrations
5	Succinic acid	a) 1717	a) c=O stretching vibrations
6	Diethyl succinate	a) 1727	a) c=O stretching vibrations
7	Diethyl fumarate	a) 1718	a) c=O stretching vibrations
		b) 970-960	b) C-H in CH=CH (trans)

Table 11

I-R Interpretation of Parent Samples

Sr. No.	Sample code	Name of sample	Frequency cm^{-1}	Assignment
1	Control	Virgin sample	a) 2860-3000 b) 1450-1465 c) 1600 d) 865-810	a) C-H stretching in alkanes b) Alkane groups might be due to asymmetric bending of methyl groups c) Aromatic groups conjugated to C=C d) C-H out of plane deformation in $\text{CR}_1\text{R}_2 = \text{CHR}_3$ compounds
2	Synthetic mixture	Synthetic mixture	a) 795-890 b) 690 c) 1790	a) C-H out of plane deformation in $\text{CR}_1\text{R}_2 = \text{CHR}_3$ b) C-H stretching in C = C (cis) c) C = O groups from anhydride
3	MAH-5	Asphalt MAH 10% 175°C/6 hr)	a) 1717 b) 1600	a) C=O groups from the anhydride b) Aromatic group conjugated to C = C
4	MAH-11	Asphalt + MAH 10% 175°C/6 hrs air blown	a) 1710-1700 b) 1600 c) 700-735	a) Saturated open chain ketonic group b) Aromatic groups conjugated to C = C c) Aromatic compounds
5	AB-1	Asphalt air blown	a) 1690	a) Ketonic group

Table 12

I-R Interpretation of Maltene Samples

Sr. No.	Sample code	Name of sample	Frequency cm^{-1}	Assignment
1	Control	Virgin asphalt	a) 825-795	a) 840-790 C-H out of plane deformation in $\text{CR}_1\text{R}_2 = \text{CHR}_3$
			b) 1600	b) aromatic compounds conjugated to C = C
2	MAH-5	Asphalt + MAH 10% 175°C/6 hr	a) 1700	a) might be ketones anhydrides or esters
			b) 1740	b) -do-
			c) 1600	c) aromatic compounds conjugated to C = C
3	MAH-11	Asphalt + MAH 10% 175°C/6 hr (air blown)	a) 1690	a) might be ketones anhydrides or esters
			b) 1600	b) aromatic compounds conjugated to C = C
4	AB-1	Air blown asphalt	a) 1690	a) might be ketones anhydrides or esters
			b) 1740	b) -do-
			c) 1600	c) aromatic compounds conjugated to C = C

Table 13

I-R Interpretation of Asphaltene Samples

Sr. No.	Sample code	Name of sample	Frequency cm^{-1}	Assignment
1	Control	a) Virgin asphalt	a) 1600	a) Aromatic groups conjugated with $\text{C} = \text{C}$
			b) 1460	b) Might be alkanes due to asymmetric bending of methyl at 1450 cm^{-1}
			c) 795	c) C-H out of plane deformation in $\text{CR}_1\text{R}_2 = \text{CHR}_3$
2	MAH-5	Asphalt + MAH 10% (175°C/6 hrs)	a) 1720	a) Might be due to acyclic ketones or anhydrides
			b) 1600	b) Aromatic group conjugated with $\text{C} = \text{C}$
3	MAH-11	Asphalt + MAH 10% 175°C/6 hrs air blown	a) 1690	a) Might be ketones or anhydrides
			b) 1720	b) Might be due to acyclic ketones or anhydride
			c) 1600	c) Aromatic group conjugated to $\text{C} = \text{C}$
4	AB-1	Asphalt air blown 175°C/6 hrs	a) 1690	a) Might be due to acyclic ketones or anhydrides
			b) 1600	b) Aromatic group conjugated to $\text{C} = \text{C}$