PILOT PLANT STUDIES ON THE UTILIZATION OF INDUSTRIAL WASTES FOR INDUSTRIAL BITUMEN MANUFACTURE

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Mr. T.P.Antony under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other Degree from any other institution.

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the supervision of Dr.D.Joseph Francis, Professor & Head, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, in the Department of Polymer Science and Rubber Technology. No part of this thesis has been presented for any other degree from any other institution.

4-12-1989

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C O N T E N T S

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Chapter 1

INTRODUCTION

I.1 GENERAL

The history of Petroleum goes back to many centuries before Christ. The Old Testament contains a number of references to large oil and gas seepages and its uses. Noah preparing the arc for the flood, seems to have been one of the first men to have realised the value of petroleum. He used it to calk the seams of his primitive vessel. But even before Noah, prehistoric man undoubtedly had seen, smelled and tasted this strange blackish-green substance.

According to the available evidence, ancient people knew more about asphalt than other forms of petroleum. In the Bible[1] there are references to "Slime" and "Pitch" - ie bitumen or asphalt, the substance left after the gases and liquids of crude oil have evaporated. The basket in which Moses floated in the Nile was water-proofed with asphalt. Arabic literature has references to "eternal fires" presumably caused by natural gas escaping from the earth. For a time ancient man probably had feared it too; strokes of lightening occasionally ignited escaping jets of gas and started fires that in some instances burned for centuries. Precisely when and to what degree ancient man first began to grasp the potential of petroleum is still matters for archeological investigation; but by 4000 B.C. when the

Summerians were beginning to keep records, it had already been put to use. The Summarians and later Assyrians and Babylonians used natural asphalt to attach blades to handles of their knives and tools, treat the sick and as mortar for their buildings. These civilizations grouped on the banks of the river Euphrates in what is now Iraq, obtained their asphalt from the "Fountains of pitch" in HIT, about a hundred miles west of Baghdad, where large seepages of petroleum existed.

There are numerous early references to "Neft" (an old Persian word for petroleum from which the English "Naphta" is derived) and to "burning waters". And in the 5th century B.C. the Greek historian Herodatus described how both bitumen and oil were obtained. For many centuries, the recorded uses of petroleum were to destroy enemies in their wars. It was a key weapon in Byzantium's defence when Arab fleets attacked Constantinople in the 7th and 8th centuries.

During the 19th century the development of machines and factories created a large demand for lubricants and lighting oils. Mutton and beef tallow and Castor oil served as lubricants. The demand for lubricants and lamp oil gave rise to a whaling industry so successful that whales were almost exterminated. In 1850 a process to produce oil from coal was patented by Abraham Genser.

In 1855 Samuel Kier built a distillation system in Pittsburg to produce "Carbon oil". This was North America's first oil refinery. Larger demand led to better methods of obtaining petroleum rather than skimming off from the surface of "oil springs". In 1857 a fifty foot well was digged in Canada. In August 1859 an oil well was made by Drake by drilling an iron pipe 70 foot long in Pennsylvania. The well produced upto 35 barrels a day and launched the Peroleum industry as it is known today.

I.2. VARIETIES OF PETROLEUM

Petroleum as it occurs in different parts of the world varies widely in composition. Certain varieties are composed of open chain hydrocarbons. Others are made up exclusively of cyclic hydrocarbons, and still others occur, showing every possible gradation between these two extremes. Numerous classifications have been proposed based on its chemical composition in general, or the presence of a substantial proportion of characteristic bodies, such as paraffin series of Hydrocarbons, the Naphthene series, sulphur derivatives, nitrogenous bodies, benzols, Terprenes[2] etc.

From the standpoint of asphalt content petroleums are divided into three groups:[3,4]

(1) Asphaltic petroleums: These carry a substantial

quantity of asphaltic bodies with solid paraffins either absent or present only in traces.

(2) Semi-asphaltic petroleums: These carry a moderate quantity of asphaltic bodies, but in any event generate or produce asphaltic bodies during the distillation process. Solid paraffins may or may not be present.

(3) Non-asphaltic petroleums: These do not carry asphaltic bodies but may generate them during the distillation process. Solid paraffins are usually present, but not necessarily so. Asphalt is manufactured from asphaltic and semi-asphaltic crude oils.

I.3. MANUFACTURE OF PAVING BITUMEN

1.3 (a) STRAIGHT REDUCTION FROM CRUDE OIL

Crude oils were originally refined by distillation using batch stills. In the stills, large amounts of steam aided the vapourisation or distillation of the more volatile constituents. When asphalt base crudes were thus processed, the resulting residuum became known as steam reduced asphalt[5,6]. With the advent of more efficient means of distillation, the terms straight-run asphalt and straight reduced asphalt became more commonly used. These terms imply that the asphalt is separated in such a way as to preserve its inherent properties[7] ie. by not being affected by cracking or oxidation as occurs in other processes.

Distillation is an integral process in crude oil refining. The initial step in distillation is under atmospheric pressure[8,9] and normally involves heating the crude oil to about 375°C through a tube heater or furnace, followed by injection into a fractionating column[10]. The lighter fractions are in this way separated as over-head products and the asphalt as a residuum. Use of steam in the distillation tower provides for lower vapour pressures of the distillate fractions, permitting the use of lower temperatures. This results in better operation, economy and the use of higher temperatures without cracking. When the distillation is operated under atmoshperic pressures, the asphalt residuum is termed atmospheric residue or topped crude. This becomes the first step in overall refining process.

Many crudes contain relatively high percentages of high boiling fractions which cannot be distilled in an atmospheric distillation unit. In order to obtain residuum of desired asphalt consistancy as well as to recover these high boiling fractions for other purposes, it became necessary to supplement the process. This was done by adding a second fractionating tower, operated under reduced pressure[10], to permit deeper cutting into the crude. This is the second stage of the distillation process[11].

The process of manufacturing asphalt by the vacuum distillation method has very little effect on the properties of an asphalt, other than on its consistancy or penetration. The crude source from which the asphalt is made, does have an appreciable effect on its physical properties. Different crudes also require different process conditions for the separation of an asphalt. This is due primarily to the make-up of the crude, ie. to the boiling characteristics of the oils present as well as to the quantity of oils to be removed. This is brought out by the relationship of atmospheric cut-point to the yield of the various penetration asphalt residuum. Cut-point as used here is the maximum vapour temperature reached during distillation.

I.3.(b) PROPANE DEASPHALTING PROCESS

Asphalt is a by-product of the propane deasphalting and fractionation process[12], which involves the precipitation of asphalt from a residuum stock by treatment with propane under controlled conditions. It has as its primary purpose the recovery of either lube or catalytic cracking stocks. Asphalt manufactured by this process, therefore, is subject to the requirements specified for these oil fractions. Propane is conventionally used in this process although propane-butane mixtures have been used with some variation in processing conditions. Worldwide there are over 45 propane deasphalting units in operation, mostly on crudes of relatively low asphalt content. These units make asphalt for paving by blending with straight reduced residues.

The process consists of a counter-current liquid-liquid extraction. The charge stock is introduced near the top of an extraction tower and the liquid propane near the bottom using solvent to oil ratios from 3/1 to 8/1. The deasphalted oil solution is withdrawn overhead and, the asphalt solution from the bottom, each being subsequently stripped of propane.

Operating pressures and temperatures are dependant on the proportion of the propane-oil mixture. Temperatures are usually selected to accommodate the charge stock; ie. a temperature must be selected in which the propane-oil mixture has suitable viscosity for fluid handling in the deasphalting tower. High solvent-oil mixtures tend to give high yields of asphalt oil and low yields of asphalt. Operating pressure and temperature are varied depending upon selectivity needed.

Basically there are small differences between asphalts prepared by propane deasphalting and those prepared by vacuum distillation, when processing the same stock. Propane precipitation does have the ability to reduce a residue further ie, to a harder asphalt product. However, propane deasphalting is conventionally applied to low asphalt content residues which are generally quite different in composition from those processed by vacuum distillation on asphalt - bearing crudes. Thus, it is difficult to make comparisons of asphalts prepared by the two processes. However, it is generally observed that for a given softening point we find lower penetrations in the case of the propane precipitation process.

Mixed propane-butane is sometimes used in the deasphalting process. This provides a slightly higher level of flexibility due to higher operating temperature, thus separating an asphalt product of higher softening point and containing a lower percentage of oil. A similar effect is obtained by mixing benzene or other aromatics with either propane or butane[13]. This permits the use of higher temperature and pressures yielding an asphalt approaching 200°C in softening point. Again the effect is to concentrate a higher percentage of asphaltenes in the asphalt product.

1.3.C DEASPHALTENING PROCESS

In recent years interest has been displayed in deasphaltening of residual stocks. This involves the use of solvents such as n-pentane, n-hexane or n-heptane at atmospheric pressure in ratios of 5/1 or greater .

The result is the precipitation of a product that is essentially asphaltenes, thus the term de-asphaltening The selectivity of this method, in terms of how well the resins and oils are separated from the asphaltenes, depends upon the ability of the process to separate the solid asphaltene product from the solvent-oil-resin solution. Such a separation is usually accomplished by filtration or by centrifuging. As yet, deasphaltening has not been reduced to refinery practice, but it takes little vision to foresee this as an eventuality.

I.4 AIR-BLOWING PROCESS FOR INDUSTRIAL BITUMEN MANUFACTURE

It has been recognised for many years that the physical properties of petroleum products change when treated with air. One of the first to report this fact was Abraham Genser in 1865[14]. Air-blowing is a process in which an asphalt stock is converted at temperatures ranging from 200° to 270°C to a product of modified properties by polymerization in presence of air. This is sometimes called asphalt oxidation with the product termed oxidised asphalt. The terms air-blowing and air-blown asphalt are preferable, however, because it has been shown[15] that dehydrogenation and polymerizations are involved and that oxygen is not added to the asphalt product except in a very minor amount. Naphthene aromatics are converted to polar aromatics and then to asphaltenes[16]. The following is the scheme of transformations during air blowing of the raw material.

In the beginning of the process

$RH + O_2 \longrightarrow R^{\bullet} + HOO^{\bullet}$

Interaction of the formed radicals with new molecule of hydrocarbon followed by disproportionation leads to the recovery of stable products.

$\dot{R} + R^1H \longrightarrow {}^{\bullet}RR^1H$

${}^{\bullet}RR^1H + R^{11}H \longrightarrow \dot{R}R^1HR^{11}H \longrightarrow$ disproportionation.

As a result of the comparatively low concentration of hydrocarbon radicals, there is less probability of their recombination ($2R^{\bullet} \rightarrow R\text{-}R$) and the interaction of the radicals with oxygen takes place to a smaller extent than with the molecules of the initial substance.

$\dot{R} + O_2 \longrightarrow RO\dot{O}$

$RO^{\bullet} + R^1H \longrightarrow ROOH + \dot{R}^1$

$ROOH \longrightarrow RO^{\bullet} + OH^{\bullet}$

$R^{11}H + {}^{\bullet}OH \longrightarrow {}^{\bullet}R^{11} + H_2O$

Continuation of the chain:

$RH + HO\dot{O} \longrightarrow {}^{\bullet}R + H_2O_2$, $H_2O_2 \longrightarrow 2\dot{O}H$

$R^1H + OH^{\bullet} \longrightarrow \dot{R}^1 + H_2O$

Air-blowing of petroleum residues or fluxes was first patented by Desmedt[17] and first put into commercial practice by Byerley[18]. Originally this was accomplished by injecting air into hot asphalt contained in a horizontal vessel or still. With the development of high pressure blowers it was found that greater efficiency could be realized by using vertical vessels or towers. Other design operating features followed such as the use of agitation and chemical catalysing agents which will be mentioned later. Published literature on air-blowing leaves much to be desired, with no complete treatise on the subject. Perhaps the reason for this problem is that there are many competing reactions involved and with very little published information that may be applied to any particular unit design. The fact that all variables mentione previously are interdependent plus a general non-uniformity of plant design and practice permits very little opportunity to standardise on methods.

1.4.(a) THE BATCH AIR-BLOWING PROCESS

The batch process for air-blowing is more commonl used than the continuous method. The essential features of the process are

a) a preheat furnace b) a compressor for air supply
c) a blowing vessel d) perforated pipes at bottom
to subdivide the gas in a fine stream or jet

Preheating is usually accomplished by a tube furnace or heater such as the automatic convective type. Direct fired batch stills or tanks with immersion heaters can also be used to accomplish the same objective. Air supply is commonly provided by compressors of the rotary type. A wide variety of vessels or drums have been adapted to air-blowing of asphalt. Frequently use is made of vessels transferred from other refinery service. Many horizontal type vessels are still in use although where new design is involved, a vertical type is preferable because of better efficiency. Basically the height of asphalt in the blowing vessel is the prime consideration for reasons dependent upon the air supply. If greater capacity is desired, the vessel should be designed with a large diameter. If shorter processing time is desired, the trend would be toward taller vessels of small diameter. The quantity of air is also a factor in the amount of conversion that takes place per unit of time; present day units are designed to operate on 15 to 50 Cu.ft of air per minute per tonne of asphalt charge.

The design of blowing vessels usually includes such features as easily removable air coils to save time in maintenance cleaning, safe and well designed sample ports etc. It has been estimated that exotherasphalt per degree farenheit of softening point rise. The effect of this exothermic heat is to raise the temperature of asphalt itself. This heat must be removed to some extent to prevent accumulation of very high temperatures which would affect the softening point-penetration relationship of the blown product. Several features have been included in the design to overcome this. One is to provide a pump-around system using a heat exchanger or spraying water directly on the top of the asphalt during blowing.

Air blowing losses will generally vary from 1/2 to 2% of the charge depending upon the volatility of the flux, temperature, time etc. Process fumes largely account for these losses. The disposal of process fumes has always been a problem with no completely satisfactory answer. These fumes contain hydrocarbons and their derivatives in both vapour and entrained form. The vapours include moisture as well as products from the reaction of air with the asphalt. Such compounds as aldehydes, ketones, sulphur and nitrogen derivatives have been identified in blowing fumes.

The vapourised compounds accounts for the disagreeable odour found in blowing fumes. Entrained oils originate from the asphalt and are representative of the more volatile hydrocarbon constituents in asphalt.

A simple knockout drum or vapour trap in the effluent line following the blowing vessel will do a great deal in deoiling these fumes. The knockout drum is equipped with water sprays which assist in deoiling. Where space is available, a simple system consists of passage of the effluent through a long horizontal air condensor and then into a vertical stack. This will trap out virtually all of the entrained oil and permit better dilution of the vapourised compounds.

Operation of batch air blowing

In batch air-blowing, temperature is the most important single variable. Other variables such as air rate, source of flux etc. are generally held constant. Preheating is generally necessary to bring the flux up to a temperature where reaction begins. For practical considerations, this is in the vicinity of 200-270°C; conversion does take place at lower temperature but is very slow. Higher starting temperatures may be used, but it is more practical to use some of the exothermic heat to reach these temperature and thus save input heat. After air has been introduced, there is a gradual temperature rise until some means is applied to hold the temperature of the batch. Water injection is used to control the temperature at a level in the vicinity of 220°C. The end-point can be predicted by testing the batch for softening point periodically. In this way it is possible to pump out the batch at a predicted time instead of waiting for a final test. As the end point is reached the batch is cooled 20°C or more as quickly as possible. This will aid in maintaining the end-point consistancy by preventing depolymerization which frequently occurs when blown asphalts are soaked at high temperatures. This is called quick freezing.

Parameters of the process

1. Nature of the raw material:

Petroleum containing 5% and more by weight of asphaltic-resinous substances are used for the purpose of air-blowing. The best raw materials for obtaining air-blown asphalts are residues of high resinous, low paraffinic petroleums eg; Arab mix, Suez blend, Kuwaity, Maxican heavy, Venezuela, Trinidad petroleums etc.,

The quality of the air-blown asphalt especially the softening point-penetration relationship depends on the nature and consistancy of the raw material. For a given softening point, the penetration of the air blown asphalt obtained from the same petroleum dependson the oil content in the raw material. The higher the oil content in the raw material, the higher is the penetration of the resulting air blown asphalt. The air blown asphalts made from propane deasphalted asphalt have higher molecular weights compared to those from vacuum distillation process. The paraffinic petroleums are not suitable. The paraffin waxes like crystalline substances do not possess the plastic and adhesive properties. The action of paraffinic compounds depends on their dispersion, structure and the permissible content of these compounds in the raw material is upto 3% by weight. The more the paraffinic content in the raw material, the more will be the flow rate of air and oxidation duration.

2. Temperature of the process:

The optimum temperature for air-blowing depends on the nature of the raw material and it is normally between 220 to 240°C. At higher temperatures upto 270°C the rate of increase of softening point increases but results in products of lower penetration for a given softening point. At temperatures above 270°C there is an intensive formation of carbenes and carboids which results in lower penetration and ductility. With rise in temperature, the diffusion constants increase and the surface tension decreases, the size of the gas bubles increase as a result of decrease in the viscosity of the liquid phase, side reactions prevail which do not help in increasing the softening point of the bitumen (Mainly dehydrogenation reactions take place resulting in the formation of carbenes and carboids). Further, at higher temperatures there is an intensive distillation out of lighter fractions. At temperature above 270°C the flow rate of air increases and the extent of utilization of oxygen of the air decreases.

3. Flow rate of air:

The flow rate of compressed air, degree of its dispersion and distribution over the cross section of oxidation tower significantly affect the intensity of the process and the properties of the bitumen. The increase in the flow rate of air up to definite limit, with other conditions being the same, leads to a proportional increase in the oxidation rate; the latter depends on the temperature of the process, construction of the oxidation tower and the nature of the raw material.

The effect of flow rate of air and oxidation duration on the quality of bitumen has not been fully determined. However, it has been found that the bitumens, oxidised in short duration, have higher penetration than the penetration of bitumen of the same softening temperature oxidised in longer duration at lower rate of air supply. This may be explained by the formation of lower molecular polar asphaltenes in the first case. When the duration of oxidation is long and the high temperature acts for a long time, molecules of CO_2 split out and the conversion of bitumens into higher molecular weight asphaltenes takes place.

4. Pressure:

With increase in pressure in the reaction zone, the diffusion of oxygen into liquid phase improves, the oxidation duration reduces and as a result of condensation of a portion of oil vapours from the gaseous phase and penetration of the resulting bitumen will be higher. The oxidation under pressure enables the use of raw material with small oil content and produce bitumens having fairly high penetration.

I.4.(b) CONTINUOUS AIR-BLOWING

Continuous air blowing has got certain advantages[19], lower equipment and maintenance cost; shorter blowing times because of more efficient use of air; less preheat capacity needed; easier to control and operate because of its continuous nature; more yield per unit of investment and less fumes to handle. If only one or two products are to be manufactured and if there is a continuous loading out or packaging of the product, most of these claims are quite valid. Consistant with the advantages of any continuous process, once the unit has been regulated to yield a product of constant quality, the relative high yield of a product per unit time and its cost become decided advantages. If a variety of blown asphalt grades are to be made, the continuous plant becomes less practical. Converting a continuous unit from one product to another requires considerable adjustment and sometimes manipulation of the charge stock. Most manufacturers are called upon to make a variety of grades of blown asphalt from different fluxes, and herein lies the versatility of the batch unit and the disadvantage of the continuous unit. Batch units also require a greater investment in tankage. In spite of this, there are relatively few continuous units in operation today.

I.4.C AIR-BLOWING WITH CATALYSTS - REVIEW OF LITERATURE

The term catalytic asphalt has been accepted[30] in spite of some question as to whether this is truly a catalytic process. Since the agents used here can not be recovered as such, technically they might better be termed chemical reactants. In any event, the general effect is to reduce blowing time, as well as to change the softening point-penetration relationship . Reduction of blowing time is an economic incentive, whereas the change in the flow properties permits the manufacture to specifications, previously not possible.[21]

Baillard oxidised a mixture of petroleum and oleic acid by means of air at 160°C[22], Busse blew air through a heated mixture of asphalt and vegetable oils in the presence of nitric acid, sulphur or sulphur dichloride,[23] Salathe blew heated air through melted native asphalt, either alone or in the presence of litharge[24], Schreir proposed blowing melted asphalt coal tar pitch, fatty acid pitch, wool fat pitch etc., with air in the presence of manganese dioxide and sulphuric acid and finally adding formaldehyde[25]. Incidently it is of interest to note that vaseline, liquid or solid paraffin wax may be converted into fatty acids by oxidation with potassium permanganate in an acid or alkaline solution or a mixture of manganese dioxide with hydrochloric or nitric acid[26].

Byerley and Mabery found that[27,28] asphalts of variable properties can be obtained depending upon the temperature and the duration of the blowing process. For the softer grades (fusing under 100°C) the Lima residuum was blown three days at 200°C, during which 2% of distillate was produced. For the harder grades (Fusing at about 200°C), the residuum was blowen 4 to 5 days at 260°C during which between 5 & 6% of distillate was recovered. The product was claimed to be resistant to changes in atmospheric temperature, and to differ from the corresponding steam - distilled asphalt by being readily soluble in petroleum benzene or naphtha. Air under suction was passed through a 6000 gallon still of the oil, at the rate of 450 Cu.ft. per minute. Ohio petroleum residue of 21-27° Baume, also Texas Gulf coast residue of 12-15 Baume were first used for this purpose.

Hayward[29,30] and Culmer[31,32] obtained patents for a similar process, according to which a mixture of petroleum residue and refined Trinidad asphalt or Gilsonite was heated to 193°C and blown for 40 hrs at the rate of 15-30 Cu.ft. air per minute, per ton asphalt. After a time, the external source of heat was removed, since it was found that the temperature of the residue increased spontaneously, due to the chemical changes induced by the action of the air. It was also found that, the oxidation progressed very rapidly at first, and then more slowly, as it approached the end of the process. The air may either be blown through the still under pressure, or else sucked through the still by subjecting the contents of the still to a partial vacuum (upto 20 inch mercury). There are proponents of both systems. The loss depends largely upon the amount of volatile matter contained in the residual oil, and varies from practically 0 upto 10% of the weight of the charge, depending of course upon the extent the product is blowen. Water and CO_2 are given off. It is contented that the vacuum process removes the oily and greasy matters from the residual oil and forms a brighter and cleaner looking blown asphalt. Non-asphaltic petroleums will yield a good grade of blown asphalt if first subjected to a high temperature and pressure which serve to convert saturated hydrocarbons into polymerized unsaturated compounds[33]. It is also contented that blown asphalts of high penetration for a high fusing point, may be produced from petrolatum, from which microcrystaline wax has been separated by dissolving in a mixture of benzene and methyl ethylketone, chilling the solution, filtering, distilling off the solvent, and finally blowing the residue[34]. Blown asphalts may likewise be produced from naphthenic residual oils or naphthenic derivatives (ie. non-asphaltic and non-paraffinic in character) obtained by extracting petroleum with propane, SO_2, aniline, phenol etc.[35]

Various catalysers and oxidising agents have been proposed for augmenting the air-blowing process, resulting in a product having a higher penetration for a given softening point[36], including finely powdered limestone[37,38], caustic soda or sodium carbonate[39], bentonite or finely powdered coke[40], sulphur[41], sulphuric acid with or without the addition of metallic persulphates or per borates[42], metallic fluoborates[43], boric acid, phosphoric acid or arsenious acid[44,45] P_2O_5 P_2S_5, P_4S_3 or P_4S_7[46,47] a mixture of P_2O_5 and a copolymer of isobutylene and styrene[48], a mixture of H_3PO_4 and boron trifluoride[49], potassium chlorate[50], chlorides or sulphates of zinc, aluminium, iron, copper or antimony[51,52]; chlorides of zinc or aluminium together with finely divided metals (eg: Fe, Al, Mg, Mn or Cu)[53], chlorides or sulphates of Zn, Al, Fe, Cu or Sb, together with a lead soap or finely divided PbO[54]; the residue obtained in the manufacture of synthetic lubricants by polymerizing hydrocarbons (eg; olefins) with $AlCl_3$ as catalyser[55]; polymerizing by heating with aluminium chloride and sulphuric acid followed by blowing with air[56], heating with metallic oxides, followed by blowing with air[57]; heating with hydrochloric acid followed by blowing with air[58]; blowing in the presence of aluminium or zinc stearate[59], copper, lead, cobalt, iron or chromium naphthenate, sulphonate, stearate or resinate[60]; cobalt, chromium, manganese, iron, nickel zinc, lead or copper naphthenate or oleate in the presence of an alkali[61]; Lead oxide (PbO) and naphthalene[62]. First blowing with air followed by heating with a halide catalyst (eg: a halide of aluminium such as $AlCl_3$, a halide of boron such as BF_3, zirconium, tantalum, copper, tin, zinc, antimony, etc.) together with hydrohalogen acid (eg: HCl, HBr, HF or HI)[63], blowing in the presence of Seleno sulphide, Thionyl perchloride, sulphuric oxyfluoride, phosphorous oxychloride, phosphorous oxy-fluoride, phosphorous thiofluoride or silicon fluorform[64], a quinone dioxide[65], basic acetylacetonate or manganese, cerium, nickel, cobalt or zinc[66], copper, iron, cobalt soaps[67], as well as the various agents referred to previously. It has been proposed that any excess catalyst be removed after the blowing operation by blowing the product with dilute hydrochloric acid and washing with hot water[68].

The use of various gases has been suggested for blowing through the melted asphalt including air under pressure[69], air followed by a mixture of air and steam in varying proportions under atmospheric or reduced pressure[70], carbon dioxide with or without air,[71] ozone[72], a mixture of air or oxygen with NO_2, or SO_2[73], a mixture of air and nitrogen oxides in the presence of HNO_3[74], carbon monoxide activated by a catalyst such as nickel or palladium, or by first heating the asphalt with cerium oxide or tin oxide and blowing as aforesaid[75], air containing up to 11.5% chlorine[76], chlorine in the presence of a "chlorine carrier" (eg: hexachlorethane[77]), chlorine followed by carbon dioxide[78], bromine or boron fluoride, air and halogens in the presence of sulphur[79], air containing a trace of a gaseous catalyst (eg: SeS, $SOCl_2$, SO_2F_2, $POCl_3$, PSF_3 $HSiF_3$ POF_3 etc.)[80], air containing a small amount of gaseous catalyst (eg: Cl_2, Cl_2O, COS, NO, NO_2, H_2S, SO_2, SO_3, ethyl mercaptan, n-butyl mercaptan ozone etc.[81]), air containing a trace of chlorine followed by heating with aluminium chloride etc[82].

The blowing of different mixtures has been suggested for the purpose of improving the characteristics of the finished product, in the way of imparting rubber like properties, greater toughness, increasing its resistance to temperature changes, augmenting its weather resistance etc. including the following, a mixture of semi asphaltic residual oil and fatty acid pitch, with or without gilsonite[83], a mixture of residual oil, pine tar and rubber[84], a mixture of residual asphalt to which latex is added[85], a mixture of residual asphalt with a phenolformaldehyde resin[86], a mixture of residual asphalt with naphthenic tar obtained upon the extraction of asphaltic or mixed base crude with phenol, furfural, cresylic acid, nitrobenzene, sulphur dioxide or the like[87], a mixture of native asphalt with the distillate obtained in the vacuum distallation of coal tar pitch[88], a mixture of residual oil or residual asphalt with vegetable drying oil[89], such as Soyabean oil[90], a mixture of residual oil and paraffin oil[91], a mixture of residual asphalt with cylinder oil stock[94], a mixture of residual asphalt and petrolatum blown with air in presence of $FeCl_3$[95], a mixture of blown asphalt, cylinder oil and calcium oleate or stearate[96], a mixture of gilsonite, residual asphalt, and fish oil pitch[97], a mixture of petroleum asphalt and peat tar[98], mixing the blown asphalt with a co-polymer of isobutylene and styrene[99], treating blown asphalt with an alkyl and an alkaline earth under heat[100], asphalt mixed with so called "soft wax" (micro crystaline wax) and lubricating oil[101], a mixture of asphalt with cracking still residue[102], blowing an aqueous-clay dispersion of residual oil with metallic driers at a comparatively low temperature[103] blowing asphalt containing a small percent of methyl polysiloxane is claimed to increase the flash point of the blown product[104] incorporating polymers of organo silicon oxide or organo Germanium oxide[105], and alternate procedure consists in heating asphalt with a substance which releases oxygen such as hydrogen peroxide, an alkyl peroxide, an arylperoxide, a tertiary butyl hydroperoxide etc.[106].

I.5 THE SCOPE OF THE PRESENT WORK

The main objectives of the investigations reported in the present thesis are the following: (1) to find out some industrial wastes as cheaper additives to augment the air-blowing polymerization process of bitumen. This will bring down the cost of production of industrial bitumen which can be applied for the manufacture of bitumenous paints, roofing and flooring materials etc. (2) to find out suitable promoters for the above additives. This will bring down the consumption of the additives (3) to help in the industrial pollution control (4) to investigate the usefulness of the industrial bitumen produced in the production of bituminous paints (5) to find out the kinetic parameters of the reactions invovled with different additives. This is essential for the design, construction and operation of new industrial bitumen plants using the additives investigated. This will also enable us to establish the mechanism of the reactions involved in the process.

Chapter 2

PILOT PLANT DESIGN AND CONSTRUCTION.

The Pilot Plant used to investigate the air-blowing polymerization process of bitumen is shown schematically in Fig.1. It was equipped with an air-flowmeter, air blowing tube, a reactor vessel, a scrubber and an exhaust pipe for the disposal of waste gases.

The compressed air from a compressor equipped with a constant pressure regulator was used for the air-blowing. The air-flowmeter used was a glass tube calibrated with a standard air-flowmeter.

The air-blowing tube was made of high carbon steel pipe and was conforming to the dimensions as given in Fig.2. There are six rows of air-holes, each row containing 20 numbers of air-holes kept at equal distance apart. It can be easily removed, cleaned and reused.

The reactor vessel was also made of high carbon steel. It was a cylindrical vessel with 12cm diameter and 48cm height. It is equipped with a valve on the top for the addition of raw material and chemicals. For drawing the samples at any desired time, a tap was provided at the bottom of the reactor. Electrical heating coils and a rheostat are provided to heat the

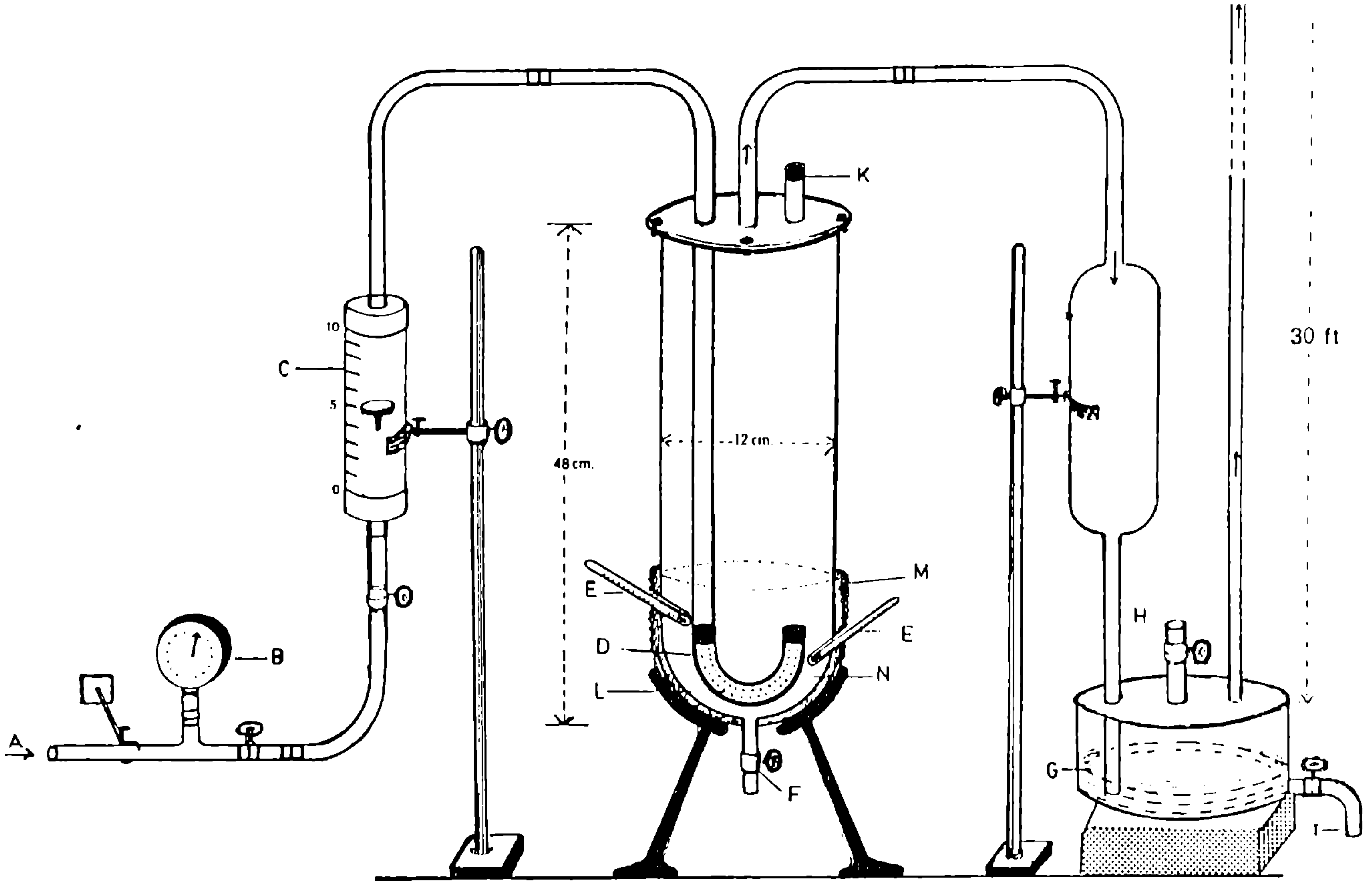
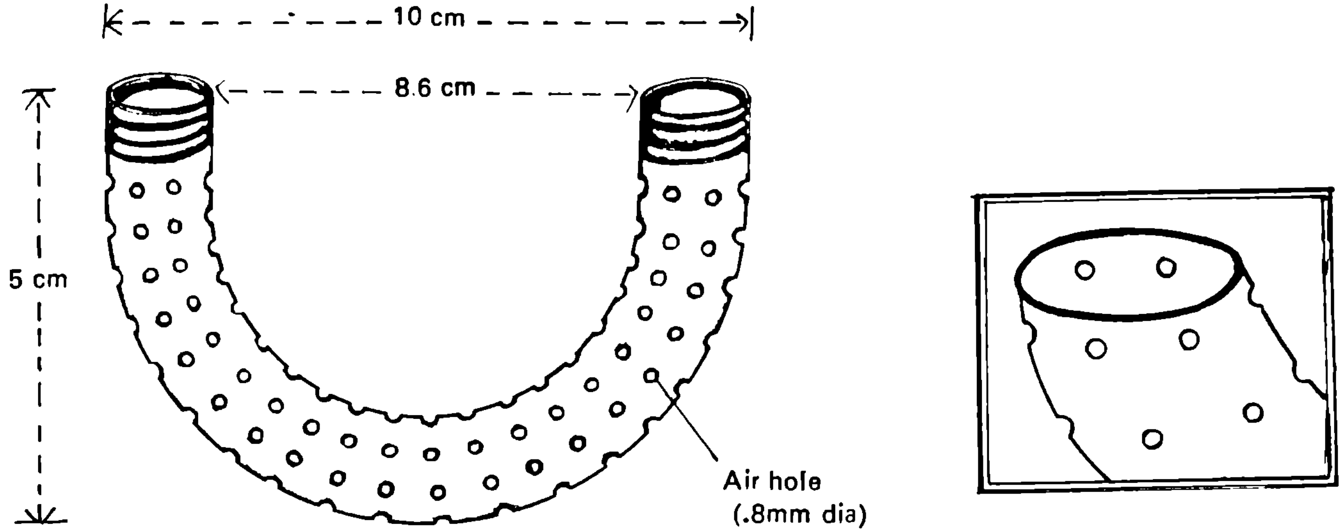


Fig. 1 PILOT PLANT USED FOR THE BITUMEN AIR-BLOWING



SIDE VIEW

CROSS SECTIONAL VIEW

Fig. 2 **AIR-BLOWING TUBE**

material taken in the reactor to any desired temperature and to keep it steady for any desired duration. The temperature of the material contained in the reactor can be read from the thermometers inserted through the sockets provided at the bottom of the reactor.

The scrubber is filled half with water. When the noxious exhaust waste gases pass through the scrubber a part of it get condensed and the remaining portion is allowed to escape into the atmosphere by means of a 30 ft. high pipe. After every run the water in the scrubber is drained off.

Chapter 3

MATERIALS AND EXPERIMENTAL METHODS

The materials used and the procedure of the experimental techniques adopted, are described in this chapter.

MATERIALS

1 The 80/100 paving bitumen derived by the vacuum distillation process was obtained by the courtesy of Cochin Refineries Ltd., Ambalamugal, Kerala.

2 The 80/100 paving bitumen made by the propane deasphalting process was obtained by the courtesy of Haldia Refinery Project, Indian Oil Corporation Ltd., Haldia, West Bengal.

3 Petroleum refinery caustic wash waste having 15% of sodium sulphide was obtained by the courtesy of Cochin Refineries Ltd., Ambalamugal, Kerala.

4 Waste PVC having a K value of 65 was obtained from Premier Cable Co. Ltd., Karukutty, Kerala.

5 Ferric chloride: Laboratory Reagent grade of Nesselers Laboratories was used.

6 Iron Powder: Laboratory Reagent grade of Ranbaxy Laboratories was used.

7 Manganese dioxide: Technical grade of B.D.H was used.

8 Potassium Permanganate: G.P.R. grade of B.D.H was used.

.9. Tetrahydrofuran: HPLC grade of E.Merck (India) Ltd. was used.

.10. Carbontetrachloride: Spectroscopic grade of Sisco Research Laboratories was used.

.11. Carbon di Sulphide: Laboratory Reagent grade of S.D. fine chemicals private Ltd. was used.

.12. Asbestos: Laboratory Reagent grade of Qualigens Fine Chemicals was used.

.13. Methanol: G.P.R grade of B.D.H was used.

.14. Trichloroethylene: G.P.R. grade of B.D.H. was used.

.15. Heptane: G.P.R. grade of B.D.H was used.

.16. Toulene: Laboratory Reagent (Rectified) grade of Ranbaxy Laboratories was used.

.17. Petroleum heavy Naphtha: Containing 25% aromatics obtained by the courtesy of Cochin Refineries Ltd., Ambalamugal was used.

.18. Cashew Nut Shell Liquid (CNSL) obtained from Indimin Sales Corp, Ahmedabad was used.

19. Formaldehyde: Formaldehyde Solution of B.D.H. (37%) was used for the investigation.

20 Hexamethylene diamine: Hexamethylene diamine of Riedel was used for the investigation.

EXPERIMENTAL PROCEDURES

1. Determination of the strength of sodium sulphide[107]

$$H_2S + I_2 \rightleftharpoons 2HI + S$$

For reasonably satisfactory results the sulphide solution must be sufficiently dilute (concentration not greater than 0.04%. Hence the test solution should be diluted accordingly) and the sulphide solution is added to excess of acidified 0.1N iodine and not conversely. Loss of Hydrogen sulphide is thus avoided and side reactions are almost entirely eliminated. (with solutions more concentrated than 0.04% the precipitated sulphur enclose a portion of the iodine and this escapes the subsequent titration with the standard sodium thiosulphate solution.) The excess of Iodine is then titrated with standard thiosulphate solution using starch as the indicator.

Method of air-blowing bitumen

The bitumen is heated to about 75-100°C above its softening point and then transferred 1 kg. of the material into the reactor. The bitumen is then heated to the desired temperature by means of electrical heating. The additive is then added through the valve provided for it. Compressed air from the line is then passed through the sample. The air-flow rate is then adjusted according to the requirement with the help of an air-flowmeter. The exhaust waste gases are passed through the scrubber and released to the atmosphere through the exhaust pipe. Samples are drawn at definite intervals of time and tested.

Determination of softening point (IS 1205-1958)

Softening point is the temperature at which the substance attains a particular degree of softening under specified conditions of the test.

Procedure: Heat the material to a temperature 75 to 100°C above its softening point. Stir until it is completely fluid and free from air bubbles and water and filter if necessary through IS sieve 30. Place the rings, previously heated to a temperature approximating to that of the molten material, on a metal plate which has been coated with a mixture of equal parts of glycerine and dextrose and fill with sufficient melt to give an excess above the level of the ring when cooled. After cooling for 30 minutes in air, level the material in the ring by removing the excess with a warmed sharp knife.

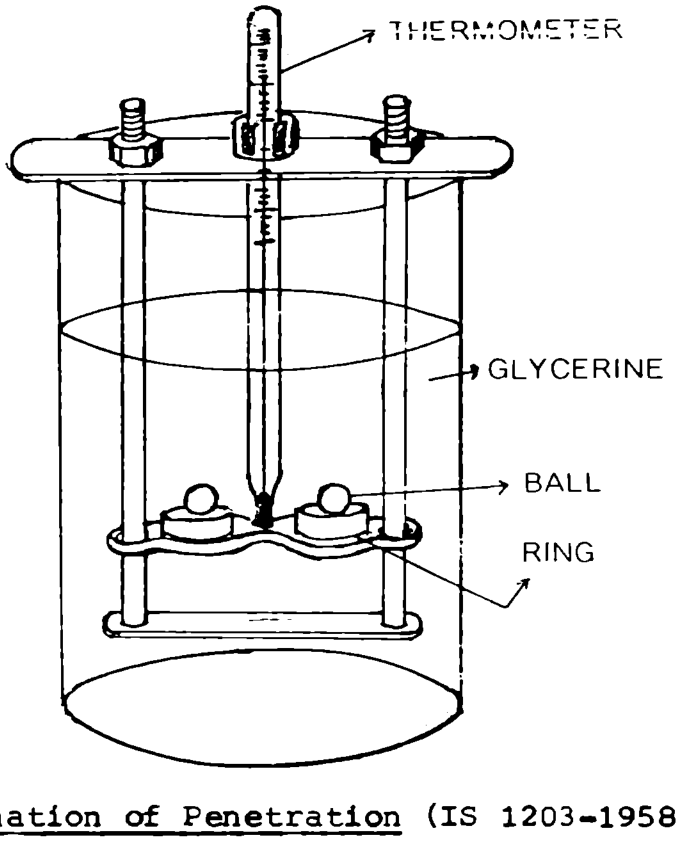
For materials of softening point below 80°C

Assemble the appratus with the rings, thermometer and ball guides in position, and fill the bath to a height of 50 mm above the upper surface of the rings with freshly boiled distilled water at a temperature of 5°C. Maintain the bath at a temperature of 5°C for 15 minutes after which place a ball previously cooled to a temperature of 5°C by means of forceps in each ball guide. Apply heat to the liquid and stir the bath so per minute until the material softens and allows the ball to pass through the ring.

For materials of softening point above 80°C

The procedure for materials of softening point above 80°C is similar to those below 80°C with the difference that glycerine is used in place of water in the bath and the starting temperature of the test is 35°C.

Record for each ring and ball the temperature shown by the thermometer at the instant the sample surrounding the ball touches the bottom plate of the support.

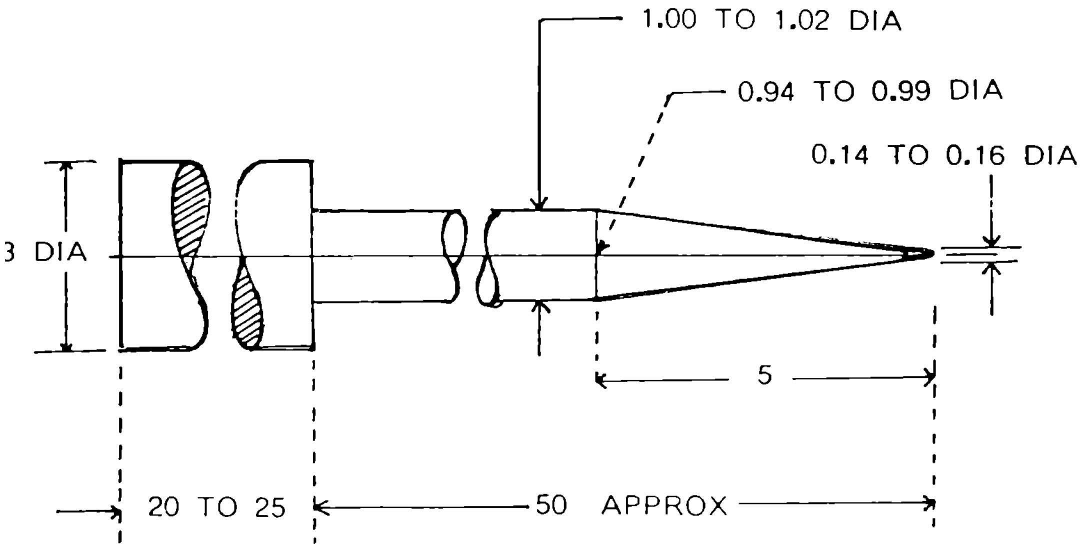


b.4. Determination of Penetration (IS 1203-1958)

Penetration is a measure of hardness or

hundredths of a centimetre) traversed by the point of a standard needle entering the material under the specified conditions of standard load, time and temperature.

The penetration needle is a highly polished, cylindrical hard steel rod, co-axial, having the shape, dimensions and tolerances given in the figure.



All dimensions in millimetres

The needle is provided with a shank approximately 3 mm in diameter into which it is immovably fixed. The taper shall be symmetrical and the point shall be 'blunted' by grinding to a truncated cone.

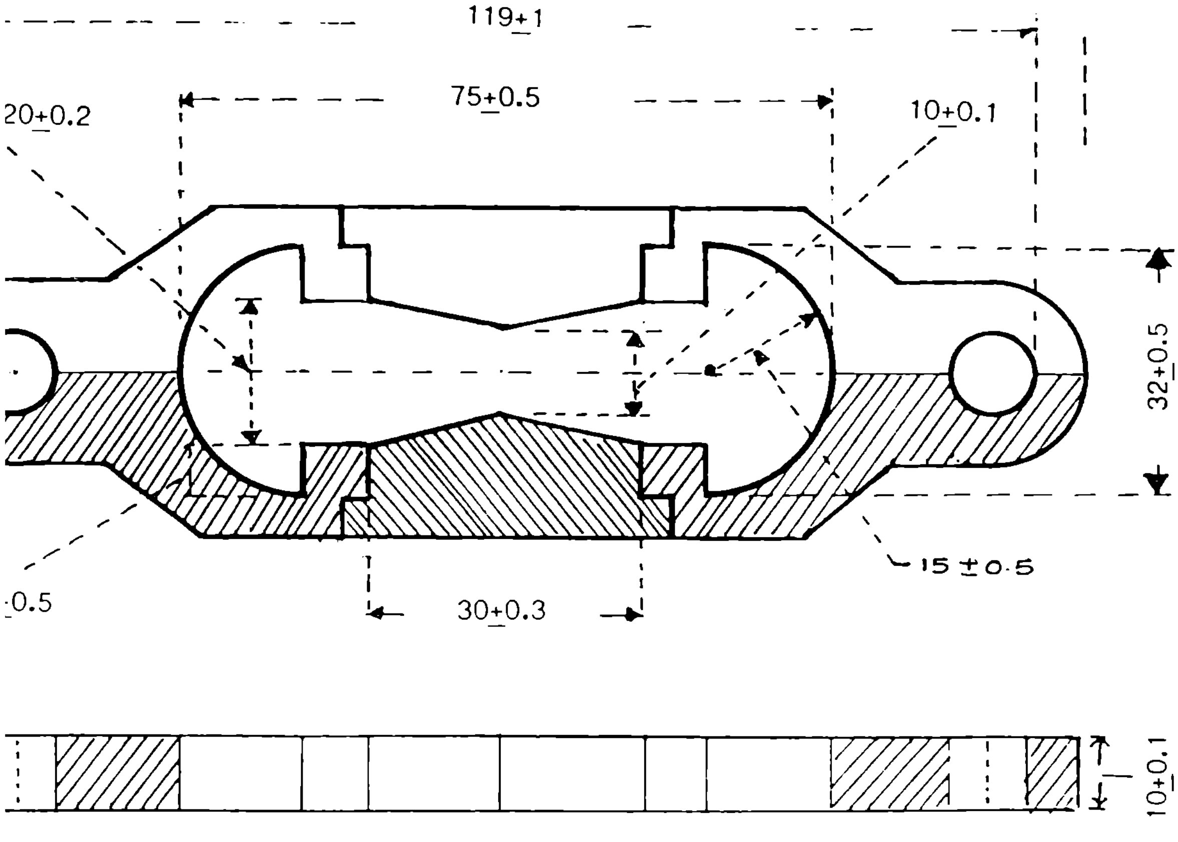
Procedure: Preparation of test sample. Soften the material to a pouring consistancy between 75°C and 100°C above the approximate softening point and stir it thoroughly until it is homogeneous and is free from to a depth at least 15 mm in excess of the expected penetration. Protect the sample from dust and allow it to cool in an atmosphere not less than 18°C for one hour. Then place it along with the transfer dish in the water bath at 25 ± 0.1°C and allow to remain for one hour. Fill the transfer dish with water from the water bath to a depth sufficient to cover the container completely. Place the sample in it and put it upon the stand of the penetration apparatus. Adjust the needle (previously washed clean with benzene, carefully dried) to make contact with the surface of the sample. The needle is loaded with the weight required to make a total moving weight (ie., the sum of the weights of the needle, carrier and superimposed weights) of 100+ 0.25gms.

Bring the pointer in the dial to zero. Release the needle for exactly five seconds. Measure the distance penetrated. Make at least three determinations at points on the surface of the sample not less than 10mm apart and not less than 10 mm from the side of the dish. The mean value of the three determinations is to be reported.

Determination of ductility (IS 1208-1958)

Ductility of a bituminous material is measured by the distance in centimeteres to which it elongate before breaking when the ends of a briquette specimen of the material of the specified form is pulled apart at a specified speed and at a specified temperature.

The test shall be conducted at a temperature of 27 ± 0.5°C and at a rate of pull of 50 ± 2.5 mm per minute. Completely melt the bituminous material to a temperature about 75°C to 100°C above the approximate softening point, until it becomes thoroughly fluid. Filter it through IS sieve 30 and then pour it to the mould as given in the figure.



All dimensions in millimetres

Assemble the mould on a brass plate and in order to prevent the material under test from sticking thoroof the sides of the mould with a mixture of equal parts of glycerine and dextrin. In filling, pour the material in a thin stream back and forth from end to end of the mould until it is more than level full. Leave to cool at room temperature for 30 to 40 minutes and then place in a water bath maintained at the specified temperature for 30 minutes after which cut off the excess bitumen by means of a hot, straight-edged knife so that mould shall be just level full.

Place the brass plate and mould with briquette specimen in the water bath and keep at 27±.5°C for about 85 to 95 minutes. Then remove the briquette from the plate, detach the side pieces and test the briquette immediately. Attach the rings at each end of the clips to the pins in the testing machine and pull the two rings apart horizontally at a uniform speed of 50±2.5mm per minute until the specimen rupture. The specific gravity of the water in the bath should be adjusted by the addition of sodium chloride so that the bituminous thread formed during the test does not touch the bottom of the bath at any time during the test. If the average of two tests does not differ by more than 5% of the mean, report the result.

Determination of specific gravity (IS 1202-1958)

Specific gravity is the ratio of the weight of a given volume of the material at a given temperature to the weight of the same volume of water at the same temperature.

Procedure: Clean, dry and weigh the specific gravity bottle together with the stopper (a). Fill it with freshly boiled, distilled water and insert the stopper firmly. Keep the bottle for not less than half an hour in a beaker of water maintained at a temperature of 27 ± $1^{o}C$. Wipe all the surplus moisture from the surface with a clean dry cloth and weig again (b).

Bring a small quantity of the material to a fluid condition by gentle application of heat, care being taken to prevent loss by evaporation. When this is sufficiently fluid, pour a quantity into the clean dry specific gravity bottle to fill it at least half. Slightly warm the bottle before filling. Keep the material from touching the sides above the final level of the bottle and avoid the inclusion of air bubbles. The use of a small funnel will prevent the contamination of the neck of the bottle. To permit escape of entangled air bubbles allow the partly filled bottle to stand for half an hour at a suitable temperature, and then cool to the specific temperature and weigh with the stopper (c). Now fill the remaining portion with distilled water maintain at the specified temperature for half an hour insert the stopper and weigh (d).

Calculation

$$\text{Specific gravity at } 27^{\circ}C = \frac{C - a}{(b-a) - (d-c)}$$

. Determination of flash point of bitumen (IS:1209-1958)

The flash point of a material is the lowest temperature at which the vapour of a substance momenterily takes fire in the form of a flash under the specified conditions of the test.

Pensky-Martens closed method is used for the determination of the flash point of bitumen. Clean and dry all parts of the cup and its accessories thoroughly before the test is started. Take particular care to avoid the presence of any solvent used to clean the apparatus after a previous test. Fill the cup with the material to be tested upto the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Take care that the locating devices are properly engaged. Insert the thermometer, light and adjust the test flame so that it is of the size of 4mm in diameter. Apply heat at such a rate that the temperature rises not less than 5°C and not more than 6°C per minute. Turn the stirrer at a rate of approximately 60 revolutions per minute.

Apply test flame at each temperature which is a multiple of 1°C upto 104°C. For the temperature range above 104°C apply the test flame at each temperature which is a multiple of 3°C, the first application of the test flame being made at a temperature at least 17°C below the actual flash point. Apply the test flame by operating the device controlling the shutter and test flame burner so that the test flame is lowered in 0.5 seconds, left in its lowered position for 1 second and quickly raised to its high position. Discontinue the stirring during the application of the test flame. The duplicate results should not differ by more than 3°C of the mean.

8. Determination of flash point of bituminous paints (IS: 101-1964: Cl.No.24)

It is determined by the Abel flash point apparatus. Fill the water bath to overflow with warm water, insert the water bath thermometer and adjust the bath temperature to 54°C at the beginning of the test. Don't apply heat to the water bath at any time during test. Adjust the temperature of the sample between 0° and 10°C. Place the cup on a level surface in good light and fill it with sample until the liquid just reaches the point of the gauge fixed to the wall of the cup. Place the cover with the slide closed on the cup and press it down so that its edge water bath. Insert the oil cup thermometer seating the collar firmly in the cover. Light the test flame and adjust its size to 4mm diameter. When the temperature of the oil reaches 18°C, apply the test flame by slowly opening the slide in the cover. Apply the test flame after every 0.5°C rise in temperature until a distinct flash occurs in the interior of the cup. Record the temperature of the sample when the flash occurs.

Determination of solubility in carbon-disulphide (IS: 1216-1958)

Procedure: Weigh about 2 gms of the dry material correct to the nearest 0.001 gm into a 200 ml conical flask and add 100 ml of carbondisulphide. Stirr the contents of the flask and then allow to stand loosely corked for a period of 1 hour. Filter the contents of the flask through the gooch crucible which has been weighed to the nearest 0.001 gm. Moisten the asbestos pad with carbon disulphide before commencing filteration and filter at a rate of more than 2 drops per second at first. Transfer the insoluble matter remaining in the flask to crucible by washing out the flask with a stream of carbon disulphide from a wash bottle. Wash the material retained in the crucible with successive small amounts of carbon disulphide until a filtrate is obtained which is not coloured. Allow the crucible to dry in air for 30 minutes after which, place it in an oven at 100°C for 1 hour. Allow the crucible to cool in dessicator and weigh.

Matter soluble in CS_2 per cent $= \frac{(W_1 - W_2)}{W_1} \times 100$

where W_1 = weight in gms of dry sample taken for the test and W_2 = weight in gms of insoluble material retained in gooch crucible.

- Determination of loss on heating (IS: 1212-1958)

Procedure: Heat the container in an oven at 100° to 110°C for 30 minutes, cool and weigh into the container 50.0 ± .5 gm of the material correct to the nearest 0.01 gm. Bring the oven to a temperature of 163 ± 1°C and place the sample container in the revolving shelf near the circumference. Close the oven and rotate the shelf during the entire test at a rate of 5 to 6 revolutions per minute, the temperature being maintained at 163 ± 1°C for 5 hours after the sample has been introduced. At the end of the specified heating period remove the containers, cool to the room temperature and weigh correct upto 0.01 gm. Report to the nearest 0.05% of the mean percentage loss in weight for the duplicate determinations.

- Determination of molecular weights by Gel Permeation Chromatography[108]

The carrier solvent used was THF at 25°C. The flow rate was set at 1 cc/minute. A column system of four columns (1-10^4, 2-400, and 1-100A^o) was used. The column packing used was Styragel. Anionically polymerised polystyrenes and polypropylene glycols were used as standards for calibration.

Determination of Carbon Hydrogen ratio

Carbon and hydrogen were determined gravimetrically as carbon dioxide and water respectively.[109]

Infra red analysis[110]

Both the Perkin-Elmer 21 and Infra cord Spectrophotometers equipped with sodium chloride prisms were used for the Infrared analyses. All fluid samples were run on sodium chloride plates with 0.05 mm teflon spacers. The solid samples were run in solutions using 0.10 gms of the sample to 10 ml of carbon tetra chloride in the region from 2.5 to 12 microns. For the solutions two 1.0 mm cells were used.

Determination of asphalt composition using solvent deasphaltening, elution-adsorption chromatography[111]

The procedure used is based upon solvent precipitation of asphaltenes followed by elution-adsorption chromatography of the petrolene fraction. Asphaltenes are first precipitated with a paraffin solvent at a high dilution ratio by the principle of disparity of molecular size and type between because of its purity and other properties that permit filtration steps without the precipitation of wax components. The chromatographic step involves the use of active alumina and elution solvents of increasing polarity.

Place 10 - 15 gm of sample in an Erlenmeyer flask and add 100 ml of n-pentane per gram of asphalt. Heat on steam bath while stirring, then let stand overnight. Filter slowly through Whatman No.1 paper in 12 cm Buchner and wash thoroughly with warm n-heptane until clear. Transfer insolubles to fresh heptane warm to 100°F, filter and wash again. Under a nitrogen atmoshere dry insolubles and weigh as asphaltenes. Concentrate petrolene heptane solution on steam bath to a volume of 50 ml. Prepare F-20 alumina by drying at 750°F for 16 hrs and store in tight glass containers. Add about 450 gms of alumina to 3.1 x 100cm chromatographic column with gentle tapping and immediately prewet with 50 ml of n-heptane. Follow prewet solvent with the 50 ml of petrolene solution and n-heptane eluant. Add more eluant and recover eluate according to the following schedule.

Eluant	Eluate Vol.ml	Fraction recovered
n-Heptane	200	Saturate
Benzene	100	Saturate
Benzene	300	Naphthene aromatics
Benzene-Methanol(1:1)	300	;;
Trichloroethylene	300	Polar aromatics
;;	;;	;;
;;	Hold up	;;

Combine eluates into tared 400 ml breakers and evaporate to dryness and constant weight using a steam bath and nitrogen purge. Weigh fractions to the nearest 0.01g and calculated weight percent.

Determination of drying time (IS: 101-1964 Cl No.7.2)

The material is brushed on 150 x 150 mm mild steel panel and allowed to air-dry under specified drying conditions.

Air-drying test was conducted at room temperature and relative humidity of 65 ± 5% in a well-ventilated chamber, free from draughts and dust, and the film exposed to diffused day light for at least six hours in each 24 hrs of drying period, care being taken to protect it from direct sunlight.

The material shall be examined after definite intervals for the following conditions.

) Surface dry

) hard dry

) tack free - the procedure of test on the dried film of the panel after a definite period is as follows.

ace the panel in one pan of a suitable balance and unterpoise it with weights. Place a further weight 2.25 kg and press on the dried film surface of the nel with the thumb till the two pans are balanced. ld for one minute and then slowly release. No sign stickiness to the thumb shall be apparent and the umb impression, if produced, shall be such as can be ped away with dry cotton wool.

termination of consistancy(IS: 101-1964 Cl.No.7.4)

Insert a clean metal rod into the original ntainer and examine the nature of settling. The terial shall not take hard inside the container and all be in such a condition that stirring easily produces smooth uniform paint suitable for application.

termination of finish (IS: 101-1964, Cl.No. 7.5)

The material, when applied on a mild steel panel brushing to give a dry film weight commensurate with e weight per 10 litre of the material as given below.

Weight of the wet material kg/10ℓ	Limits of dry film weights g/m
Upto 12	27 -34
from 12-14	34 -44
from 14-16	44 -54
from 16-18	54 -68
over 18	68 -80

The panel is allowed to dry in a vertical position under specified conditions, shall dry to a hard, firmly adherent, flexible and smooth film free from sagging and wrinkling with a matt, semi-glossy or glossy surface in accordance with the requirements of the material specification. The film so produced shall be of normal opacity and in no way inferior to a film prepared in the same manner and at the same time from the approved sample, when examined not earlier than 48 hrs and not later than 100 hrs after application.

<u>Determination of colour</u> (IS 101-1964, Cl.No. 11)

The material is brushed on a 150 x 150 mm mild steel plate in two normal coats. The second coat shall be applied after the first coat has become hard dry. The colour of the paint film shall be compared in diffused daylight with the specified colour 24 hrs after the application of the second coat. The colour of the paint film shall be a close match to the specified colour. Photoelectric reflectionmeter is used as an aid to objective measurement of colour and for recording reflectance characteristics of reflecting surfaces that are to be examined under normal diffused daylight. Any suitable photo-electric reflectionmeter using three filters, amber, green and blue along with I.C.I (International Commission on Illumination) illuminant may be used for this purpose.

Stripping test (IS: 101-1964 Cl No. 17)

Procedure: apply a coat of the material by brushing to a 150 x 50 mm, 0.315mm tinned plate to give a dry film. Allow the panel to air-dry in a horizontal position for 48 hrs under the specified drying conditions. Test the dried film in the apparatus under such a load that scratch is produced showing the bare metal surface. The scratch so produced shall be free from jagged edges.

Determination of Flexibility and adhesion
(IS: 101-1964, Cl No. 16)

Procedure: Apply a coat of material by brushing to a 100 x 50 x.0315mm tinned plate, to give a dry film weight commensurate with the weight per 10 litres of the material as already prescribed in III b (17). Allow panel to air dry in a horizontal position. After air drying, bend the panel double 44.5mm from the upper edge over a 6.25mm diameter rod with the paint film outside. Close the hinge in a regular manner without jerking in not less than 1 second and not more than 1½ seconds. Remove the panel carefully from the hinge. The paint film shall not show damage, detachment or cracking when examined under x 10 magnification.

Protection against corrosion under conditions of condensation (IS: 101-1964 Cl No. 18)

Procedure: Clean the metal panel. Apply one coat of the paint on both sides of the mild steel panel to give a dry film weight of the material as specified in III b (17). Keep the painted panel in a vertical position at room temperature for 24 hrs to air dry and then at a temperature of 60 - 65°C for one hour. Cool the panel to room temperature and protect the edge to a depth of 5mm with a suitable protecting composition (consisting of 3 parts by weight of paraffin wax and 1 part by weight of Carnauba wax) which shall have melting point above 50°C and then suspend it vertically in corrosion cabinet. After exposure under these conditions for seven days, remove the panel and examine for signs of deterioration of the paint film. Remove 25mm strip of the film from the centre of the panel carefully with a non-corrosive paint remover neglecting 25mm portion of the exposed surfaces from each end and examine the exposed metal for signs of corrosion.

The metal surface shall show no sign of corrosion; changes in appearance and condition of the paint film shall not be taken into consideration in deciding about acceptability.

Keeping properties of paints (IS: 101-1964 Cl No.31)

When stored under cover in a dry place in the original sealed container under normal temperature conditions the material shall retain the properties prescribed in the material specifications for one year after the date of manufacture.

Determine the water resistance of paints (IS: 158-1968 appendix A)

Apply a coat of the material, by brushing to the inside surface of a clean tin container, with a lever lid, 125 mm high and 90 mm in diameter, to give a dry film weight commensurate with the weight in kg/10ℓ of the material as specified in III b (17). Allow the paint film to air dry for seven days. At the end of this period store water in the container for 24 hrs and then rinse the container thoroughly with water. Then fill the container with water. Allow the water to remain in contact with the paint film for 3 days with lid closed. Examine the water for odour and taste at the end of this period. Then take the water from the container in a beaker, heat it to boiling, cool it and again examine for odour and test if the paint film remains firmly adherent and imparts no unpleasant odour or taste to water.

Determination of resistance to acid (IS: 158-1968 App.B)

Apply a coat of the material by brushing, to a 150 x 50 mm clean glass panel to give a dry film weight commensurate with the weight in kg/10ℓ of the material as specified in III b (17). Allow the panel to air dry in a horizontal position for 24 hrs under standard conditions. Immerse a panel partially in dilute sulphuric acid (1:20 v/v) for 24 hrs. Take out the panel wash carefully and examine the immersed portion of the film after drying for one hour. The material shall be deemed to have passed the test if the paint film on the panel shows no signs of softening, blistering, cracking, dulling or change of colour.

Determination of resistance to alkali

(IS: 158-1968 Appendix C)

Partially immerse a panel, prepared as described in III b (24) in the aqueous solution of sodium carbonate (5% anhydrous sodium carbonate in water w/v) for four hrs. Take out the panel, wash and examine the immersed portion of the film after drying for one hour. The material shall be deemed to have passed the test if the paint film for the panel shows no signs of softening, blistering, cracking, dulling or change of colour.

Resistance to chlorine (IS: 158-1968 Appendix D)

Immerse three quarters of a panel prepared as prescribed in III b (24), in chlorine water (0.05% w/v) in a suitable glass container, which is either covered with black paper or painted outisde with black paint and keep in a dark place for 72 hrs. After this period take out the panel wash and examine the immersed portion of the film after drying for 24 hrs. The material shall be deemed to have passed the test if the paint on the panel shows no blistering and cracking. Sunlight dulling and change of colour shall not be a cause of rejection.

Determination of resistance to heat
(IS: 158-1968 Appendix E)

Apply a coat of the material by brushing, to a 150x100x0.800 mm clean mild steel panel to give a dry film weight commensurate with the weight in kg/10ℓ of the material as prescribed III b (17). Allow the panel to air dry in a horizontal position for 24 hrs. Heat the panel in a vertical position in an electrical furnace the temperature of which is gradually raised from room temperature upto a temperature of 300°C in one and half hrs time. Maintain the panel at the max. temperature of 300°C for half an hour. Remove the panel from the furnace, cool to room temperature and immerse in water at room temperature for 24 hrs. Take out the panel and examine it after air drying for one hr. The material shall be deemed to have passed the test if the film remains firmly adherent and shows no sign of cracking, blistering or flaking. Formation of hairlines shall not be a cause of rejection.

Chapter 4

UTILIZATION OF PETROLEUM REFINERY CAUSTIC WASH WASTE FOR THE MANUFACTURE OF INDUSTRIAL BITUMEN

INTRODUCTION

Industrial bitumen of various grades are manufactured by the air-blowing polymerization of paving bitumen in presence of additives like Phospherous pentoxide, Ferric chloride etc. Paving bitumen is manufactured mainly by two different processes (1) by the vacuum distillation process and (2) by the propane deasphalting process. The additives used for the bitumen air-blowing are costly and hence the high cost of production of industrial bitumen. This necessitated the development of cheaper additives that will make the process an economic one.

IV(a).1 AIR-BLOWING OF BITUMEN WITHOUT ANY ADDITIVE

EXPERIMENTAL

Paving bitumen (80/100 grade) obtained by the vacuum distillation process (Cochin Refinery) and by the propane deasphalting process (Haldia Refinery) were used as the raw materials.

The raw material is heated to around 125°C, made homogenous by stirring with a glass rod, and one Kg of the material is transferred to the reactor as described in Chapter II. By means of electrical heating the material in the reactor is heated to 220°C and made to remain steady at that temperature

COCHIN PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 220 °C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

uration f blow-ng hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1	1.011	53	25	20	$>$300	99.95	$<$0.01
2	1.013	60	21	10	$>$300	99.92	$<$0.01
3	1.016	69	16	8	$>$300	99.89	$<$0.01
4	1.020	77	12	6	$>$300	99.85	$<$0.01
4.5	1.022	85	9	4	$>$300	99.83	$<$0.01
5	1.025	91	7	3	$>$300	99.81	$<$0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 240°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow-g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1	1.012	56	20	10	$>$ 300	99.94	$<$0.01
2	1.015	69	17	7	$>$300	99.90	$<$0.01
3	1.019	83	6	3	$>$300	99.86	$<$0.01
4	1.024	103	0	0	$>$ 300	99.81	$<$0.01
4.5	1.027	112	0	0	$>$ 300	99.78	$<$0.01
5	1.030	123	0	0	$>$300	99.76	$<$0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 260°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1	1.013	60	15	6	$>$300	99.93	$<$0.01
2	1.017	80	5	1	$>$300	99.85	$<$0.01
3	1.022	106	0	0	$>$300	99.80	$<$0.01
4	1.028	138	0	0	$>$300	99.74	$<$0.01
4.5	1.031	155	0	0	$>$300	99.71	$<$0.01
5	1.035	174	0	0	$>$300	99.68	$<$0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 220^{o}C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ation blow- hrs.	Specific gravity @ 27^{o}C	Softening point ^{o}C	Penetration 1/10 mm	Ductility cm	Flash point ^{o}C	Solubility in CS$_2$ % wt.	Loss on heating % wt.
1	1.016	49	25	19	$>$300	99.94	$<$0.01
2	1.018	54	21	14	$>$300	99.90	$<$0.01
3	1.021	61	17	9	$>$300	99.87	$<$0.01
4	1.025	67	13	7	$>$300	99.83	$<$0.01
5	1.030	75	9	5	$>$300	99.79	$<$0.01
6	1.036	84	5	3	$>$300	99.72	$<$0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 240°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

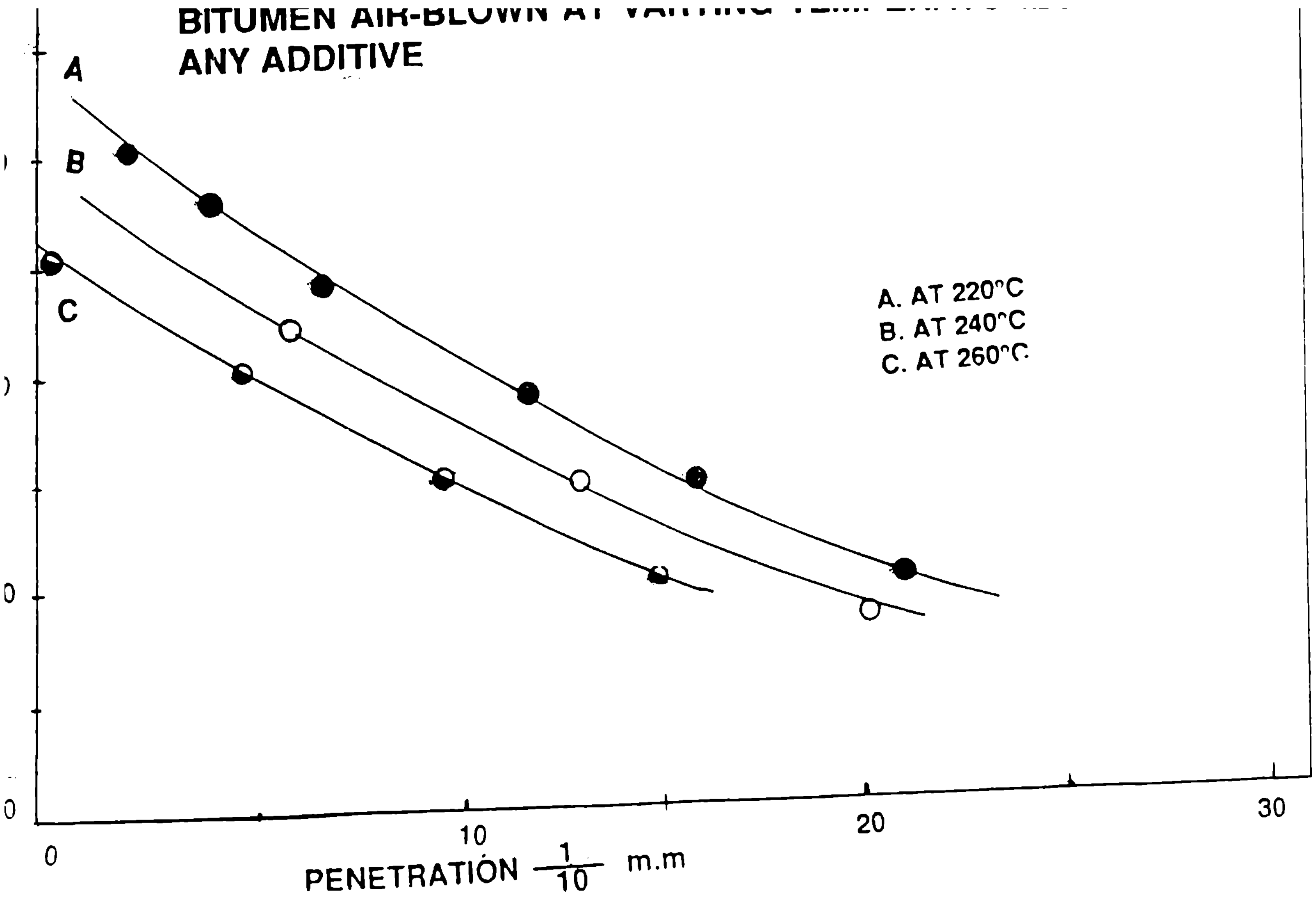
ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubi- lity in CS_2 % wt.	Loss on heating % wt.
1	1.017	51	21	14	>300	99.93	<0.01
2	1.020	59	15	8	>300	99.89	<0.01
2.5	1.022	64	11	6	>300	99.86	<0.01
3	1.024	69	9	4	>300	99.84	<0.01
4	1.029	81	4	2	>300	99.79	<0.01
5	1.035	95	0	0	>300	99.74	<0.01

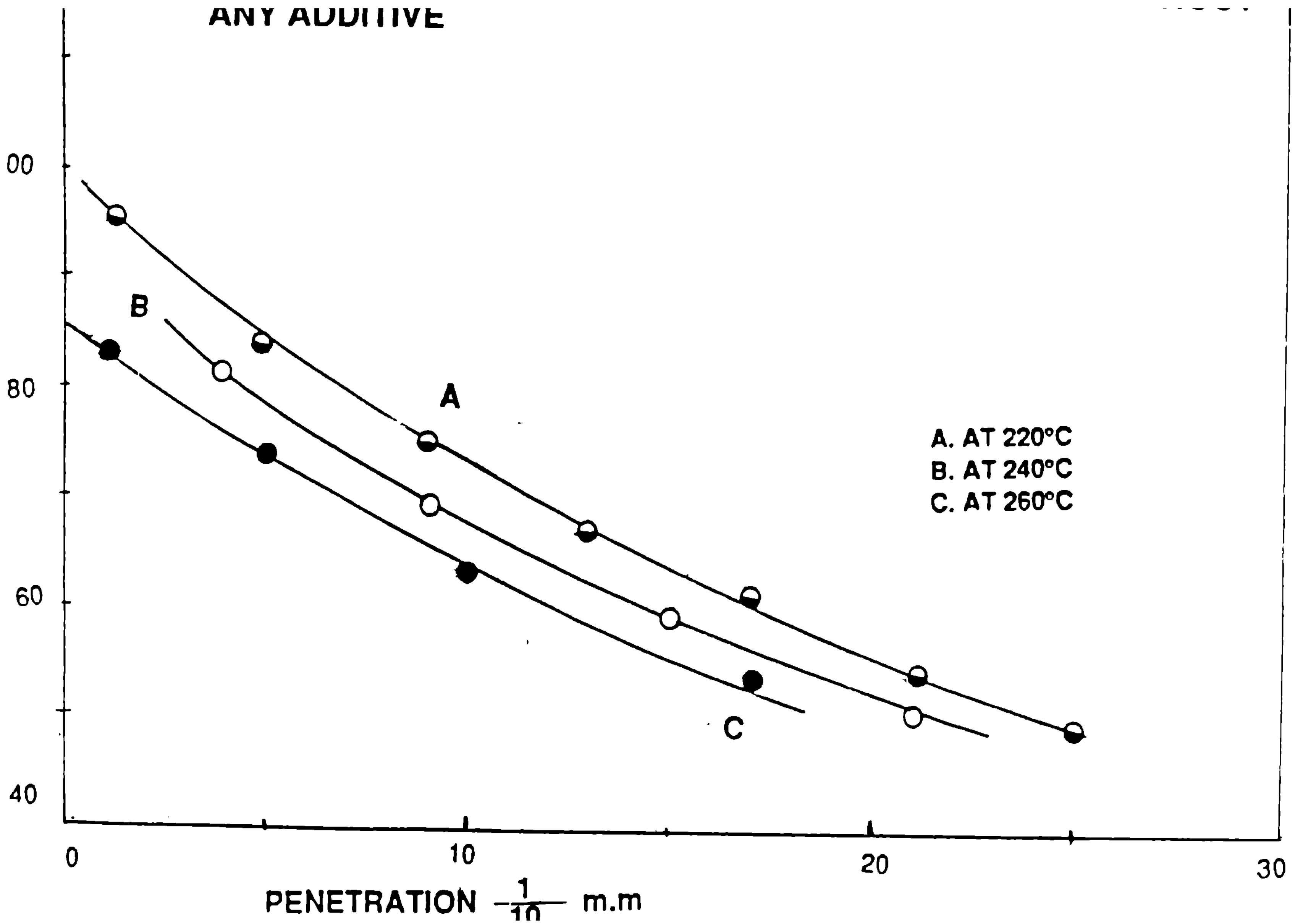
HALDIA PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT 260°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow-g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1	1.018	54	17	9	>300	99.92	<0.01
2	1.022	66	10	6	>300	99.83	<0.01
2.5	1.024	70	5	2	>300	99.81	<0.01
3	1.027	83	1	0	>300	99.78	<0.01
4	1.033	98	0	0	>300	99.72	<0.01
5	1.040	122	0	0	>300	99.65	<0.01

BITUMEN AIR-BLOWN AT VARYING
ANY ADDITIVE




ANY ADDITIVE
00
80
60
40
0
10
20
30
PENETRATION $\frac{1}{10}$ m.m
A
B
C
A. AT 220°C
B. AT 240°C
C. AT 260°C

by means of a rheostat. Air is then blown into the material by means of an air-blowing tube and adjusted the rate of flow of air to be 5ℓ per min. per kg. sample with the help of the regulator provided on the air-flow meter. Samples are drawn at definite intervals of time and tested. The process was repeated at 240°C and 260°C also.

RESULTS AND DISCUSSION

The results are given in Tables 1 to 6. The effect of temperature on the softening-point penetration relationship are given in Figs.1 & 2.

From tables 1 to 6 it is clear that the polymerization process is very slow and hence not economical. Another observation is that the rate of conversion of Haldia bitumen is poor compared to that of Cochin bitumen Hence Haldia bitumen requires a longer air-blowing time compared to Cochin bitumen. It is of course possible to increase the rate of conversion by raising the temperature of the process. But it has a drawback that it resul in products of poor softening point-penetration relationship as it is evident from Fig.1 & 2. According to the IS 702-1961 there are different grades of industrial bitumen depending upon the softening point-penetration relationship. They are mainly 75/30, 85/25, 85/40, 90/15, 105/25, 115/15, 135/10 and 155/6.

the second one penetration. A grade 75/30 should have the softening point between 70 to 80 and penetration between 25 to 35). From Figs. 1 & 2 it is clear that the manufacture of the different grades of industrial bitumen by air-blowing without any additive is impossible.

IV(a).2 AIR-BLOWING OF BITUMEN IN PRESENCE OF PETROLEUM REFINERY CAUSTIC WASH WASTE

In Petroleum Refineries, hydrogen sulphide present in liquified petroleum gas and naphtha fractions is removed by the caustic washing process. An aqueous solution of sodium hydroxide of strength 10 to 20% is used for this purpose. Hydrogen sulphide reacts with caustic soda resulting in the formation of sodium sulphide

$$2\ \mathrm{Na\ OH} + H_2S \underset{\text{above } 50^{\circ}\mathrm{C}}{\overset{\text{below } 50^{\circ}\mathrm{C}}{\rightleftharpoons}} Na_2S + 2H_2O$$

Caustic wash is then discharged to the waste water treatment sytem and then disposed to the inland waters. It was thought worthwhile to examine whether the sodium sulphide present in the caustic wash waste could function as an additive in the industrial bitumen manufacture.

TABLE - 7

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2.0% SODIUM SULPHIDE @ 220°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point°C	Solubility in CS_2 % wt.	Loss on heating % wt.
.5	1.017	53	59	70	>300	99.86	<0.01
.0	1.020	61	56	67	>300	99.82	<0.01
.5	1.023	70	46	59	>300	99.77	<0.01
.0	1.027	80	38	52	>300	99.71	<0.01
.5	1.031	92	31	22	>300	99.65	<0.01
.0	1.037	105	26	15	>300	99.59	<0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2.0% SODIUM SULPHIDE AT 240°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
0.5	1.018	55	53	66	>300	99.85	<0.01
1.0	1.021	67	37	50	>300	99.81	<0.01
1.5	1.024	79	28	19	>300	99.76	<0.01
2.0	1.030	96	19	12	>300	99.66	<0.01
2.5	1.036	115	11	6	>300	99.54	<0.01
3.0	1.042	138	5	4	>300	99.46	<0.01
3.3	1.046	154	1	0.5	>300	99.39	<0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2.0% SODIUM SULPHIDE AT 260°C

THE AIR-FLOW RATE BEING 5 $L\ MIN^{-1}$ PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
.5	1.019	58	35	45	>300	99.86	<0.01
.0	1.022	71	27	19	>300	99.79	<0.01
.5	1.027	91	16	9	>300	99.64	<0.01
.0	1.033	113	6	3	>300	99.54	<0.01
.5	1.040	140	0	0	>300	99.44	<0.01
.0	1.047	175	0	0	>300	99.36	<0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITH 2.0% SODIUM SULPHIDE AT 220°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
.0	1.025	54	53	64	>300	99.81	<0.01
.0	1.027	67	43	52	>300	99.76	<0.01
.0	1.032	80	35	28	>300	99.68	<0.01
.0	1.037	101	22	12.5	>300	99.62	<0.01
.5	1.039	112	18	9.5	>300	99.54	<0.01
.0	1.049	158	1	0.5	>300	99.42	<0.01

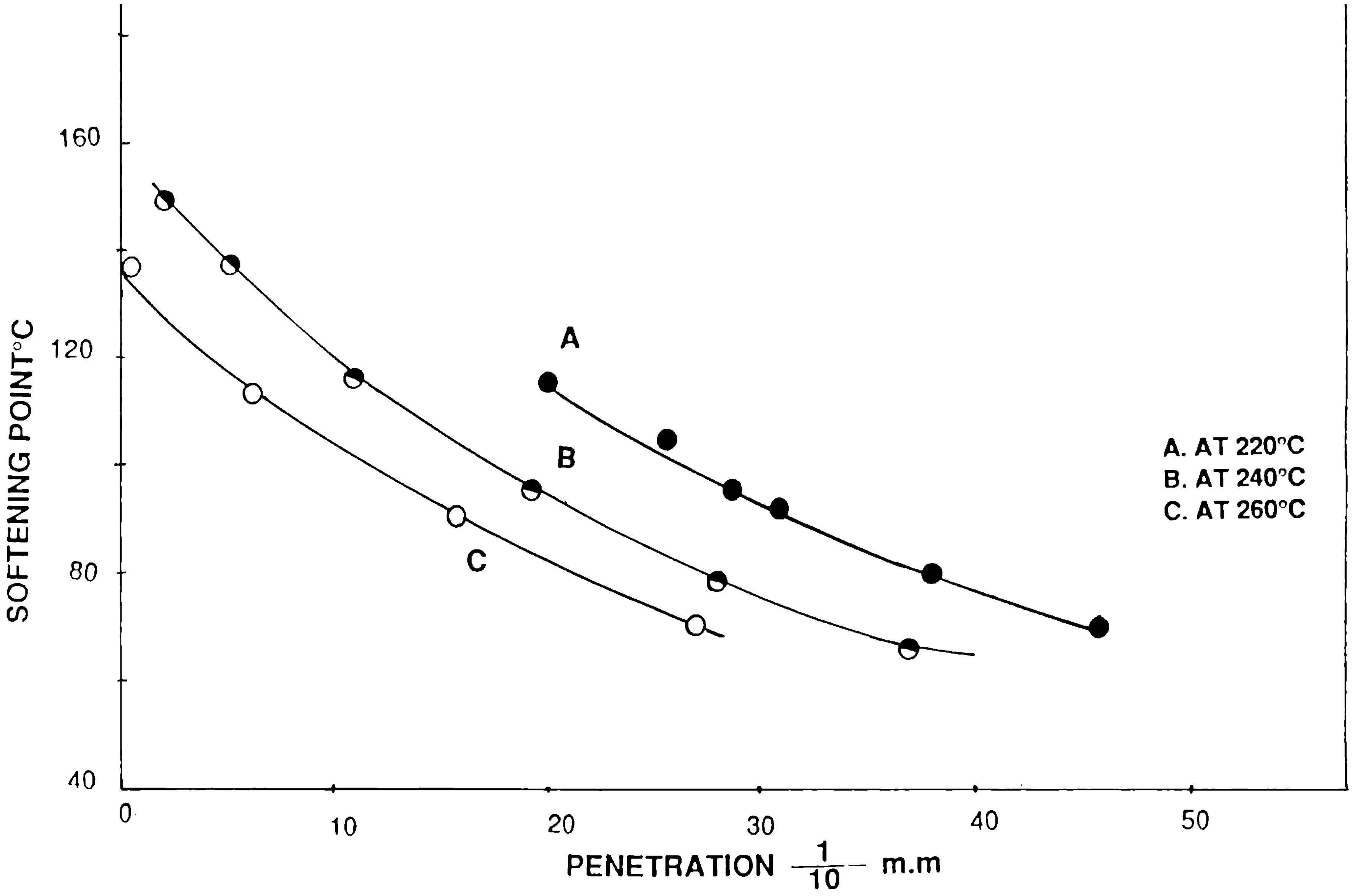
THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

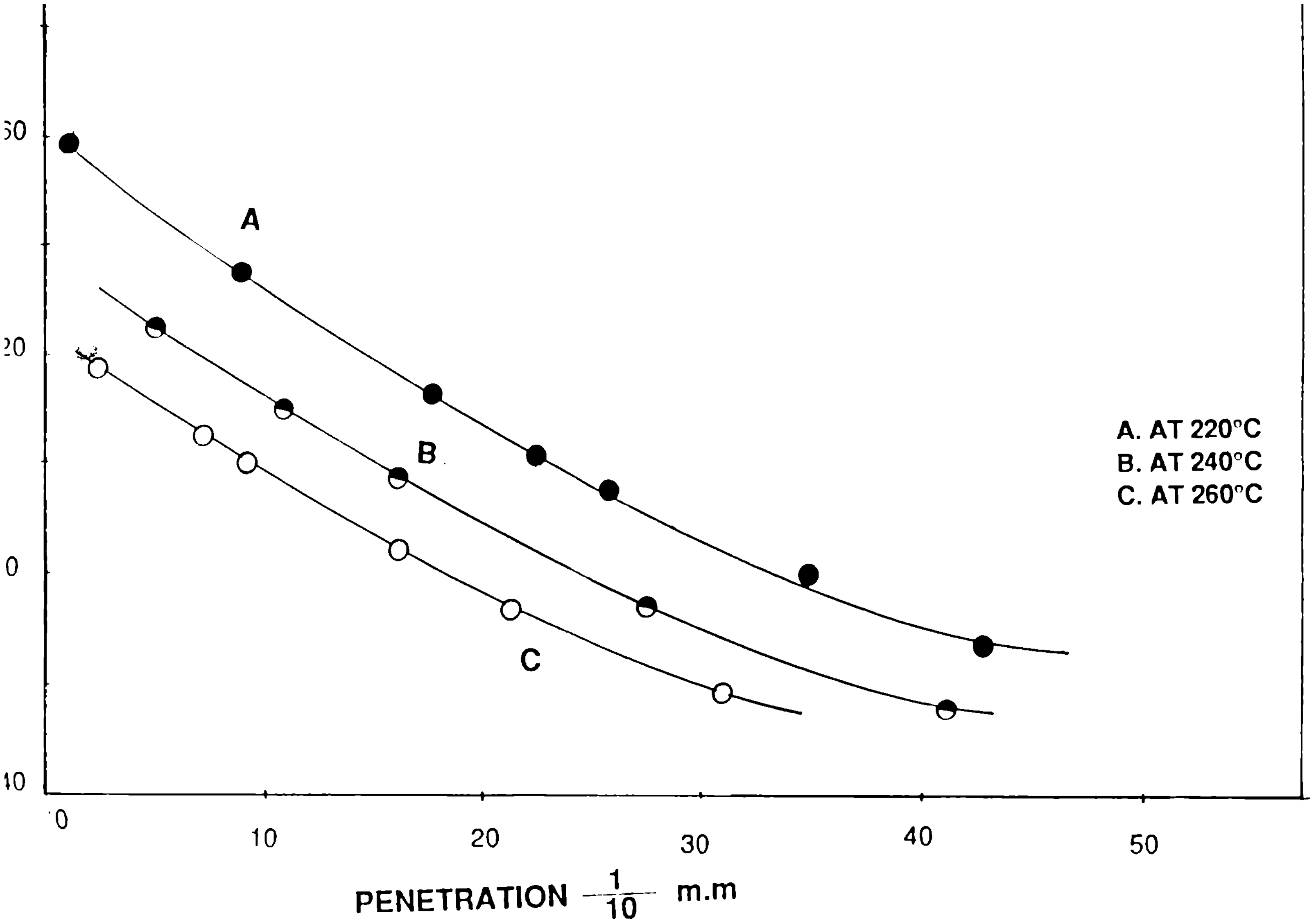
ation blow- hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
.0	1.026	58	41	50	>300	99.79	<0.01
.0	1.030	75	30	19	>300	99.72	<0.01
.0	1.035	98	16	8	>300	99.59	<0.01
.5	1.037	110	11	5	>300	99.54	<0.01
.0	1.040	125	5	2.5	>300	99.49	<0.01
.5	1.044	150	0	0	>300	99.42	<0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITH 2.0% SODIUM SULPHIDE AT 260°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
.0	1.027	61	30	20	>300	99.76	<0.01
.0	1.032	85	16	8	>300	99.74	<0.01
.5	1.035	101	9	4.5	>300	99.60	<0.01
.0	1.038	118	2	1.0	>300	99.44	<0.01
.0	1.048	165	0	0	>300	99.34	<0.01


A
B
C
A. AT 220°C
B. AT 240°C
C. AT 260°C
SOFTENING POINT°C
160
120
80
40
0
10
20
30
40
50
PENETRATION $\frac{1}{10}$ m.m


30
20
0
40
0
10
20
30
40
50
PENETRATION $\frac{1}{10}$ m.m
A
B
C
A. AT 220°C
B. AT 240°C
C. AT 260°C

EXPERIMENTAL

The raw materials are air-blown with Petroleum refinery caustic wash waste containing 2.0% Sodium sulphide at varying temperatures, the air flow rate being 5ℓ/min/kg sample.

RESULTS AND DISCUSSION

The results are given in Tables 7 to 12. The softening point penetration relationship of the blown bitumen are given in Fig. 3 & 4.

From Tables 7 to 12 it is evident that there is a considerable increase in the rate of conversion. Air blowing in presence of 2% sodium sulphide at 220°C reduces the air-blowing time by about 60% as compared to that without any additive. Another observation is that, Cochin bitumen requires lesser air blowing time than Haldia bitumen. A comparative study of Figs. 1 to 4 makes it clear that there is considerable improvement in the softening point penetration relationship compared to the air blown product without any additive. In this case also with rise in temperature the softening point-penetration relationship of the air-blown product deteriorates. This is attributed to the blowing losses of oil that become considerable as the temperature increases. This is also in agreement with the observations already made by Lockwood[112] and Hoiberg[113]. But by suitably selecting the temperature of air blowing it is easily possible to make all the ten different grades of industrial bitumen. Another observation is that compared to the air-blown products from Haldia bitumen the Cochin bitumen possesses better softening point-penetration relationship.

IV(a).3 AIR-BLOWING OF BITUMEN IN PRESENCE OF FERRIC CHLORIDE

Ferric chloride is a widely used additive for the manufacture of Industrial Bitumen. So it was thought worthwhile to compare the efficacy of sodium sulphide with that of the conventional additive ferric chloride.

EXPERIMENTAL

One kg. of the raw material was heated to 220°C added 0.75% ferric chloride and air-blown at the rate of 51 /minute / kg of raw material. The air-blowing process was repeated at temperatures 240 and 260°C in a similar manner.

RESULTS AND DISCUSSION

The results are presented in Tables 13 to 18. The softening point penetration relationship of the products are given in Figs. 5 and 6. From the results it is evident that sodium sulphide is equally effective as Ferric chloride in reducing the air blowing period. Figs. 3 to 6 show that Sodium sulphide is equally effective in improving the softening point-penetration

COCHIN PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 220°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubi- lity in CS_2 % wt.	Loss on heating % wt.
.5	1.020	54	63	73	>300	99.85	<0.01
.0	1.022	62	60	70	>300	99.81	<0.01
.5	1.025	73	47	59	>300	99.76	<0.01
.0	1,028	86	37	52	>300	99.69	<0.01
.5	1.033	99	31	22	>300	99.62	<0.01
.0	1.039	116	24	15	>300	99.56	<0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 240°C THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
0.5	1.021	56	55	66	>300	99.84	<0.01
1.0	1.024	69	38	52	>300	99.80	<0.01
1.5	1.028	84	28	20	>300	99.74	<0.01
2.0	1.033	100	20	12.5	>300	99.66	<0.01
2.5	1.038	126	10	5.5	>300	99.59	<0.01
3.0	1.045	154	1	0.5	>300	99.51	<0.01

COCHIN PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 260°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubi- lity in CS_2 % wt.	Loss on heating % wt.
).5	1.022	59	37	49	>300	99.82	<0.01
l.0	1.025	75	27	18	>300	99.77	<0.01
l.5	1.030	84	22	14	>300	99.71	<0.01
2.0	1.034	120	7	3	>300	99.63	<0.01
2.5	1.042	155	2	1	>300	99.55	<0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 220°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
.0	1.028	56	55	64	>300	99.81	<0.01
.0	1.031	70	42	50	>300	99.74	<0.01
.0	1.035	89	33	28	>300	99.65	<0.01
.5	1.038	97	28	17	>300	99.58	<0.01
.0	1.040	115	20	11	>300	99.46	<0.01
.5	1.048	150	4	2.0	>300	99.36	<0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 240°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG. SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1.0	1.029	59	42	62	>300	99.77	<0.01
2.0	1.033	77	29	17	>300	99.69	<0.01
2.5	1.035	89	22	13	>300	99.64	<0.01
3.0	1.038	102	15	7.0	>300	99.59	<0.01
3.5	1.041	120	10	5.0	>300	99.49	<0.01
4.0	1.044	138	4	2.0	>300	99.44	<0.01

HALDIA PAVING BITUMEN AIR-BLOWN WITH 0.75% FERRIC CHLORIDE AT 260°C

THE AIR-FLOW RATE BEING 5 L MIN^{-1} PER KG SAMPLE

ration blow- g hrs.	Specific gravity @ 27°C	Softening point °C	Penetration 1/10 mm	Ductility cm	Flash point °C	Solubility in CS_2 % wt.	Loss on heating % wt.
1.0	1.030	62	31	15.0	>300	99.76	<0.01
2.0	1.035	85	13	5.5	>300	99.68	<0.01
2.5	1.037	102	10	2.5	>300	99.63	<0.01
3.0	1.040	125	3	1.0	>300	99.58	<0.01
3.5	1.045	148	0	0	>300	99.47	<0.01
4.0	1.048	175	0	0	>300	99.42	<0.01

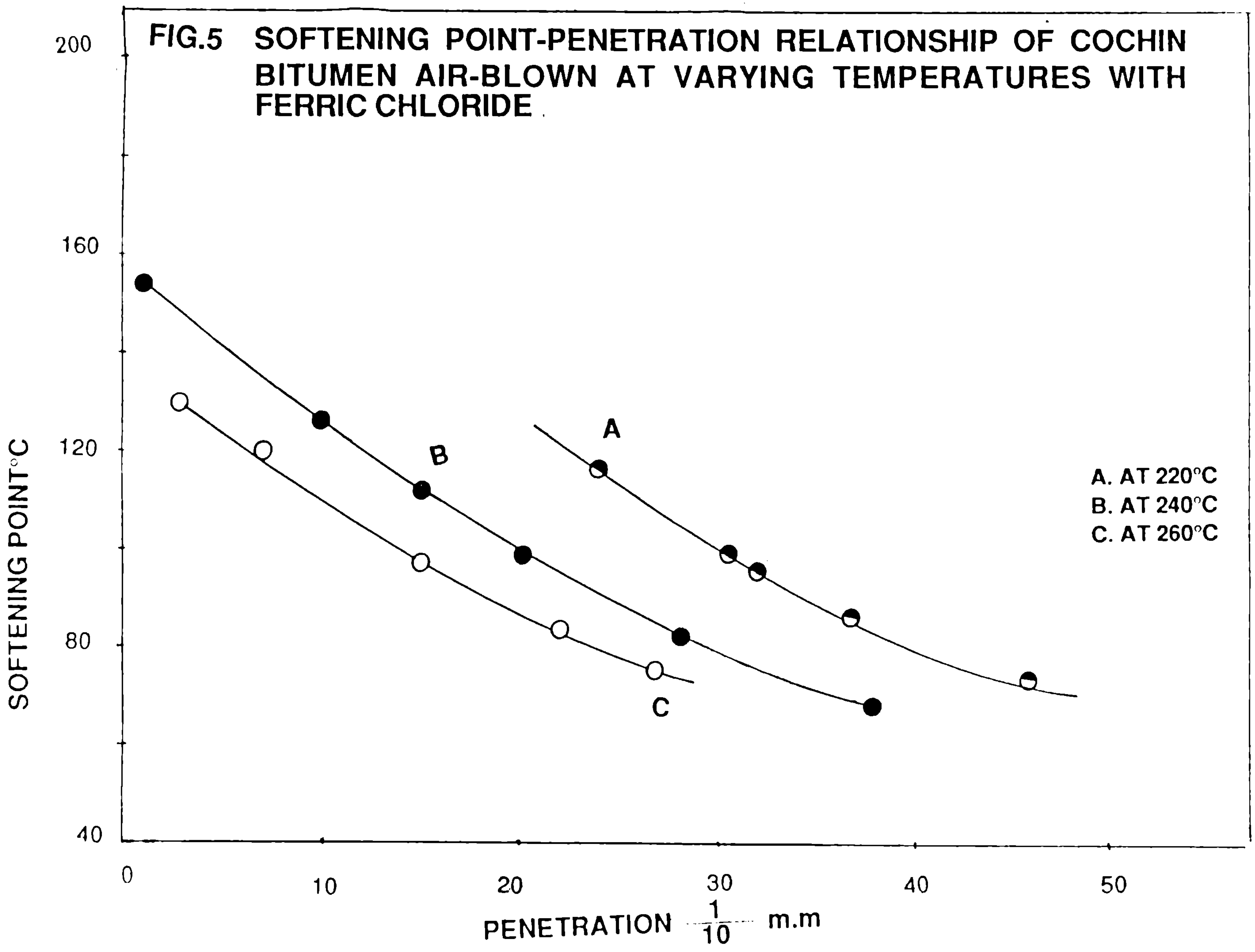
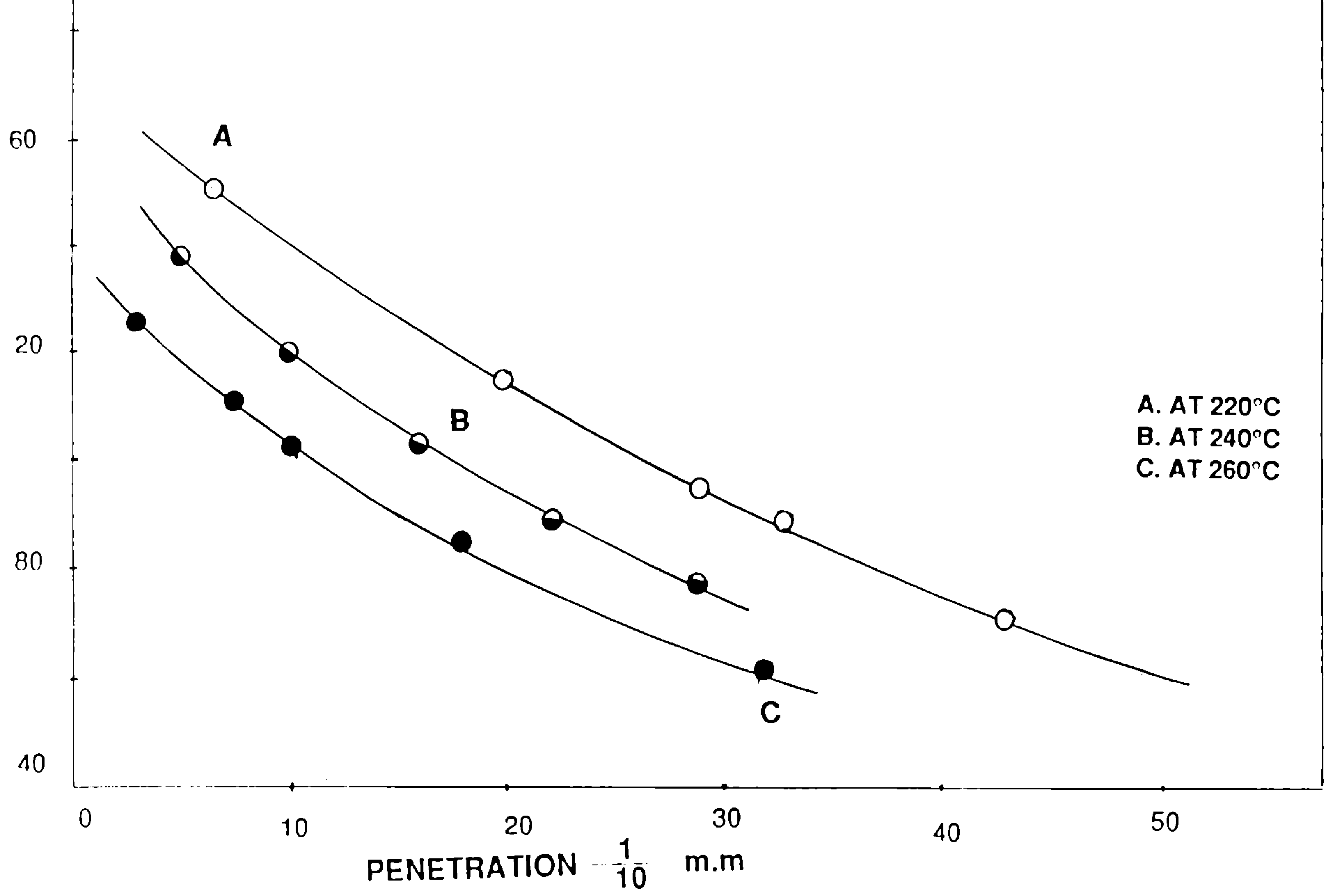


FIG.5 SOFTENING POINT-PENETRATION RELATIONSHIP OF COCHIN BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH FERRIC CHLORIDE.

FIG.6 SOFTENING POINT-PENETRATION RELATIONSHIP OF HALDIA BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH FERRIC CHLORIDE



vation is that in the case of ferric chloride also there is deterioration in softening point-penetration relationship with rise in temperature. But by suitably selecting the temperature of the process all the ten different grades of industrial bitumen could be manufactured.

IV(b) CHARACTERISATION OF THE AIR BLOWN BITUMEN

IV(b).1 INFRA-RED ANALYSIS

Figs. 7 and 8 show the infrared spectra of the air-blown Cochin and Haldia bitumen. An increase in the intensity of the absorption band at 8.7 microns and 9.4 microns are observed. The absorption at 8.7 microns is attributed to the formation of disulphides and that at 9.4 microns is due to the formation of thiophenic compounds. Tucker[114] after a number of studies have confirmed that the absorption band at 8.7 microns is due to the disulphides.Hartough[115] confirmed the absorption band at 9.4 microns as due to the thiophenic compounds.

There is the possibility for the formation of three types of bonds in this process, the Sulphur-carbon bonds, Carbon-Carbon bonds and Sulphur-hydrogen bonds. Sulphur is known to react with hydro-carbons in bitumen to form polysulphides at about 125°C.[135] A study of literature concerning the sulphurization of bitumen reveals that a chemical reaction takes place between

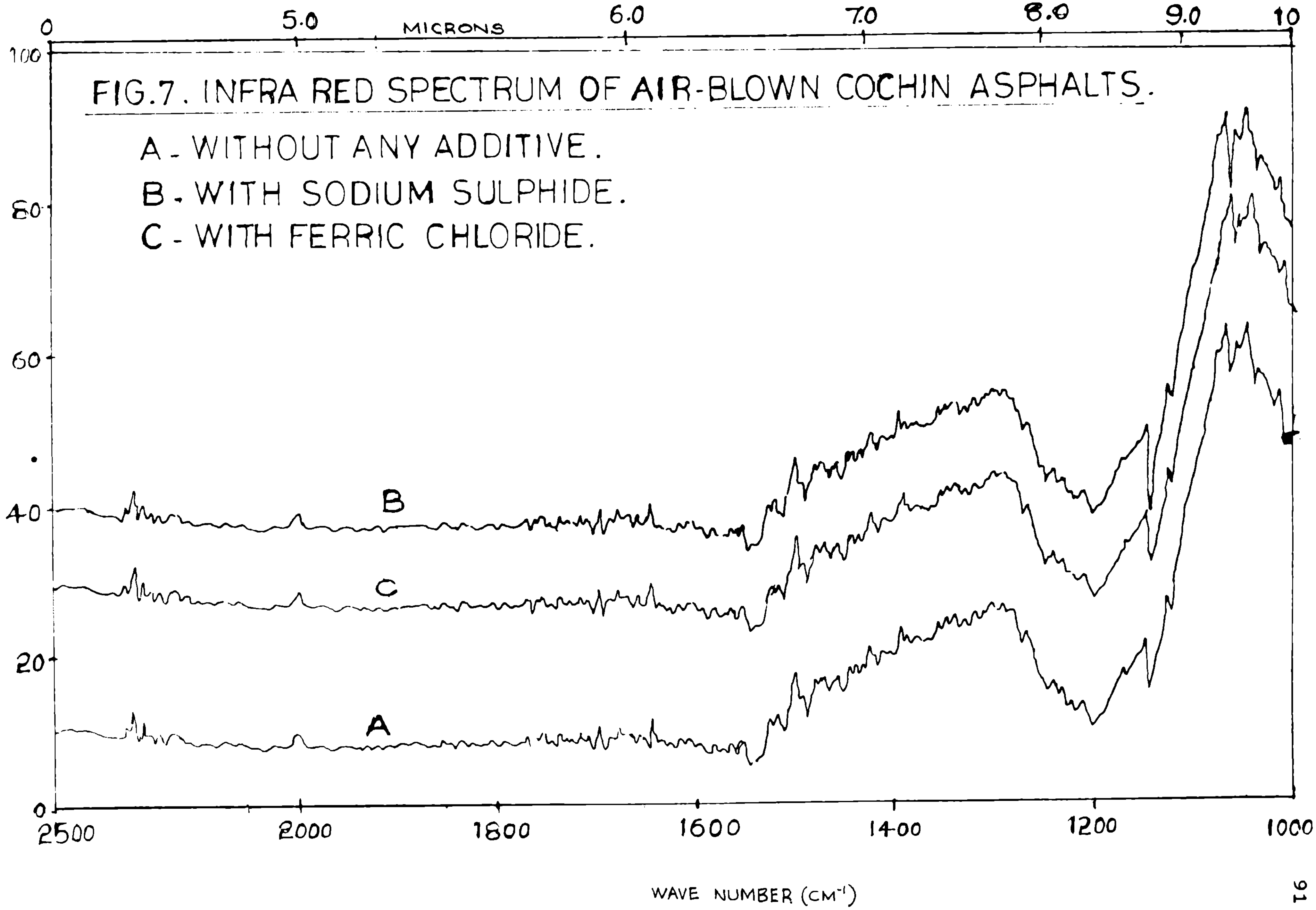


FIG.7. INFRA RED SPECTRUM OF AIR-BLOWN COCHIN ASPHALTS.

A - WITHOUT ANY ADDITIVE.
B - WITH SODIUM SULPHIDE.
C - WITH FERRIC CHLORIDE.

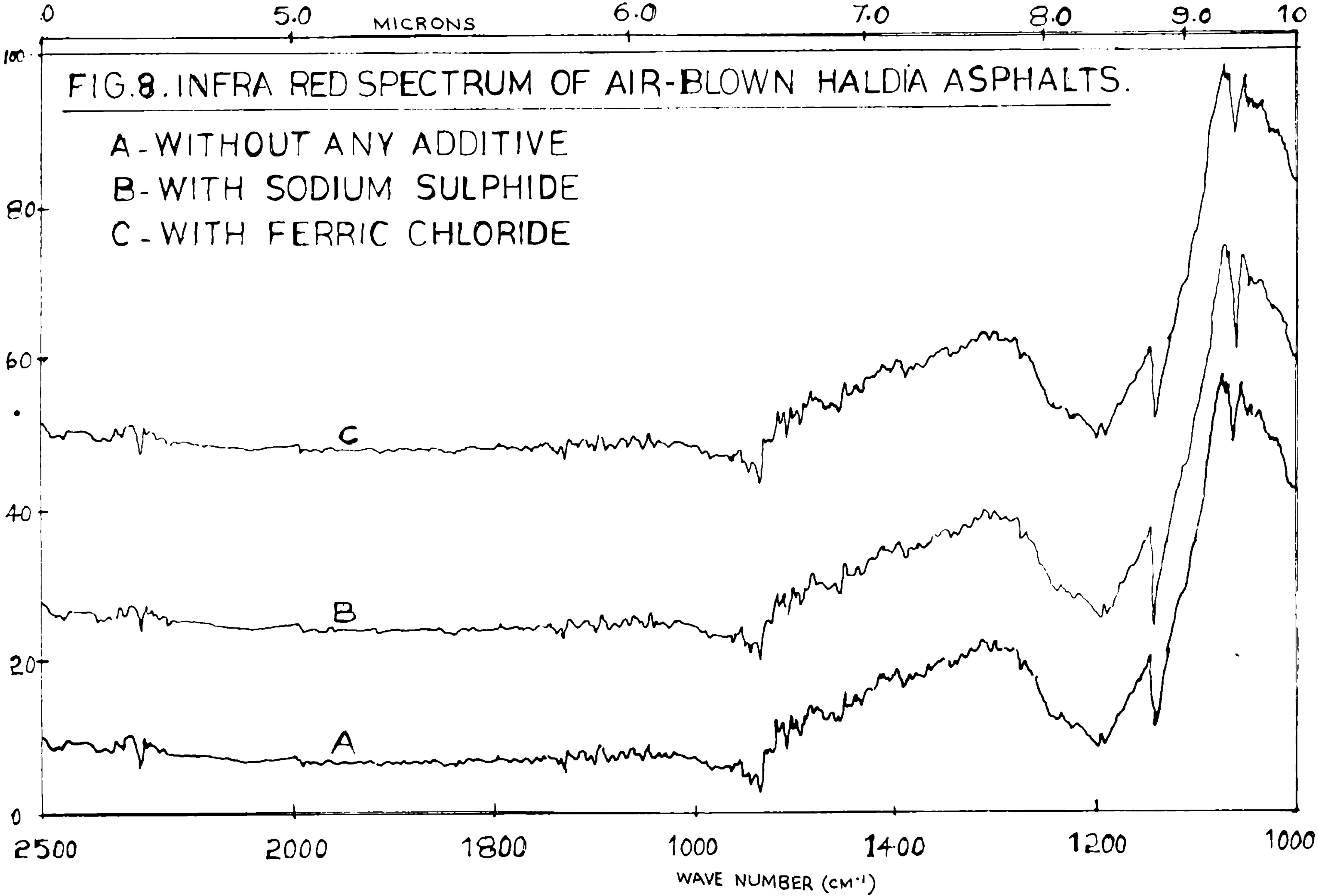


FIG.8. INFRA RED SPECTRUM OF AIR-BLOWN HALDIA ASPHALTS.

TABLE - 19

EFFECT OF ASPHALTENE CONTENT AND ITS MOLECULAR WEIGHT ON SOFTENING POINT - PENETRATION RELATIONSHIP

Bitumen Air-blown @ 220°C		Softening point °C	Penetration 1/10 mm	Asphaltene content (% wt)	Molecular wt. of asphaltenes	
					Mw	Mn
COCHIN	Without any additive	95	4	26.0	20200	9900
	With sodium sulphide	95	29	33.4	17100	8700
	With ferric chloride	95	32	34.6	16500	8450
HALDIA	Without any additives	95	1	27.2	22400	12100
	With sodium sulphide	95	26	34.4	19000	10450
	With ferric chloride	95	29	35.8	18400	10150

FIG.9. GEL PERMEATION CHROMATOGRAPHS OF THE ASPHALTENE FRACTIONS OF THE COCHIN AIR-BLOWN ASPHALTS.

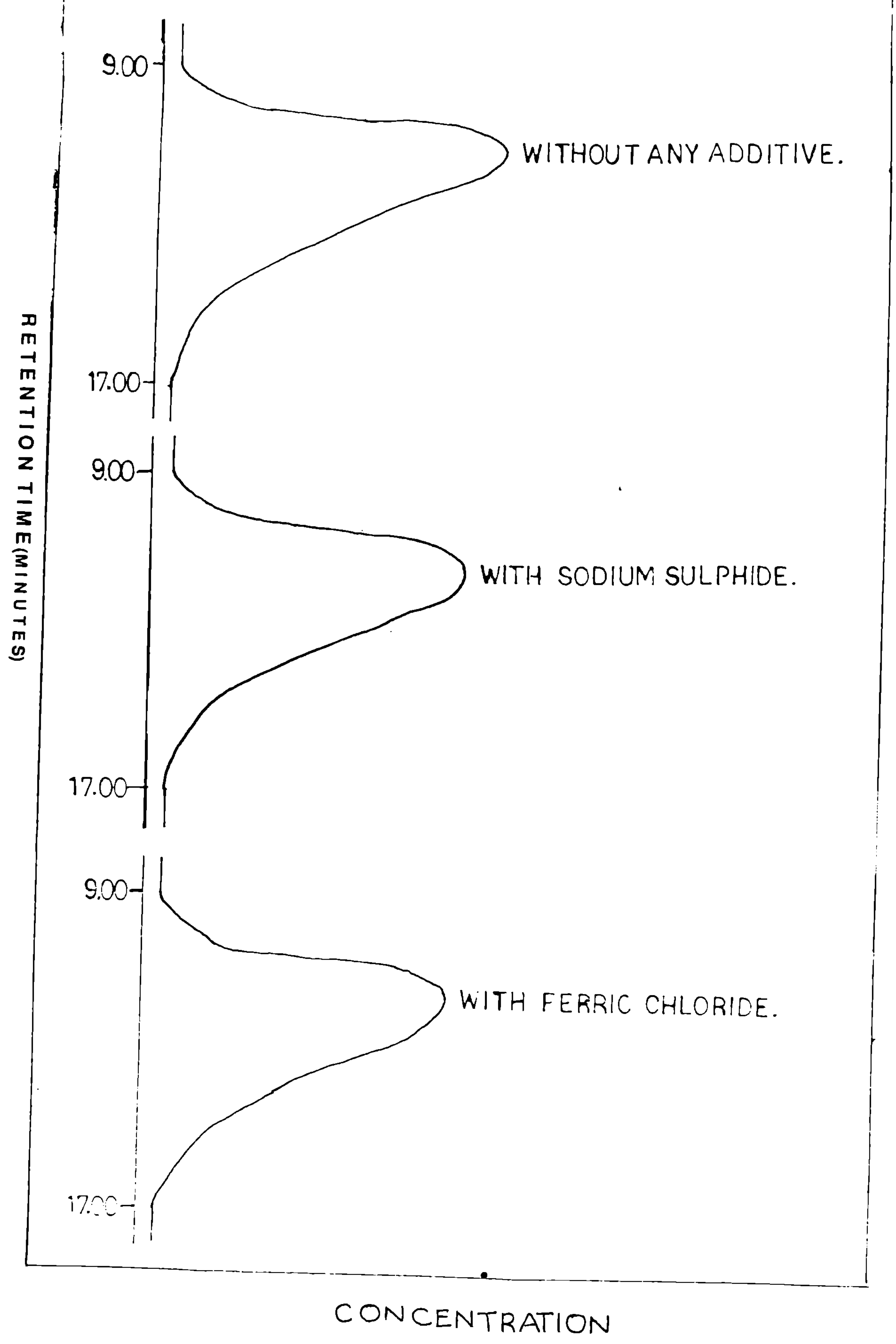
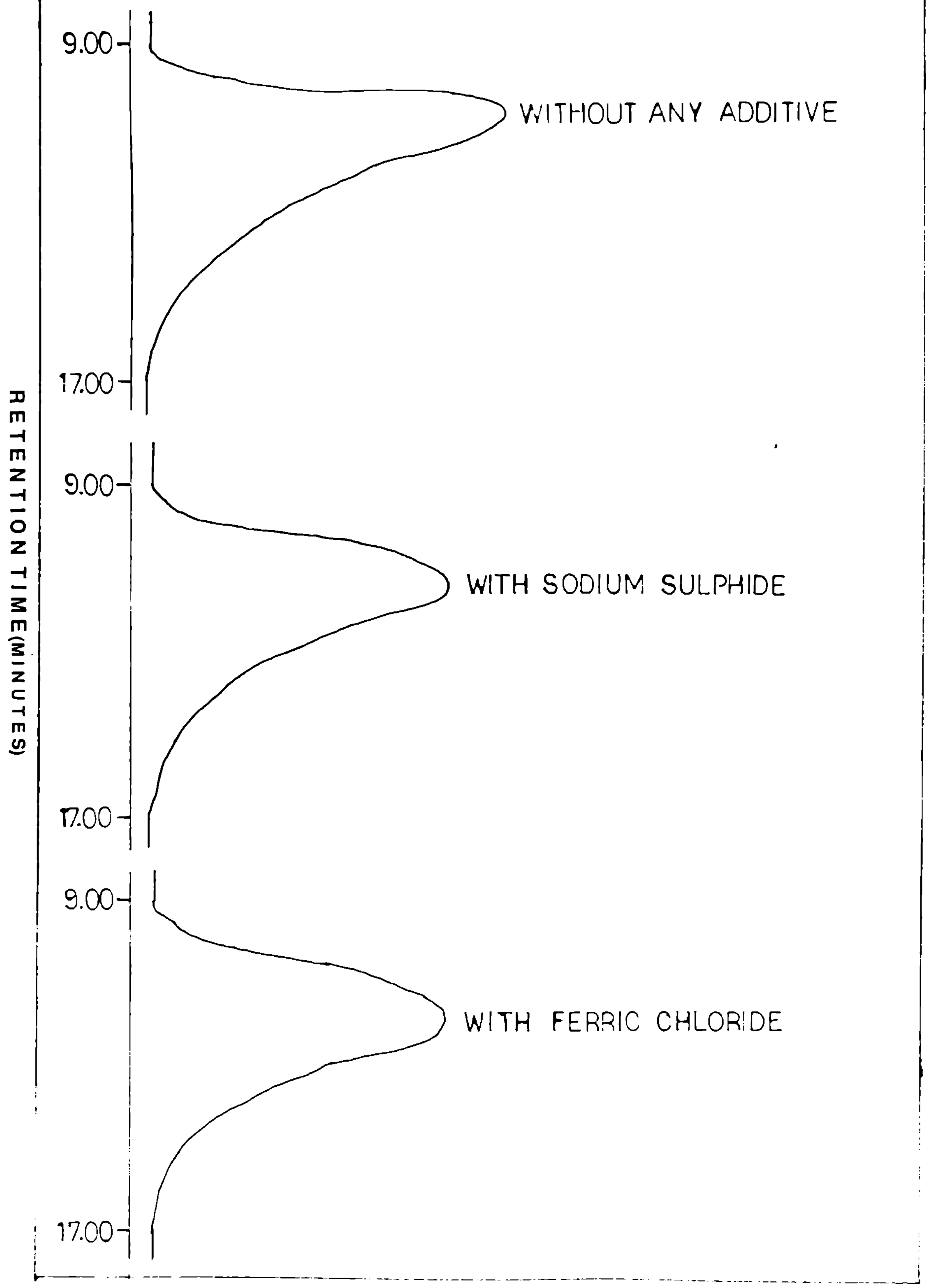


FIG.10. GEL PERMEATION CHROMATOGRAPHS OF THE ASPHALTENE FRACTIONS OF THE HALDIA AIR-BLOWN ASPHALTS.



sulphur and different hydrocarbons constituents of bitumen @ about 200°C. The reaction proceeds by a free radical mechanism initiated by the formation of sulphur free radicals at high temperatures[136].

The increase in the intensity of the bands at 8.7 microns and 9.4 microns is due to the formation of disulphides and thiophenic compounds respectively during the air-blowing polymerization in presence of sodium sulphide.

IV(b).2 MOLECULAR WEIGHT DETERMINATION BY GEL PERMEATION CHROMATOGRAPHY.

During the bitumen air blowing process Naphthene aromatic fraction present in the bitumen is converted to polar aromatics which then polymerize to form asphaltenes[134]. So it was thought worthwhile to find out the asphaltene contents and their molecular weights in the air-blown bitumen. The results are given in Table 19. The gel permeation chromatographs are presented in Figs. 9 and 10.

From Table 19 it can be observed that when the air-blown bitumen products possess high asphaltene contents of low molecular weights (softer asphaltenes), the softening point-penetration relationship will be better. It is in agreement with the observations already made by Dark[116].

IV(b).3 EFFECT OF THE RAW MATERIAL ON SOFTENING POINT-PENETRATION RELATIONSHIP

From Table 19 it can be observed that Cochin air blown bitumen possess better softening point-penetration relationship as compared to those of Haldia air blown bitumen. An attempt was made to distinguish their behaviour by studying the physical properties of the raw materials. Their physical properties are as given below:

Test properties	Cochin Paving bitumen	Haldia paving bitumen
1. Softening point °C	46	44
2. Penetration 1/10 mm	85	82
3. Flash point °C	330	332
4. Ductility cms.	>100	>100
5. Specific gravity	1.007	1.019

As the above physical properties don't give any clue to the solution of the problem, the chemical composition analyses of the raw materials were carried out by column chromatography (Adsorption - elution chromatography) the results of which are as follows in terms of percentage composition.

Fraction	Cochin paving bitumen	Haldia paving bitumen
1. Saturates	8.9	5.0
2. Naphthene aromatics	46.6	43.9
3. Polar aromatics	34.8	38.0
4. Asphaltenes	9.7	13.1

The inferior softening point-penetration relationship of the air-blown products from Haldia bitumen may be attributed to the presence of lower content of saturates. During the air blowing process the saturates are not affected but the Naphthene-aromatics are transformed to polar aromatics which further get polymerised to high molecular weight asphaltenes.

Thus it can be concluded that eventhough the physical properties of the two different raw materials are practically the same there is significant difference in their chemical composition especially as far as the saturate contents are concerned. This is because they are manufactured by two different processes, Cochin bitumen by the vacuum distillation process and Haldia bitumen by the propane deasphalting process. However, our studies show that by suitably adjusting the temperature of the air-blowing process it is possible to manufacture all the ten different grades of industrial bitumen as per IS 702-1961 from both the raw materials.

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IV(c) KINETIC STUDIES ON BITUMEN AIR-BLOWING

IV(c).1 METHOD OF CALCULATION OF RATE CONSTANTS

It is already reported that asphalt air blowing behaves kinetically as a first order reaction with respect to the hydrocarbon reactants in bitumen[117]. The data usually available to the designer and to the operator as a measure of reaction completion is only the rise in softening point of the asphalt[118]. Thus the designer and operator need a simpler type of analysis using softening point as the variable.

The simplest type of reaction that fits batch air blowing is an irreversible, first order reaction. The differential equation for such a reaction can be written as

$$\frac{-dC}{dt} = kC$$

Where C is the concentration of the reactants in bitumen. Since the concentration of the reactant materials is inversely proportional to the softening point of the asphalt, $C = \frac{a}{S}$, where S is the softening point. Substituting this in the differential equation and integrating, the equation becomes,

$$k = \frac{1}{t}\,\ell n\,\frac{St}{So}\ ,$$

where S_o is the initial softening point and St is the softening point at any time t. The next step is to check out this equation with the actual test data and see how well it fits.

TABLE - 20

COCHIN PAVING BITUMEN AIR-BLOWN WITH DIFFERENT FLOW RATES OF AIR AT 220°C

Air flow rate in L/MIN/Kg.	Duration of blowing in hours	Softening Point °C	First order rate constant hour^{-1}
4	1	51	0.10
	2	57	0.11
	3	64	0.11
	4	72	0.11
	5	81	0.11
5	1	53	0.14
	2	60	0.14
	3	69	0.14
	4	77	0.13
	5	88	0.14
6	1	54	0.16
	2	62	0.15
	3	72	0.15
	4	83	0.15
	5	95	0.15

TABLE - 21

HALDIA PAVING BITUMEN AIR-BLOWN WITH DIFFERENT FLOW RATES OF AIR AT 220°C

Air flow rate in L/Min/Kg sample	Duration of blowing in hours	Sotening Point °C	First order rate constant hour^{-1}
4	1	48	0.09
	2	53	0.09
	3	58	0.09
	4	64	0.09
	5	70	0.09
5	1	49	0.11
	2	54	0.10
	3	61	0.11
	4	67	0.11
	5	76	0.11
6	1	50	0.13
	2	56	0.12
	3	63	0.12
	4	70	0.12
	5	79	0.12

TABLE - 22

COCHIN PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT VARYING TEMPERATURES, THE AIR-BLOW RATE BEING 5 L $MIN.^{-1}$ Kg. SAMPLE

Duration of blowing hrs.	@ 220°C		@ 240°C		@ 260°C	
	Softening Point°C	First order rate constants hr^{-1}	Softening point°C	First order rate constants $hour^{-1}$	Softening point °C	First order rate constants hr^{-1}
0	46	-	46	-	46	-
1	53	0.14	56	0.20	60	0.27
2	60	0.14	69	0.20	80	0.28
3	69	0.14	83	0.21	106	0.28
4	77	0.13	101	0.20	138	0.27
4.5	85	0.14	112	0.20	155	0.27
5	91	0.14	123	0.20	174	0.27

TABLE - 23

HALDIA PAVING BITUMEN AIR-BLOWN WITHOUT ANY ADDITIVE AT VARYING TEMPERATURES, THE AIR-FLOW RATE BEING 5 L MIN^{-1}Kg. SAMPLE

Duration of blowing hrs.	@ 220°C		@ 240°C		@ 260°C	
	Softening Point°C	First order rate constants hr^{-1}	Softening point°C	First order rate constants $hour^{-1}$	Softening point °C	First order rate constants hr^{-1}
0	44	-	44	-	44	-
1	49	0.11	51	0.15	54	0.20
2	54	0.10	59	0.15	66	0.20
3	61	0.11	69	0.15	83	0.21
4	67	0.11	81	0.15	98	0.20
5	76	0.11	95	0.15	122	0.20

FIG.11 BITUMEN AIR-BLOWN AT 220°C WITH VARYING AIR-FLOW RATES.

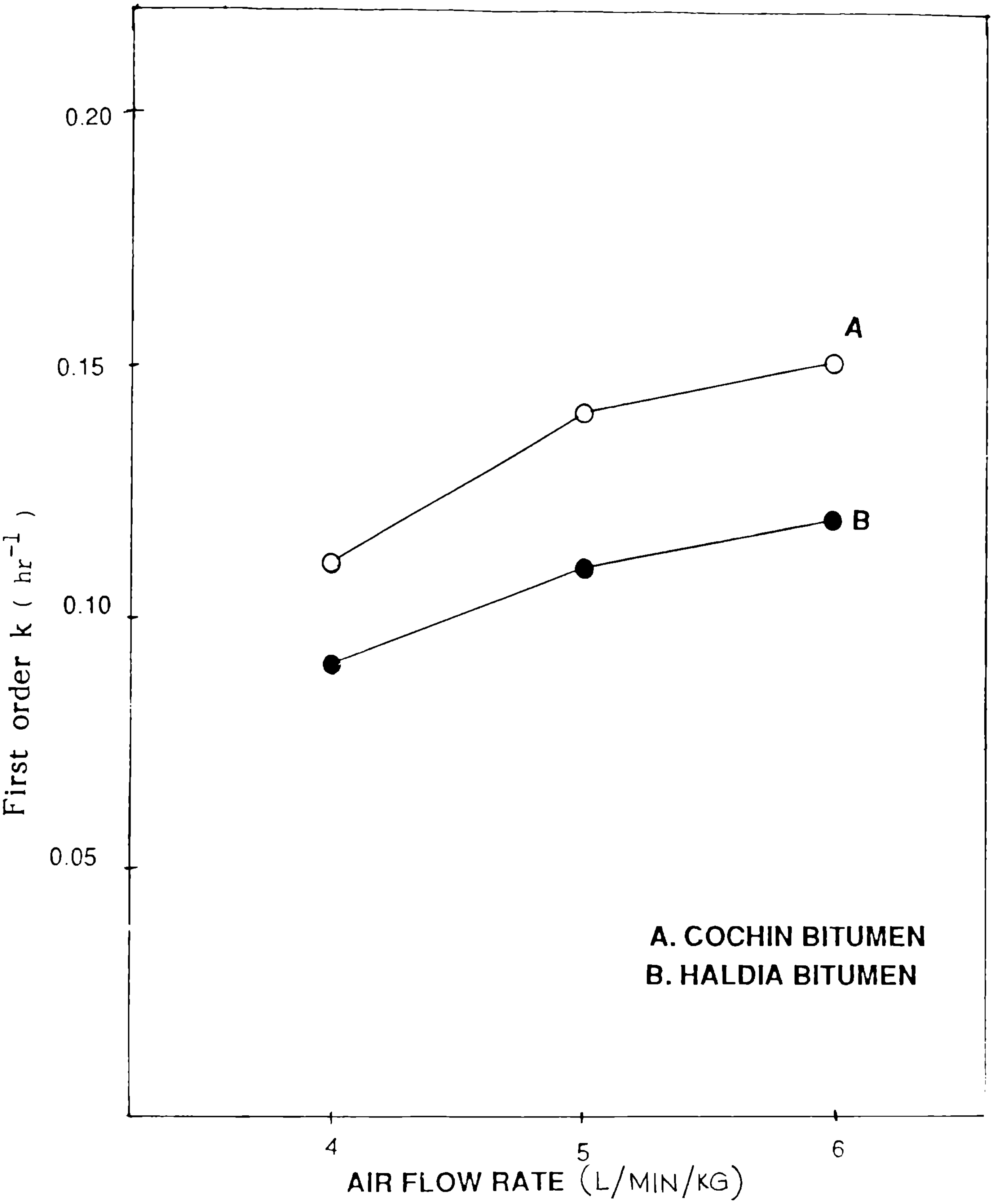


TABLE - 24

COCHIN PAVING BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF SODIUM SULPHIDE AT 220°C

Concentration of Sodium Sulphide %	Duration of blowing hours	Softening Point °C	First order rate constant $hour^{-1}$
1.5%	1.0	57	0.21
	1.5	64	0.22
	2.0	70	0.21
	2.5	77	0.21
	3.0	86	0.21
2.0%	1.0	61	0.29
	1.5	70	0.28
	2.0	80	0.28
	2.5	92	0.28
	3.0	105	0.28
2.5%	1.0	62	0.30
	1.5	72	0.30
	2.0	83	0.30
	2.5	97	0.30
	3.0	112	0.30

TABLE - 25

HALDIA PAVING BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF SODIUM SULPHIDE AT 220^{o}C

Concentration of Sodium Sulphide %	Duration of blowing hours	Softening Point ^{o}C	First order rate constant hour^{-1}
1.5%	1.0	52	0.16
	2.0	61	0.16
	3.0	71	0.16
	4.0	82	0.16
	4.5	89	0.16
2.0%	1.0	54	0.21
	2.0	67	0.21
	3.0	82	0.21
	4.0	101	0.21
	4.5	112	0.21
2.5%	1.0	55	0.23
	2.0	69	0.22
	3.0	87	0.23
	4.0	109	0.23
	4.5	122	0.23

TABLE - 26

COCHIN PAVING BITUMEN AIR-BLOWN AT THE AIR-FLOW RATE OF 5L/MIN/KG. SAMPLE WITH 2.0% SODIUM SULPHIDE AT VARYING TEMPERATURES

Duration of blowing hrs.	@ 220°C		@ 240°C		@ 260°C	
	Softening Point °C	First order rate constants $hour^{-1}$	Softening Point °C	First order rate constants $hour^{-1}$	Softening Point°C	First order rate constants $hour^{-1}$
0	46	-	46	-	46	-
0.5	53	0.28	55	0.36	58	0.46
1.0	61	0.29	67	0.38	71	0.44
1.5	70	0.28	79	0.36	91	0.45
2.0	80	0.28	96	0.37	113	0.45
2.5	92	0.28	115	0.37	140	0.45
3.0	105	0.28	138	0.37	175	0.45

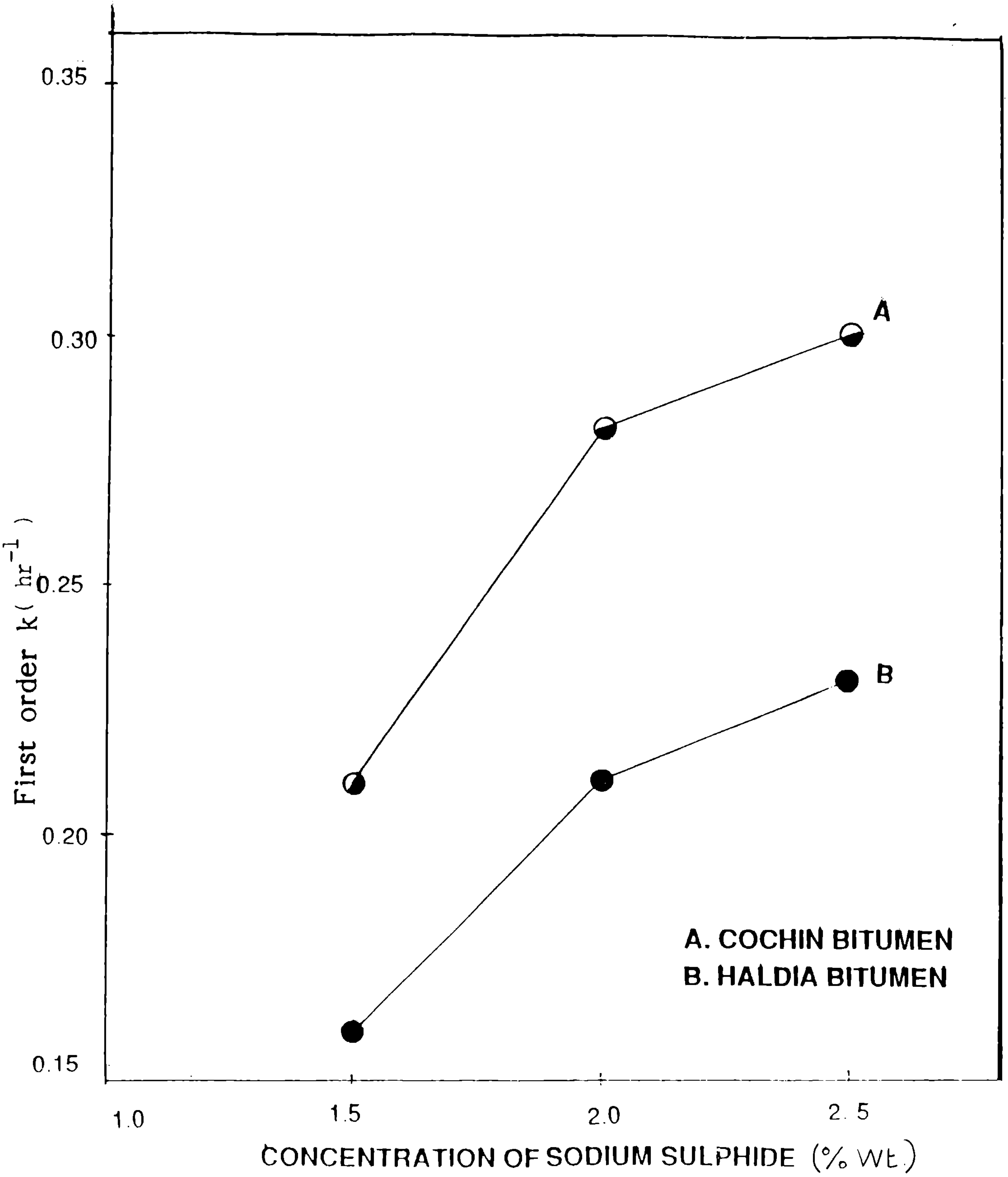
TABLE - 27

HALDIA BITUMEN AIR-BLOWN AT THE AIR FLOW RATE OF 5L/MIN/KG. SAMPLE WITH 2.0%

SODIUM SULPHIDE AT VARYING TEMPERATURES

Duration of blowing hrs.	@ 220°C		@ 240 °C		@ 260°C	
	Softening Point °C	First order rate constants hour^{-1}	Softening Point °C	First order rate constants hour^{-1}	Softening Point °C	First order rate constants hour^{-1}
0	44	-	44	-	44	-
1	54	0.21	58	0.28	61	0.33
2	67	0.21	75	0.27	85	0.33
3	80	0.20	98	0.27	118	0.33
4	101	0.21	125	0.26	165	0.33
4.5	112	0.21	150	0.27	-	-

FIG.12 BITUMEN AIR-BLOWN AT 220°C WITH VARYING CONCENTRATIONS OF SODIUM SULPHIDE



IV(c).2 BITUMEN AIR-BLOWING WITHOUT ANY ADDITIVE

To find out the optimum rate of flow of air required for the process, asphalt is air blown with different rates of flow of air at 220°C. The results are given in Tables 20 and 21. It can be observed that the optimum air flow rate required for the process is 5ℓ / min. per kg. sample.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS

In order to determine the temperature coefficients of the process, the process was carried out at varying temperatures. Using the mean velocity constants obtained, the Arrhenius plots are drawn as in Figs.14 and 15. The activation energies in Kcal per mole for Cochin bitumen and Haldia bitumen are found to be 8.78 and 7.86 respectively.

IV(c).3 BITUMEN AIR BLOWN WITH SODIUM SULPHIDE

In order to find the optimum concentration of sodium sulphide required for the process, the raw materials are air blown at 5ℓ/min per kg. sample at 220°C in presence of varying concentrations of sodium sulphide. The results are given in Tables 24 and 25. It can be seen that the optimum concentration of sodium sulphide required for the process is 2.0%.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS

The process was carried out at varying temperatures. The results are presented in Tables 26 & 27. The Arrhenius plots are drawn using the mean velocity constants. The activation energies in KCal/mole for

Cochin bitumen and Haldia bitumen are found to be 6.50 and 6.04 respectively.

Based on the above experimental results the following reaction mechanism is suggested.

(1) Formation of free radicals

$$RH + O_2 \longrightarrow R^{\bullet} + HOO^{\bullet}$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + H_2S \longrightarrow ROOH + HS^{\bullet}$$

$$HS^{\bullet} + O_2 \longrightarrow HOO^{\bullet} + \ddot{S}^{\bullet}$$

$$ROOH \longrightarrow RO^{\bullet} + \dot{O}H$$

$$RH + HOO^{\bullet} \longrightarrow \dot{R} + H_2O_2$$

$$H_2O_2 \longrightarrow 2\ \dot{O}H$$

$$RH + \dot{O}H \longrightarrow \dot{R} + H_2O$$

$$RH + \ddot{S} \longrightarrow \dot{R} + HS^{\bullet}$$

$$RH + HS^{\bullet} \longrightarrow \dot{R} + H_2S$$

(2) Polymerization by Chain reaction

$$\dot{R} + \underset{\substack{\text{Unsaturated}\\ \text{compound}}}{R^{\bullet}H} \longrightarrow R^{\bullet}R'H$$

$$\dot{R}\ R'H + R''H \longrightarrow \dot{R}\ R'H\ R''H$$

$$R\ R'H\ R''H \xrightarrow{\text{disproportionation}} \text{stable products}$$

(3) Crosslinking reaction

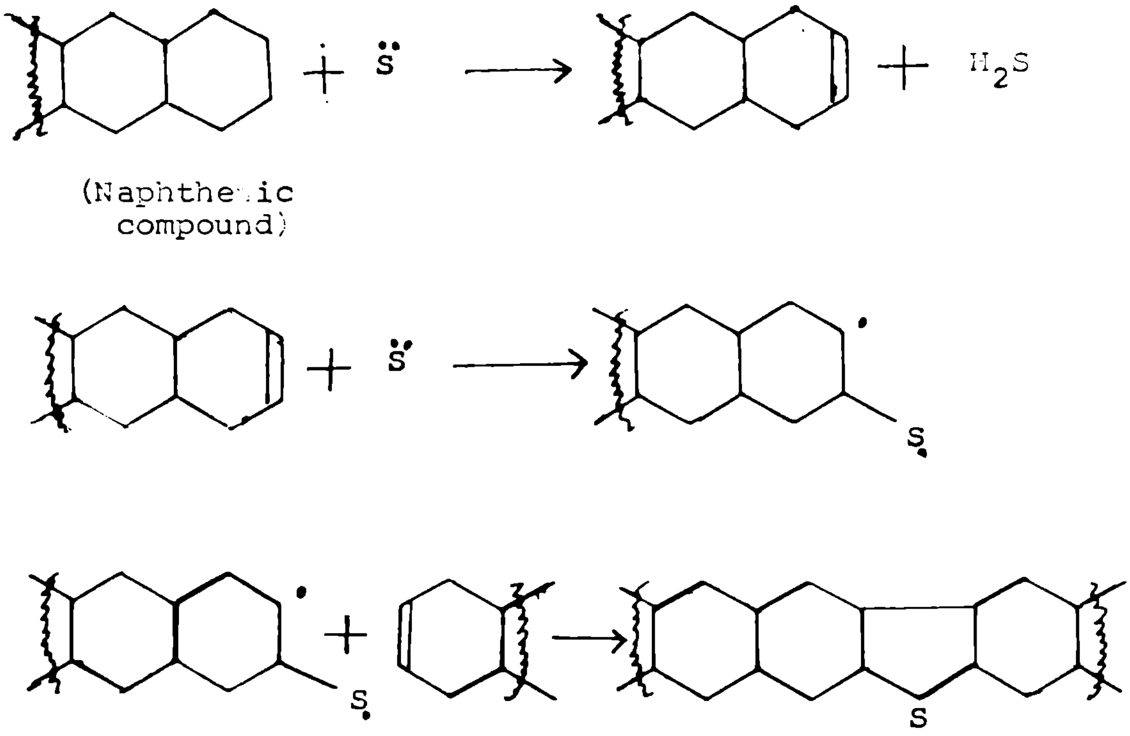
(a) formation of disulphides

$$\dot{R} + \ddot{S} \longrightarrow R - \dot{S}$$

$${}^{\bullet}R^1 + \ddot{S} \longrightarrow R^1 - \dot{S}$$

$$R\text{-}\dot{S} + R^1 - \dot{S} \longrightarrow R\text{-}S\text{-}S\text{-}R^1$$

(b) Formation of thiophenic compounds.



Sulphur is reported to be more powerful than oxygen in the abstraction of hydrogen from hydrocarbons in bitumen[137]. The effect of sodium sulphide in the polymerization of bitumen is attributed to the formation of sulphur free radicals.

IV(c).4 BITUMEN AIR BLOWN WITH FERRIC CHLORIDE

In order to find the optimum concentration of ferric chloride required for the process the raw materials were air blown with 5 ℓ/min per kg. at 220°C with varying

TABLE - 28

COCHIN BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF FERRIC CHLORIDE AT 220°C

Concentration of ferric chloride	Duration of blowing hours	Softening Point °C	First order rate constant hour^{-1}
0.5%	1.0	58	0.23
	1.5	63	0.21
	2.0	73	0.23
	2.5	81	0.23
	3.0	91	0.23
0.75%	1.0	62	0.31
	1.5	73	0.29
	2.0	86	0.31
	2.5	99	0.31
	3.0	116	0.31
1.0%	1.0	64	0.33
	1.5	77	0.34
	2.0	89	0.33
	2.5	106	0.33
	3.0	125	0.33

TABLE - 29

HALDIA BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF FERRIC CHLORIDE AT 220°C

Concentration of ferric chloride	Duration of blowing hours	Softening Point °C	First order rate constant $hour^{-1}$
0.5%	1.0	52	0.17
	2.0	62	0.17
	3.0	74	0.17
	3.5	79	0.17
	4.0	87	0.17
0.75%	1.0	56	0.23
	2.0	70	0.23
	3.0	89	0.23
	3.5	97	0.23
	4.0	112	0.23
1.0%	1.0	56	0.24
	2.0	72	0.25
	3.0	92	0.25
	3.5	105	0.25
	4.0	118	0.25

TABLE - 30

COCHIN PAVING BITUMEN AIR-BLOWN AT THE AIR FLOW RATE OF 5 L/MIN/KG SAMPLE WITH 0.75% FERRIC CHLORIDE AT VARYING TEMPERATURES

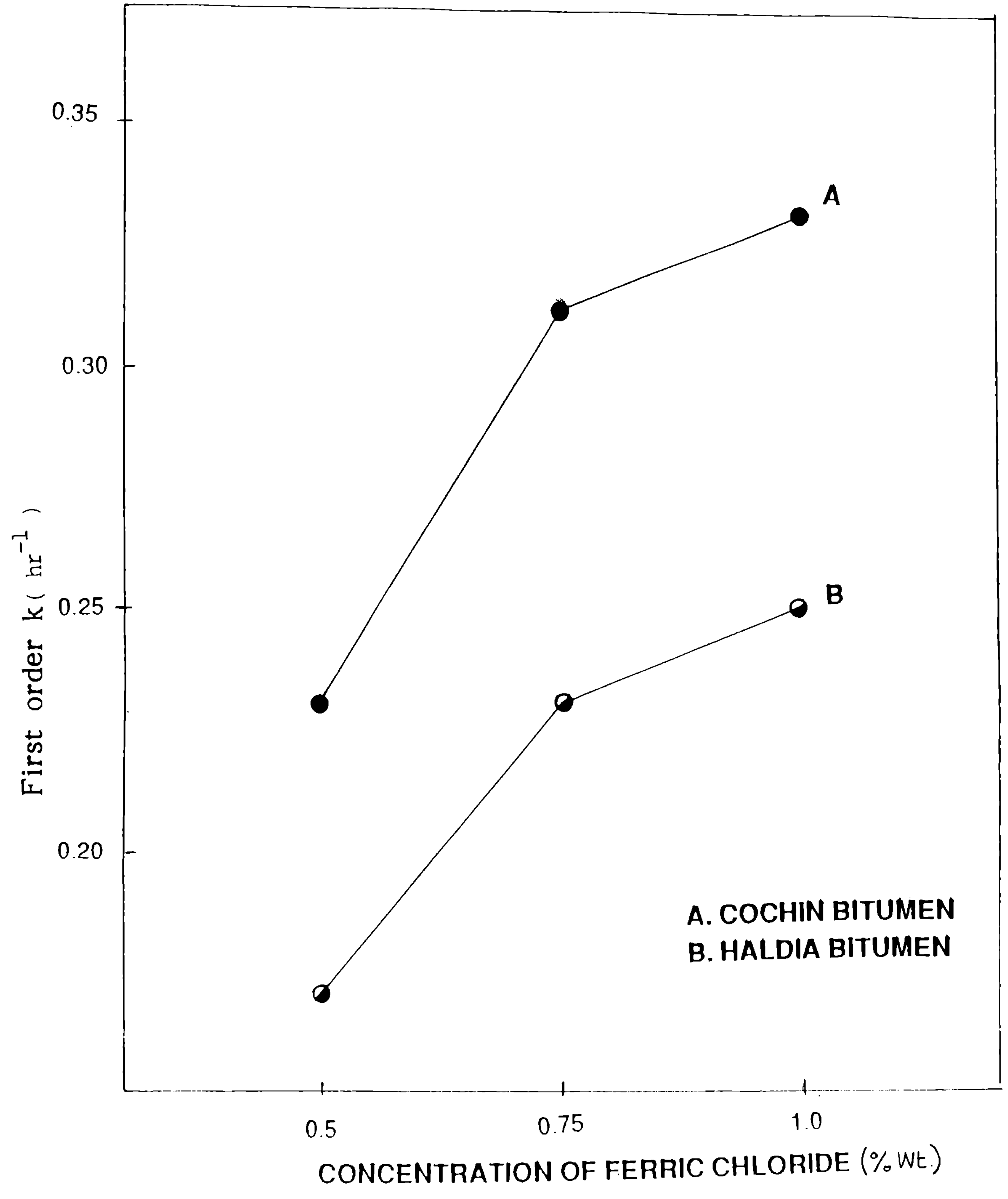
Duration of blowing hrs.	@ 220°C		@ 240°C		@ 260°C	
	Softening Point °C	First order rate constants hour^{-1}	Softening Point °C	First order rate constants hour^{-1}	Softening Point°C	First order rate constants hour^{-1}
0	46	-	46	-	46	-
0.5	54	0.32	56	0.39	59	0.50
1.0	62	0.31	69	0.41	75	0.49
1.5	73	0.29	84	0.40	94	0.48
2.0	86	0.31	100	0.39	120	0.48
2.5	99	0.31	126	0.40	155	0.49
3.0	116	0.31	154	0.40	-	-

TABLE - 31

HALDIA BITUMEN AIR-BLOWN AT THE AIR-FLOW RATE OF 5 L/MIN/KG. SAMPLE WITH 0.75% FERRIC CHLORIDE AT VARYING TEMPERATURES

Duration of blowing hrs.	@ 220°C		@ 240°C		@ 260°C	
	Softening Point °C	First order rate constants hour^{-1}	Softening Point °C	First order rate constants hour^{-1}	Softening Point °C	First order rate constant hour^{-1}
0	44	-	44	-	44	-
1.0	56	0.23	59	0.29	62	0.35
2.0	70	0.23	77	0.28	85	0.33
3.0	89	0.23	102	0.28	125	0.35
3.5	97	0.23	120	0.29	148	0.35
4.0	115	0.24	138	0.29	175	0.35

FIG.13 BITUMEN AIR-BLOWN AT 220°C WITH VARYING CONCENTRATIONS OF FERRIC CHLORIDE



concentrations of ferrichloride. The results are given in Tables 28 and 29.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS

The process was carried out at varying temperatures. The mean velocity constants were used for making the Arrhenius plots. The activation energies in KCal/mole for Cochin and Haldia bitumen are found to be 6.23 and 5.77 respectively.

Based on the above experimental results the following reaction mechanism is suggested.

1. The formation of free radicals as a result of valency conversions of iron.

$$FeCl_3 + RH \longrightarrow \overset{\bullet}{R} + FeCl_2 + HCl$$

$$FeCl_3 + H_2O \longrightarrow FeCl_2 + HCl + \overset{\bullet}{O}H$$

$$FeCl_2 + O_2 \longrightarrow Fe^{2+}.....\ O_2 \longrightarrow Fe^{3+}....\ O_2 \overset{H^+}{\rightleftharpoons} Fe^{3+} + HOO^{\bullet}$$

2. Increase in the probability of hydrocarbon radicals coming in contact with oxygen as a result of the increase in their concentration in the starting period of oxidation.

$$\overset{\bullet}{R} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + {}^{1}RH \longrightarrow ROOH + {}^{\bullet}R^{1}$$

$$ROOH \longrightarrow RO^{\bullet} + \overset{\bullet}{O}H$$

$$R^{11}H + \overset{\bullet}{O}H \longrightarrow R^{\bullet 11} + H_2O$$

$$RH + HOO^{\bullet} \longrightarrow \overset{\bullet}{R} + H_2\ O_2$$

$$H_2O_2 \longrightarrow 2\ OH^{\bullet}$$
$$R^1H + {}^{\bullet}OH \longrightarrow {}^{\bullet}R^1 + H_2O$$

3. Besides ordinary decomposition of hydroperoxide and peroxide radicals with the formation of aldehydes, ketones and alcohols, they interact with bivalent iron.

$$FeCl_2 + ROOH \longrightarrow FeCl_2OH + RO^{\bullet}$$
$$ROO^{\bullet} + FeCl_2 \longrightarrow ROO\ FeCl_2$$

4. Interaction of trivalent iron with the oxidation products having reducing properties with the regeneration of Fe^{2+} and with the separation of water.

$$FeCl_2OH + RCHO \longrightarrow FeCl_2 + H_2O + {}^{\bullet}RCO$$

5. Acceleration of decomposition of peroxides with bivalent iron.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$
$$Fe^{3+} + OH^{-} \longrightarrow Fe^{2+} + OH^{\bullet}$$
$$RH + OH^{\bullet} \longrightarrow {}^{\bullet}R + H_2O$$

6. Polymerization

$${}^{\bullet}R + \underset{\text{(unsaturated compound)}}{R^1H} \longrightarrow {}^{\bullet}R\ R^1H$$
$$R\ R^1H + R^{11}H \longrightarrow R\ R^1H\ R^{11}H$$
$$R\ R^1H\ R^{11}H \xrightarrow{\text{disproportionation}} \text{stable products}$$

FIG.14 ARRHENIUS PLOTS OF AIR-BLOWN COCHIN BITUMEN

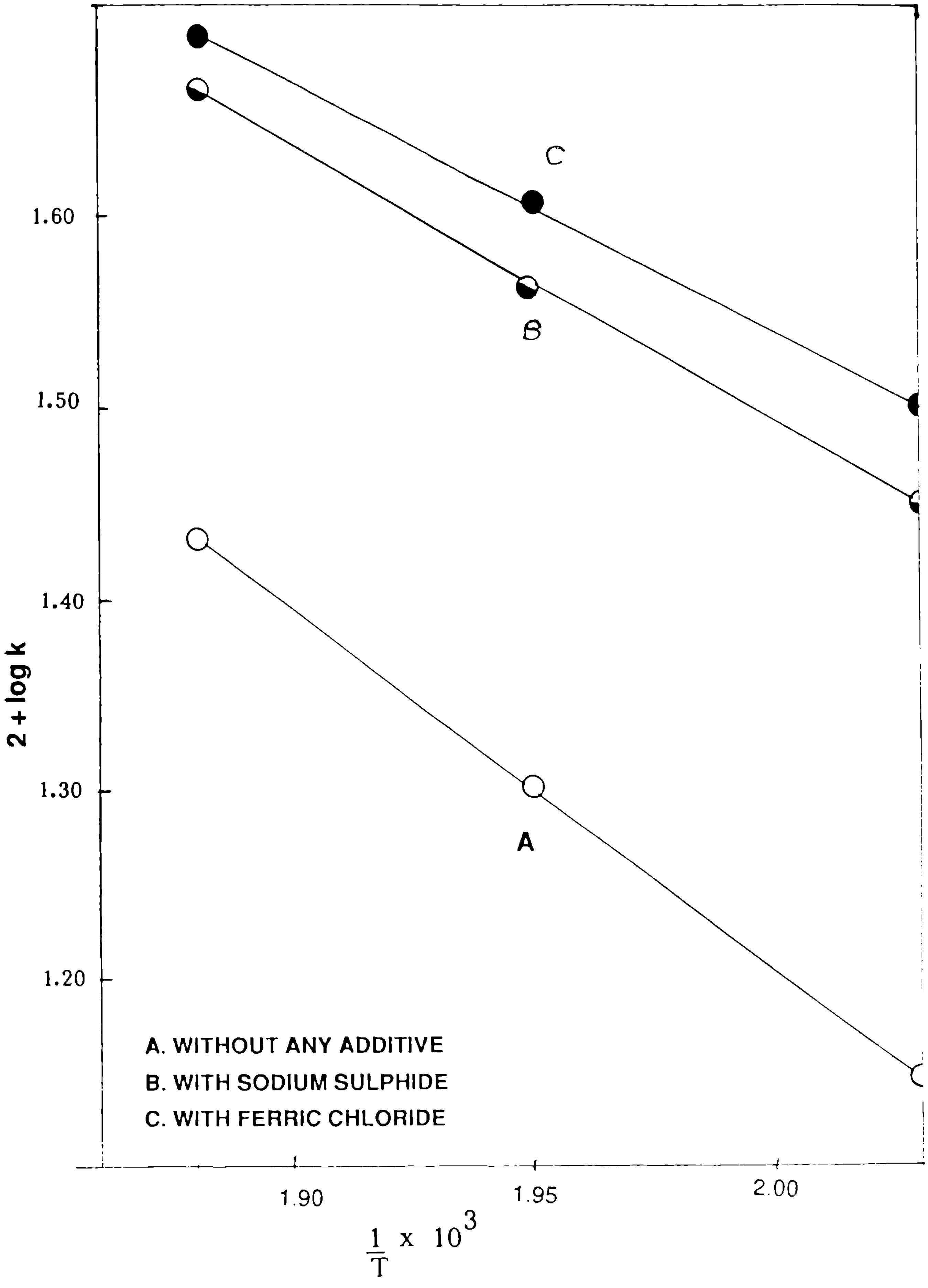
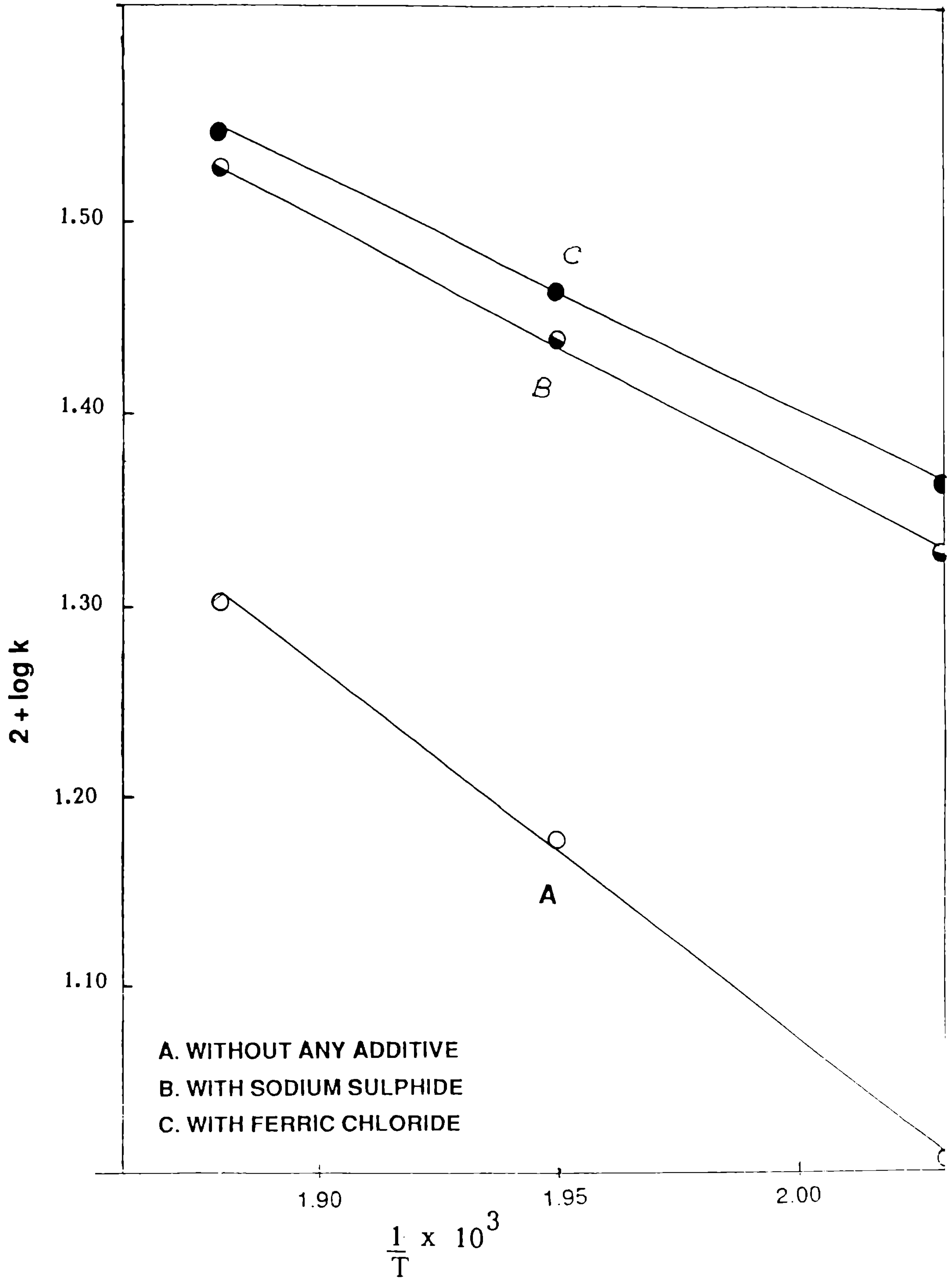


FIG.15 ARRHENIUS PLOTS OF AIR-BLOWN HALDIA BITUMEN



SUMMARY

Petroleum refinery caustic wash waste is found to be an excellent additive for bitumen air blowing. This additive in concentrations of the order of 2.0% reduces the blowing time to the extent of about 60% and is economically advantageous in industrial bitumen manufacture. Since there is a tremendous increase in the production of industrial bitumen in the recent years it is important to know the mechanism of air-blowing in detail. The present study also gives the physico-chemical characteristics of the reactions involved.

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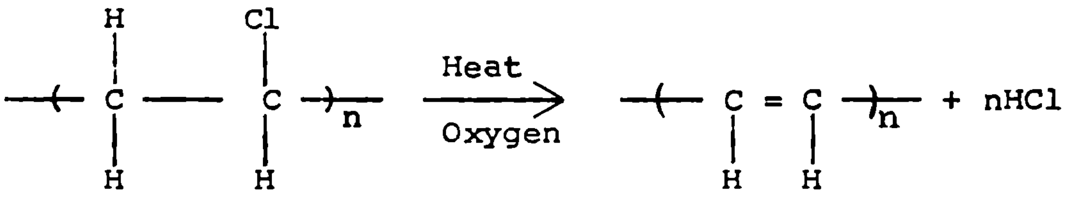
Chapter 5

UTILIZATION OF WASTE PVC FOR THE MANUFACTURE OF INDUSTRIAL BITUMEN

INTRODUCTION

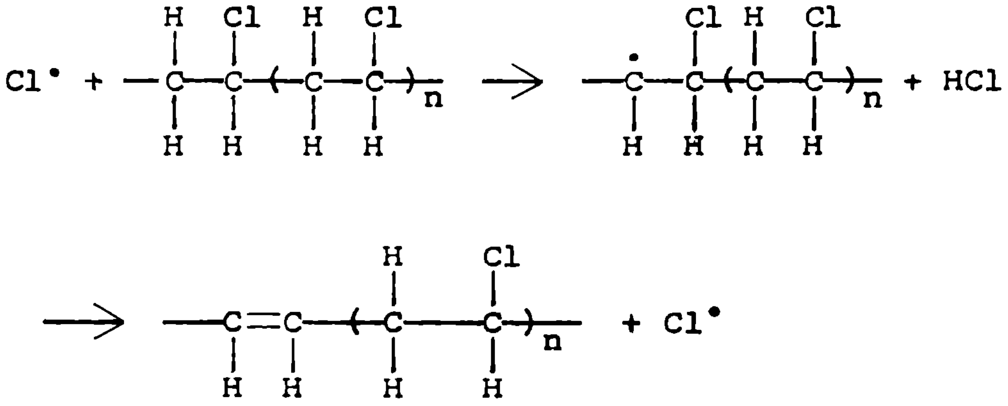
In cable industries ordinary PVC is used for insulation purposes. Owing to mechanical fault or power failure during the process, a large quantity of PVC becomes waste. Presence of metallic impurities like copper or aluminium reduces their insulation capacity, rendering them unsuitable for the insulation purposes. It is already known that upon exposure to temperatures as low as 100-120°C, PVC undergoes a degradation reaction that releases hydrochloric acid and form long polyene sequence of conjugated double bonds.[119,120] The dehydrochlorination reaction can be represented as follows :



$$-\!\left(\underset{H}{\overset{H}{C}} - \underset{H}{\overset{Cl}{C}}\right)_n \xrightarrow[\text{Oxygen}]{\text{Heat}} -\!\left(\underset{H}{C} = \underset{H}{C}\right)_n + n\mathrm{HCl}$$

Since these polyenes appear at very low levels of dehydrochlorination,[121,122] they must result from a zipper mechanism, in which the first double bond activates the formation of the second conjugated double bond and so on until long polyenes are formed. Many mechanisms have been proposed but a free radical mechanism and an ion pair mechanism seem to be preferred.[123,124]

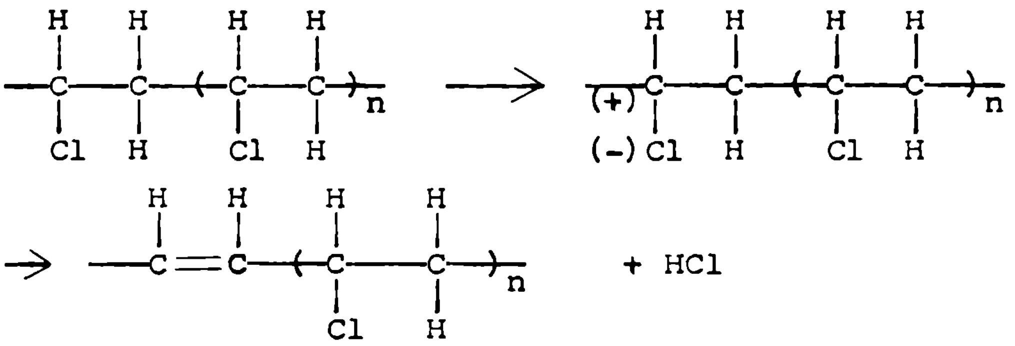
Acceleration by radical producers[125] and detection of the unpaired electron spins in the degraded PVC support the free radical mechanism. A variety of reaction sequences have been suggested and for example we have those of Arlman and Winkler.



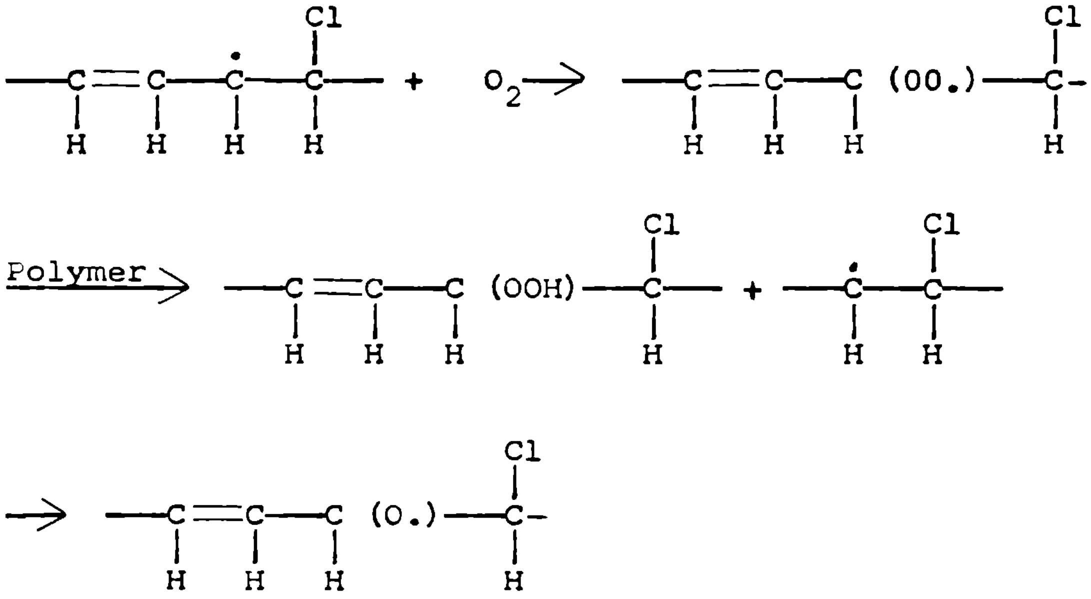
$$Cl^{\bullet} + -CH_2-CHCl-(CH_2-CHCl)_n- \longrightarrow -\overset{\bullet}{C}H-CHCl-(CH_2-CHCl)_n- + HCl \longrightarrow -CH=CH-(CH_2-CHCl)_n- + Cl^{\bullet}$$

The results of Frederic and Tedder[126] indicate that abstraction of each type of hydrogen atom is equally possible. This suggests that a free radical chain reaction, being an efficient process for hydrochloric acid elimination, will be the more important reaction.

On the other hand hydrochloric acid being an extremely powerful catalyst for further release of hydrochloric acid,[127,128] an ionic mechanism may be operative. This type of mechanism is discussed by Marks, Benten and Thomas.[129]



It was already observed that[130] the effect of oxygen is larger in increasing the rate of hydrogen chloride evolution. This effect is best explained on the basis of an initiated oxidation that both limits the length of the conjugated sequence produced and leads to peroxy groups that give chain branching due to decomposition.



V.a.1. MANUFACTURE OF INDUSTRIAL BITUMEN USING WASTE PVC.

It is already reported that hydrochloric acid is an efficient polymerization catalyst for bitumen.[131] Polyenes were found to be capable of improving the softening point-penetration relationship of bitumen.[132] Therefore it was thought worthwhile to find out whether waste PVC is useful as polymerization catalyst for bitumen.

EXPERIMENTAL

Waste PVC required for the catalytic study was obtained by the courtesy of Premier Cable Co. Ltd., Angamali, Kerala. It was having a K value of 65. Paving bitumen of grade 80/100 obtained by the courtesy of Cochin Refineries Ltd., (Manufactured by the vacuum distillation process) and Indian Oil Corporation, Haldia Refinery Project, West Bengal (manufactured by the propane deasphalting process) were used as the raw materials. The characteristics of the raw materials use are given in Chapter IV.

One kg. of paving bitumen was taken in the reactor vessel, heated to 220°C, mixed with 2.0% waste PVC and air-blown at the rate of 5ℓ/min/kg of raw material. The samples were drawn at definite intervals

TABLE - 1

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2.0% WASTE PVC AT 220°C

THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.015	62	67	76	>300	99.87	<0.01
1.5	1.020	72	55	67	>300	99.82	<0.01
2	1.025	84	43	58	>300	99.76	<0.01
2.5	1.026	98	35	48	>300	99.69	<0.01
3	1.034	118	27	15	>300	99.64	<0.01
3.5	1.044	133	23	12.5	>300	99.59	<0.01

TABLE - 2

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2% WASTE PVC AT 240°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.016	56	62	68	>300	99.88	<0.01
1	1.019	68	42	56	>300	99.86	<0.01
1.5	1.022	84	32	30	>300	99.80	<0.01
2	1.025	102	22	13	>300	99.72	<0.01
2.5	1.032	125	14	6	>300	99.65	<0.01
3	1.039	152	4	2.5	>300	99.57	<0.01

TABLE - 3

COCHIN PAVING BITUMEN AIR-BLOWN WITH 2% PVC AT 260°C

THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.017	60	42	55	>300	99.87	<0.01
1	1.020	78	28	20	>300	99.84	<0.01
1.5	1.025	99	18	10	>300	99.78	<0.01
2.0	1.030	128	8	5.0	>300	99.70	<0.01
2.5	1.042	165	0	0	>300	99.62	<0.01

TABLE - 4

HALDIA PAVING BITUMEN AIR-BLOWN WITH 2.0% PVC AT 220°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.022	55	62	66	>300	99.88	<0.01
1.5	1.025	62	53	60	>300	99.82	<0.01
2	1.027	68	46	54	>300	99.80	<0.01
2.5	1.030	75	44	50	>300	99.77	<0.01
3	1.033	85	39	45	>300	99.72	<0.01
3.5	1.036	95	34	22	>300	99.46	<0.01

TABLE - 5

HALDIA PAVING BITUMEN AIR-BLOWN WITH 2% PVC AT 240°C,

THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.023	59	50	52	>300	99.84	<0.01
1.5	1.025	68	38	46	>300	99.80	<0.01
2	1.028	79	31	20	>300	99.76	<0.01
2.5	1.031	92	24	14	>300	99.71	<0.01
3	1.034	105	18	8	>300	99.65	<0.01
4	1.045	142	5	2.0	>300	99.56	<0.01

TABLE - 6

HALDIA PAVING BITUMEN AIR-BLOWN WITH 2.0% PVC AT 260°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.025	63	37	24	>300	99.83	<0.01
1.5	1.029	76	27	15	>300	99.79	<0.01
2	1.032	92	18	8	>300	99.74	<0.01
2.5	1.035	108	11	4.0	>300	99.69	<0.01
3	1.038	128	5	2.0	>300	99.64	<0.01
3.5	1.042	154	0	0	>300	99.60	<0.01

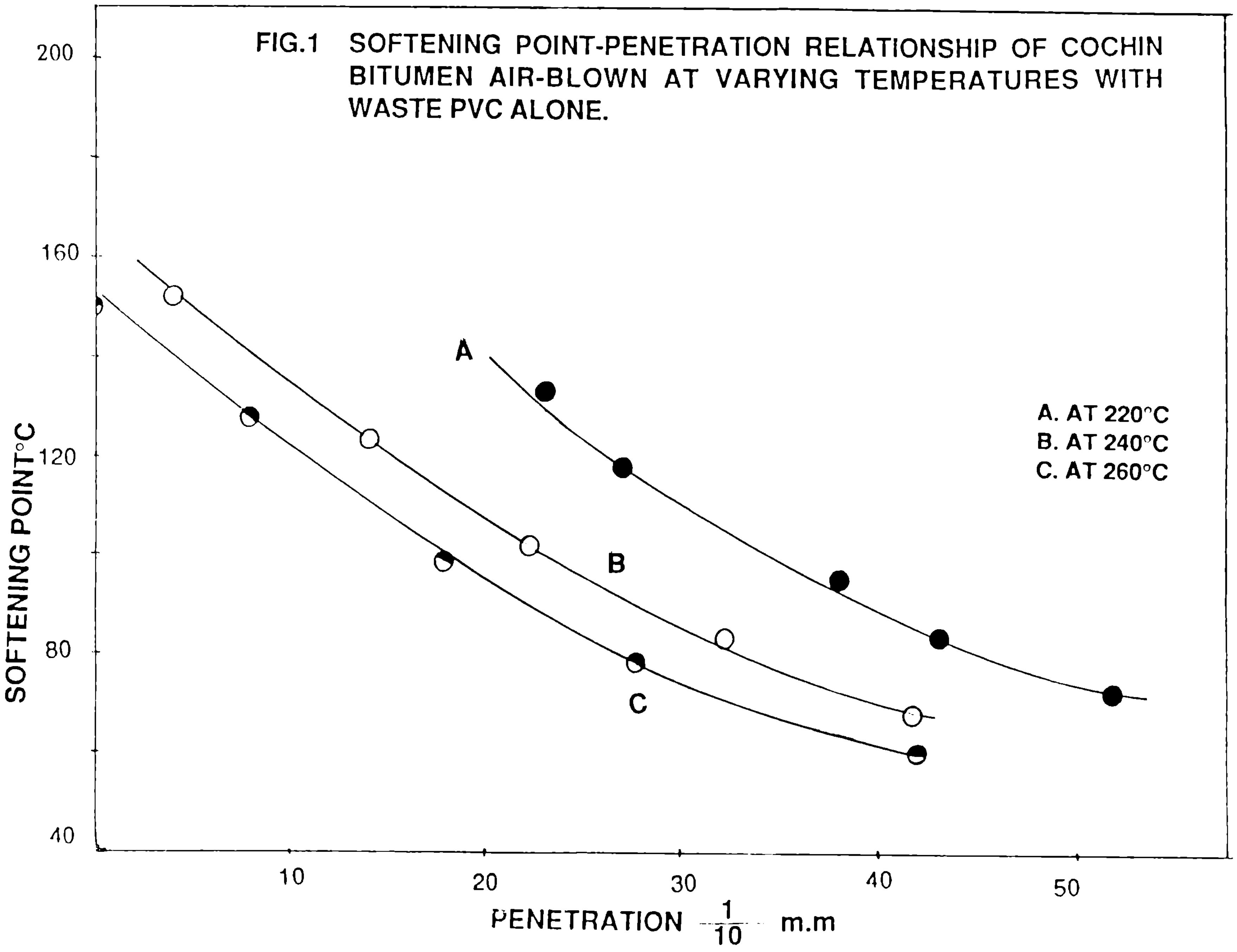


FIG.1 SOFTENING POINT-PENETRATION RELATIONSHIP OF COCHIN BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC ALONE.

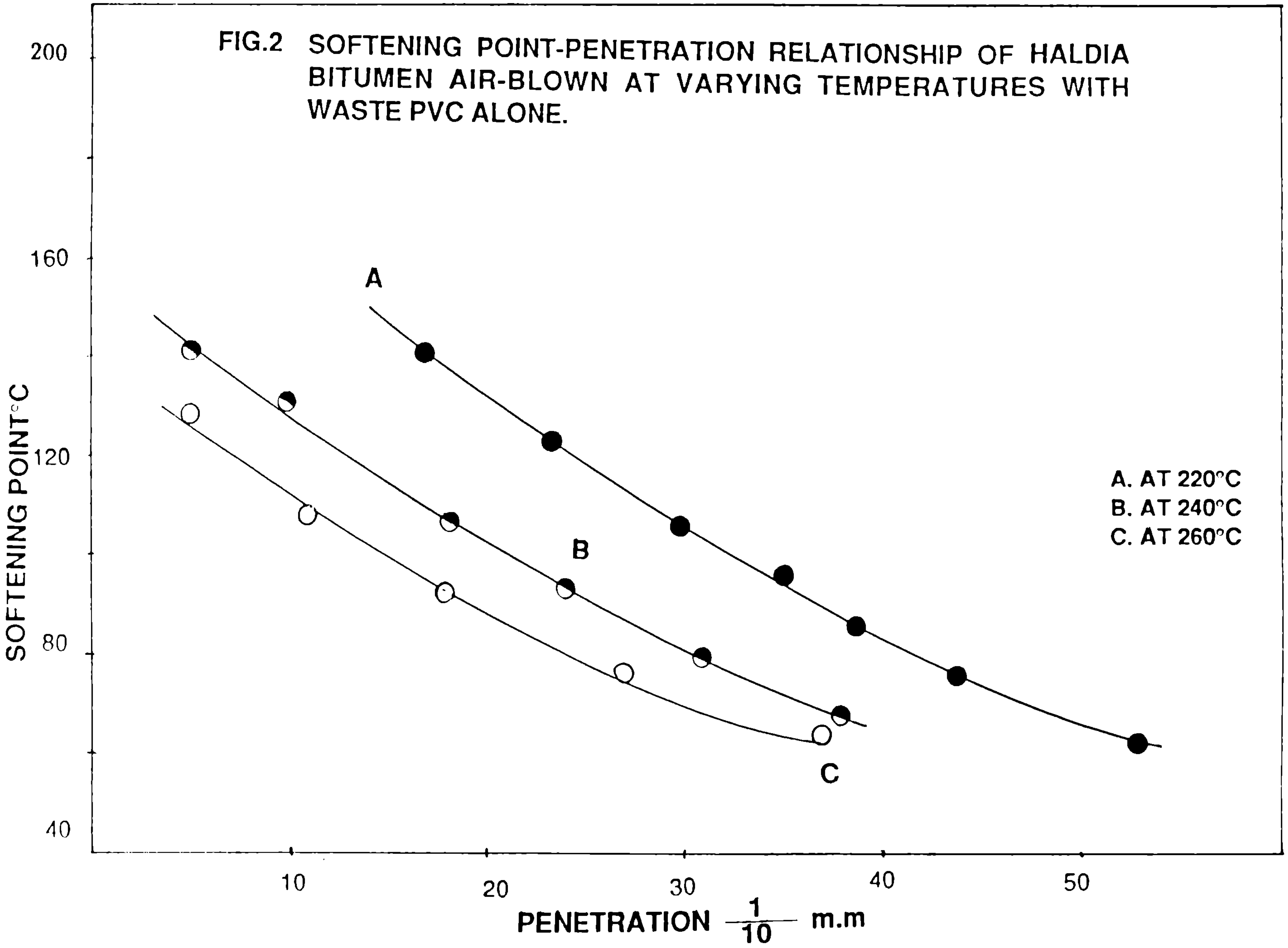


FIG.2 SOFTENING POINT-PENETRATION RELATIONSHIP OF HALDIA BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC ALONE.

of time and analysed. The process was repeated at 240°C and 260°C also.

RESULT AND DISCUSSION

The analytical data of the air-blown products are presented in Tables 1 to 6. From the tables it can be observed that waste PVC is very effective in reducing the duration of air-blowing. 2% PVC is capable of reducing the blowing time to about 60% compared to that without any additive. Blowing time is proportional to the cost of production. Hence the utilization of waste PVC is advantageous; it will make the process economical. Another observation is that compared to Haldia bitumen, Cochin bitumen requires lesser air blowing times. Figures 1 & 2 presents the plot of softening point vs penetration at various temperatures. It can be observed that with rise in temperature, the softening point-penetration relationship deteriorates. It is already reported that during air-blowing, oil losses becomes considerable as the temperature goes up. The inferior softening point-penetration relationship is attributed to the low oil content in the air blown products.[112] But it was found that by suitably selecting the temperature of air-blowing it is easily possible to manufacture all the ten different grades of industrial bitumen as per IS 702-1961.

Another observation is that compared to the air blown products from Haldia bitumen, the Cochin bitumen possess a better softening point penetration relationship. A comparative study with ferric chloride air-blown products (Chapter IV) shows that PVC air-blown products are much superior in softening point penetration relationship.

V.a.2. AIR BLOWING OF PAVING BITUMEN IN PRESENCE OF PVC AND IRON POWDER

The promoting effect of iron powder on the catalytic activity of waste PVC is investigated.

EXPERIMENTAL

One kg of the raw material is taken in the reactor vessel, heated to 220°C, added 1% waste PVC and air blown at the rate of 5ℓ/min/kg raw material. Samples were drawn at definite intervals of time and analysed. The process was repeated with 0.3% iron powder alone, 1% PVC along with 0.3% iron powder also. In order to evaluate the effect of temperature, the process was carried out at 240°C and 260°C also.

RESULT AND DISCUSSION

The analytical data of the various air blown products are presented in Tables 7 to 14. From Tables

TABLE - 7

COCHIN BITUMEN AIR-BLOWN WITH IRON POWDER AND MANGANESE DIOXIDE SEPARATELY AT 220°C AND 5L/MIN/KG AIR-FLOW RATE

Duration of blowing hours	Softening point °C		
	Without any additive	With Iron Powder	With Manganese dioxide
0	46	46	46
1	53	53	54
2	60	60	62
3	69	70	74
4	77	78	83
5	88	88	96

TABLE - 8

HALDIA BITUMEN AIR-BLOWN WITH IRON POWDER AND MANGANESE DIOXIDE SEPARATELY AT 220°C AND 5L/MIN/KG AIR-FLOW RATE

Duration of blowing hours	Softening point °C		
	Without any additive	With Iron Powder	With Manganese dioxide
0	44	44	44
1	49	49	50
2	54	54	56
3	61	62	64
4	67	66	72
5	75	75	81

TABLE - 9

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 220°C

THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.016	54	68	75	>300	99.87	<0.01
1	1.020	64	58	69	>300	99.84	<0.01
1.5	1.023	75	47	60	>300	99.79	<0.01
2	1.026	88	38	53	>300	99.72	<0.01
2.5	1.030	105	30	22	>300	99.65	<0.01
3	1.037	125	23	15.0	>300	99.60	<0.01

TABLE - 10

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 240°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.018	58	58	71	>300	99.86	<0.01
1	1.022	72	38	53	>300	99.83	<0.01
1.5	1.026	90	27	18	>300	99.77	<0.01
2	1.030	110	18	11.5	>300	99.69	<0.01
2.5	1.036	138	9	5.0	>300	99.62	<0.01
3.0	1.042	170	0	0	>300	99.54	<0.01

TABLE - 11

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 260°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Solubility in CS_2%wt.	Flash point °C	Loss on heating % wt.
0.5	1.019	60	41	55	99.84	>300	<0.01
1	1.023	80	26	18	99.80	>300	<0.01
1.5	1.028	104	14	8	99.74	>300	<0.01
2	1.036	135	3	2.5	99.66	>300	<0.01
2.5	1.044	178	0	0	99.58	>300	<0.01

TABLE - 12

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 220^{o}C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27^{o}C	Softening point ^{o}C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Solubility in CS_2%wt.	Flash point ^{o}C	Loss on heating % wt.
1	1.024	57	58	60	99.84	>300	<0.01
1.5	1.026	63	49	54	99.80	>300	<0.01
2	1.029	72	44	50	99.77	>300	<0.01
2.5	1.032	82	38	45	99.73	>300	<0.01
3	1.036	92	33	20	99.68	>300	<0.01
5	1.046	150	10	5	99.45	>300	<0.01

TABLE - 13

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 240°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point $^{\circ}$C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point $^{\circ}$C	Solubility in CS_2 %wt.	Loss on heating % wt.
1	1.025	61	45	50	>300	99.80	<0.01
1.5	1.029	71	34	24	>300	99.76	<0.01
2	1.031	83	28	15	>300	99.72	<0.01
2.5	1.033	98	20	10.5	>300	99.68	<0.01
3	1.036	114	14	6.0	>300	99.62	<0.01
3.5	1.040	134	7	2.5	>300	99.56	<0.01

TABLE - 14

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% IRON POWDER AT 260°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.026	66	31	19.0	>300	99.79	<0.01
1.5	1.028	79	23	12.5	>300	99.75	<0.01
2	1.030	96	15	6.5	>300	99.71	<0.01
2.5	1.034	118	6	2.5	> 300	99.66	<0.01
3	1.038	140	0	0	> 300	99.61	<0.01

FIG.3 SOFTENING POINT-PENETRATION RELATIONSHIP OF COCHIN BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC AND IRON POWDER

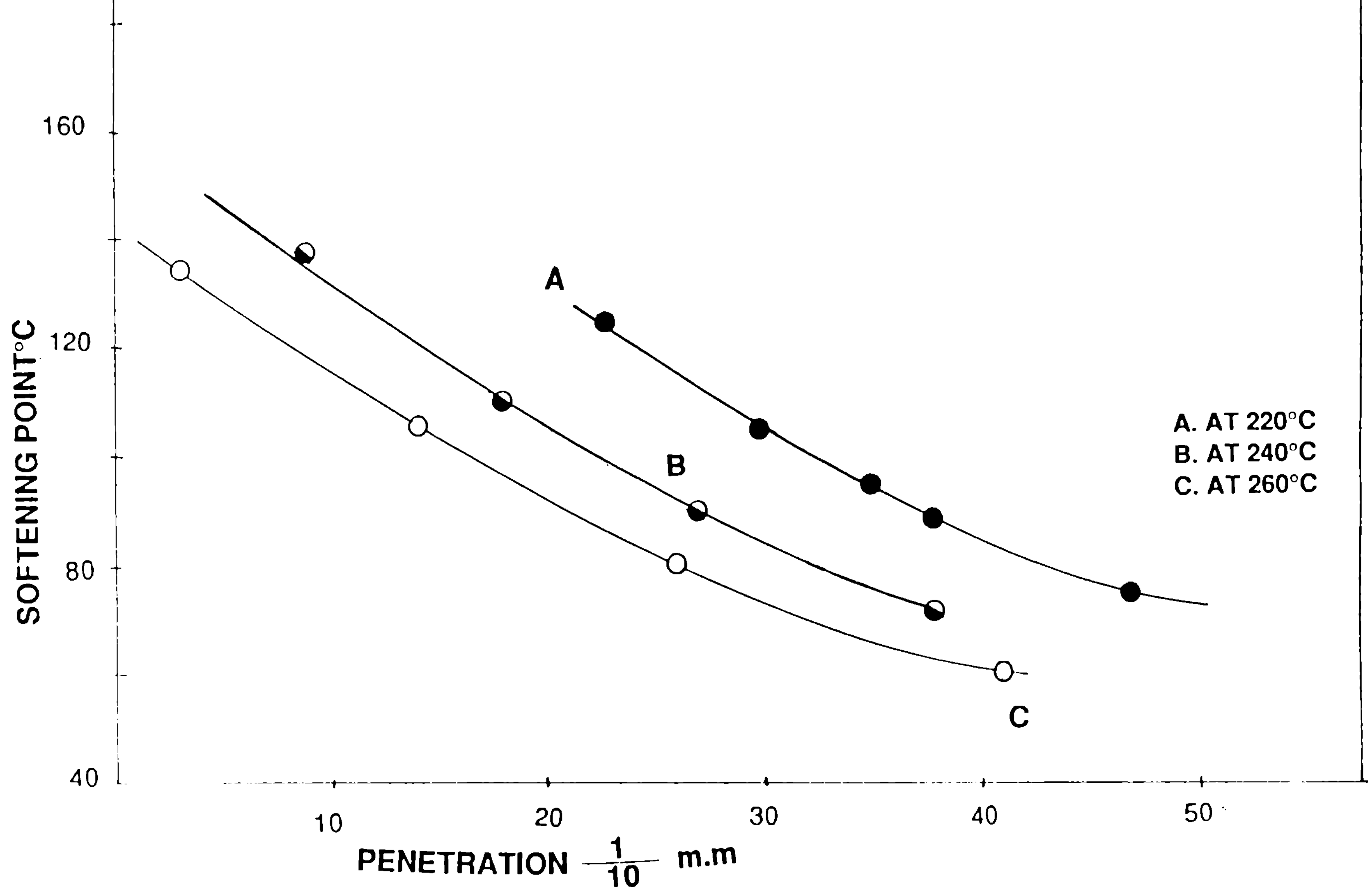
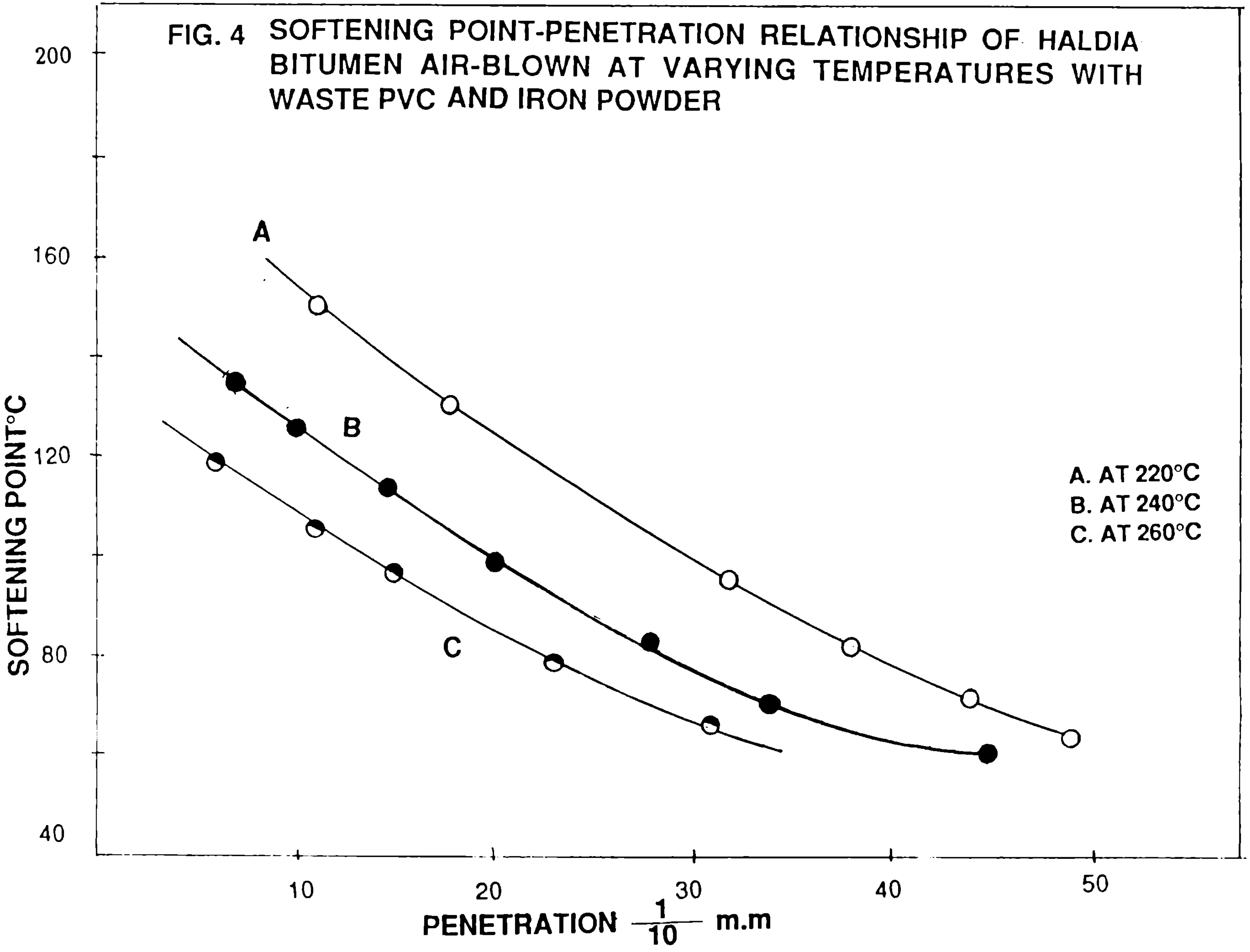


FIG. 4 SOFTENING POINT-PENETRATION RELATIONSHIP OF HALDIA BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC AND IRON POWDER



7 and 8 it can be observed that iron powder alone is not at all effective in bitumen air-blowing polymerization. From the Tables 22, 23, 26 & 27 it can be observed that the rate of bitumen polymerization with PVC catalyst is considerably increased by the addition of iron powder. The effect of iron as a promoter for PVC catalyst is attributed to the formation of ferric chloride during the process, which in turn is more effective than hydrochloric acid in catalysing the polymerization. Figures 3 and 4 represents the plot of softening point vs penetration at different temperatures. A comparative study with air-blown products with PVC shows that the softening point penetration relationship of the products with PVC and iron powder is slightly inferior. However, it can be seen that they are much superior to those made with ferric chloride, a conventional catalyst.

V.a.3. AIR BLOWING OF PAVING BITUMEN IN PRESENCE OF PVC AND MANGANESE DIOXIDE

The synergistic effect of manganese dioxide and waste PVC on the air-blowing polymerization of bitumen is investigated.

TABLE - 15

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 220°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.016	54	66	72	>300	99.88	<0.01
1	1.019	64	56	67	>300	99.85	<0.01
1.5	1.022	73	49	62	>300	99.80	<0.01
2	1.025	87	37	52	>300	99.74	<0.01
2.5	1.029	102	30	22	>300	99.67	<0.01
3	1.036	120	22	13.5	>300	99.62	<0.01

TABLE - 16

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 240^{o}C,

THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27^{o}C	Softening point ^{o}C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point ^{o}C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.017	57	57	69	>300	99.88	<0.01
1	1.021	70	37	52	>300	99.84	<0.01
1.5	1.024	86	29	21	>300	99.78	<0.01
2	1.028	105	19	12	>300	99.70	<0.01
2.5	1.034	132	9	5.0	>300	99.63	<0.01
3	1.041	163	0	0	>300	99.55	<0.01

TABLE - 17

COCHIN PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 260°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
0.5	1.018	60	38	50	>300	99.86	<0.01
1	1.022	78	26	18	>300	99.82	<0.01
1.5	1.027	102	14	7	>300	99.76	<0.01
2	1.032	135	2	1	>300	99.68	<0.01
2.5	1.042	172	0	0	>300	99.60	<0.01

TABLE - 18

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 220°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.023	56	57	60	>300	99.86	<0.01
1.5	1.026	63	48	55	>300	99.81	<0.01
2	1.029	70	44	51	>300	99.78	<0.01
2.5	1.032	80	38	46	>300	99.75	<0.01
3	1.035	90	33	21	>300	99.70	<0.01
5	1.044	148	10	3.0	>300	99.44	<0.01

TABLE - 19

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 240°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2 %wt.	Loss on heating % wt.
1	1.024	60	43	50	>300	99.82	<0.01
1.5	1.026	70	33	21	>300	99.78	<0.01
2	1.029	80	27	14.5	>300	99.74	<0.01
2.5	1.032	95	21	11.0	>300	99.69	<0.01
3	1.035	110	14	6.5	>300	99.63	<0.01
3.5	1.040	128	6	2.5	>300	99.57	<0.01

TABLE - 20

HALDIA PAVING BITUMEN AIR-BLOWN WITH 1% PVC AND 0.3% MANGANESE DIOXIDE AT 260°C, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	Specific gravity at 27°C	Softening point °C	Penetration $\frac{1}{10}$ m.m.	Ductility Cms.	Flash point °C	Solubility in CS_2%wt.	Loss on heating % wt.
1	1.025	65	30	19.0	>300	99.81	<0.01
1.5	1.028	78	22	11.5	>300	99.77	<0.01
2	1.031	95	14	6.5	>300	99.72	<0.01
2.2	1.033	101	11	5.0	>300	99.70	<0.01
2.5	1.035	115	6	2.5	>300	99.67	<0.01
3	1.039	135	0	0	>300	99.62	<0.01

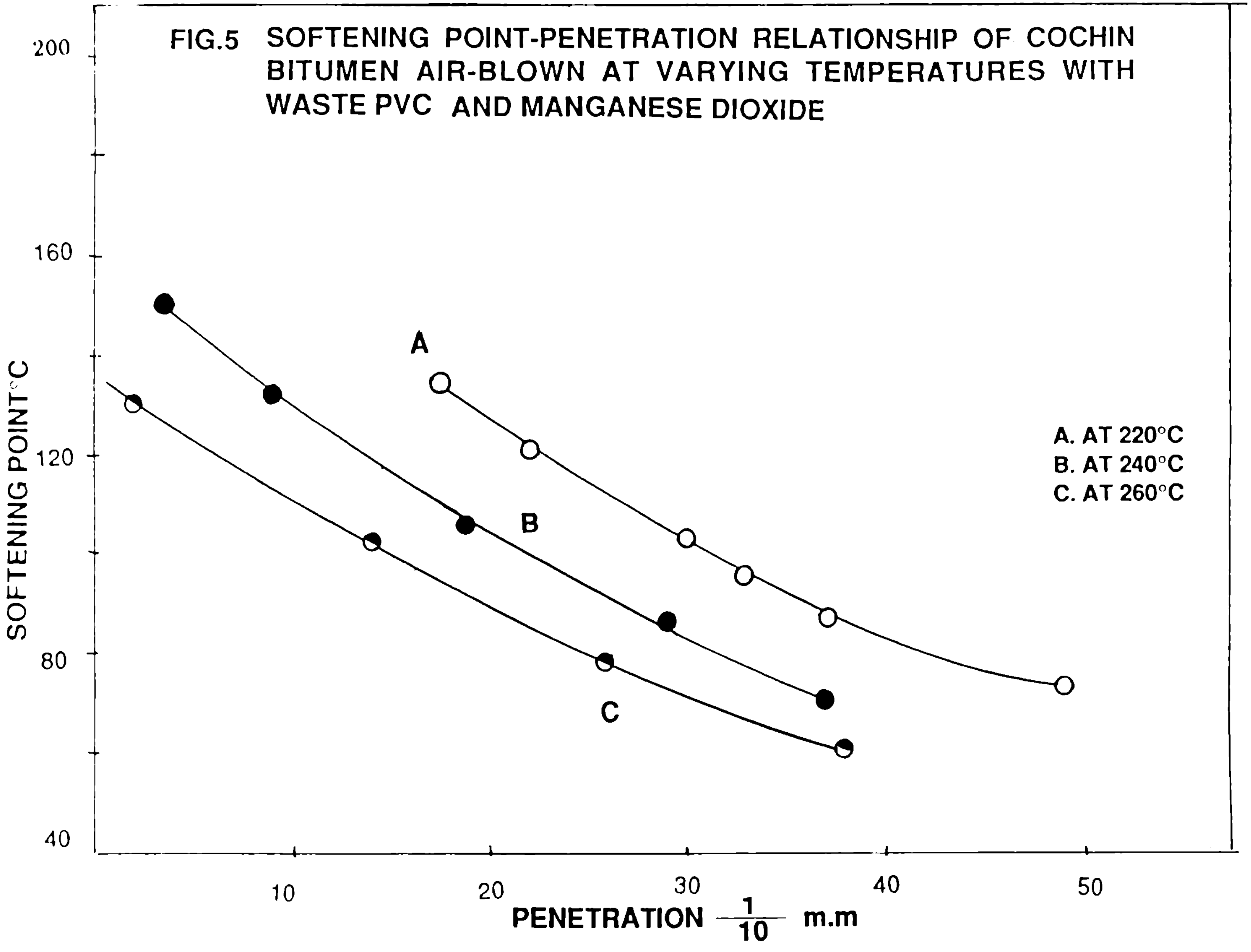


FIG.5 SOFTENING POINT-PENETRATION RELATIONSHIP OF COCHIN BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC AND MANGANESE DIOXIDE

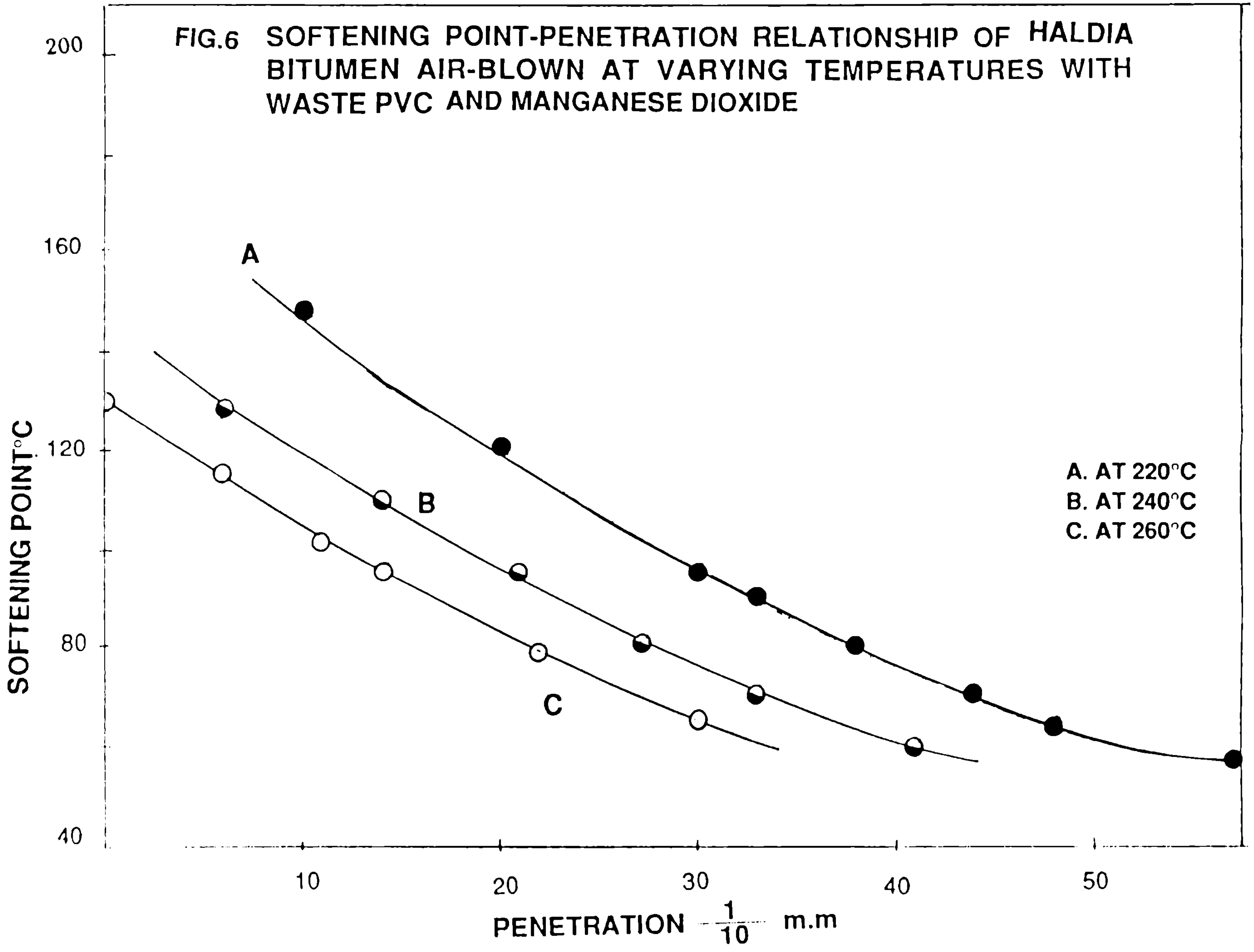


FIG.6 SOFTENING POINT-PENETRATION RELATIONSHIP OF HALDIA BITUMEN AIR-BLOWN AT VARYING TEMPERATURES WITH WASTE PVC AND MANGANESE DIOXIDE

EXPERIMENTAL

One kg of the raw material is taken in the reactor vessel and heated to 220°C. Added 1% PVC to the raw material and air-blown at the rate of 5ℓ/min/kg. Samples were drawn at definite intervals of time and analysed. The experiment was repeated with 0.3% manganese dioxide alone and 1% PVC along with 0.3% manganese dioxide. In order to evaluate the effect of temperature studies were made at 240°C and 260°C also.

RESULT AND DISCUSSION

The analytical data are presented in Tables 7, 8, 15 to 20, 30 & 31. From the results it can be observed that the rate of bitumen polymerization in presence of waste PVC and manganese dioxide together is more than the sum of their individual rates.

Figures 5 and 6 present the plot of softening point vs penetration. A comparative study reveals that the softening point penetration relationship is slightly inferior to that with PVC alone. However, it can be seen that the softening point penetration relationship with PVC and manganese dioxide is much superior to that of ferric chloride, a conventional catalyst.

V.b. CHARACTERIZATION OF AIR BLOWN BITUMEN

V.b.1. INFRARED SPECTRA

Figures 7 and 8 show the infrared spectra of the air-blown Cochin and Haldia bitumen in carbon-tetra-chloride. It can be observed that there is considerable increase in the intensity of the band at 2950 cm^{-1}. This is attributed to the presence of polyolefins in the product.[133] The improved softening point-penetration relationship of the waste PVC air-blown bitumen is attributed to the presence of polyenes formed by the degradation of PVC. This is fully in agreement with the observations already reported that polyenes are capable of improving the softening point penetration relationship of bitumen.

V.b.2. MOLECULAR WEIGHT DETERMINATION BY GEL-PERMEATION CHROMATOGRAPHY

During the bitumen air-blowing process naphthene aromatic fraction present in the bitumen is converted to polar aromatics which then polymerize to form asphaltenes. So it was thought worthwhile to find out the asphaltene contents and their molecular weights in the air-blown bitumen. The results are presented in Table 21. The Gel permeation chromatographs are given in figures 9 and 10.

FIG:7 INFRA RED SPECTRA OF AIR-BLOWN COCHIN BITUMEN

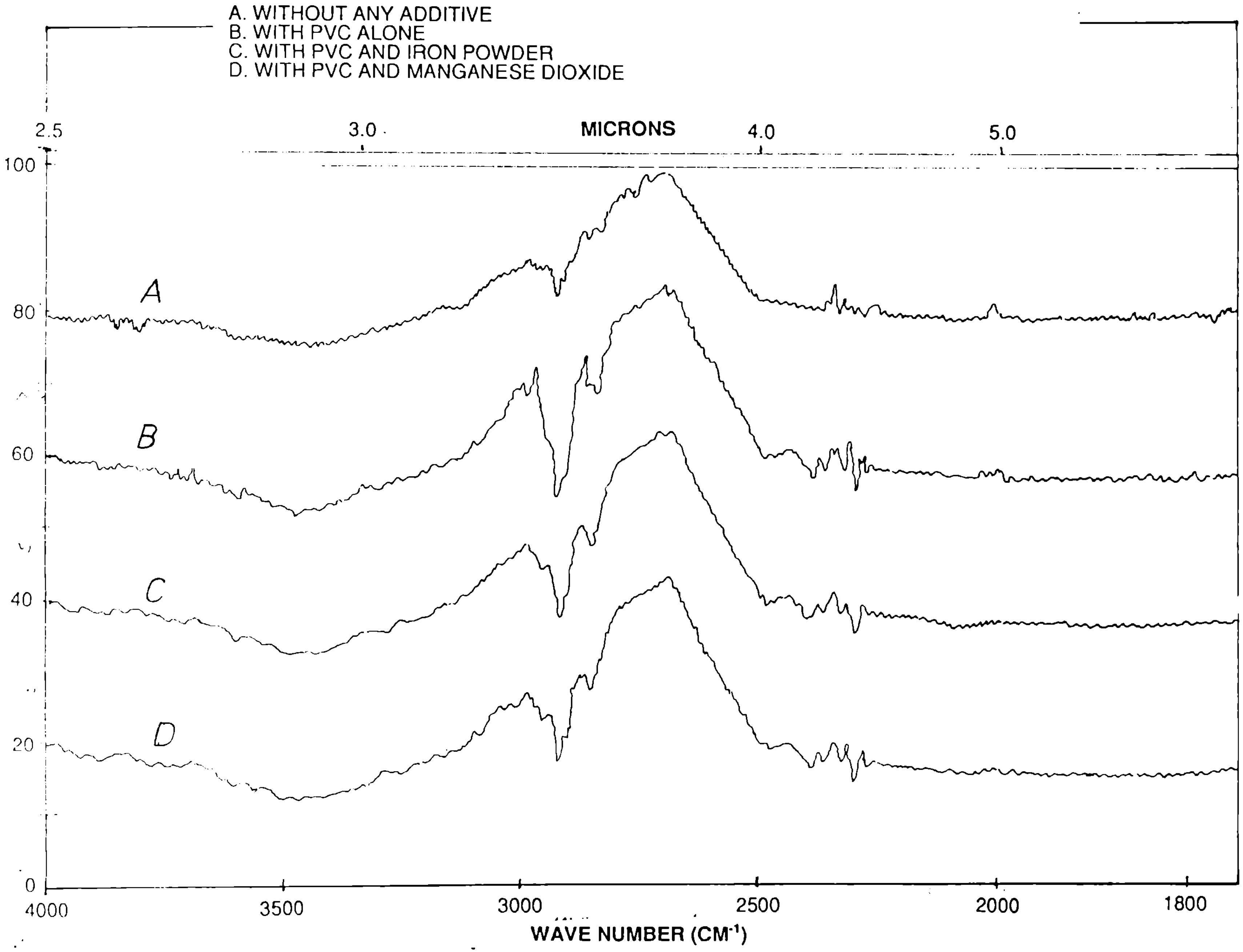


FIG:8 INFRA RED SPECTRA OF AIR-BLOWN HALDIA BITUMEN

A. WITHOUT ANY ADDITIVE
B. WITH PVC ALONE
C. WITH PVC AND IRON POWDER
D. WITH PVC AND MANGANESE DIOXIDE

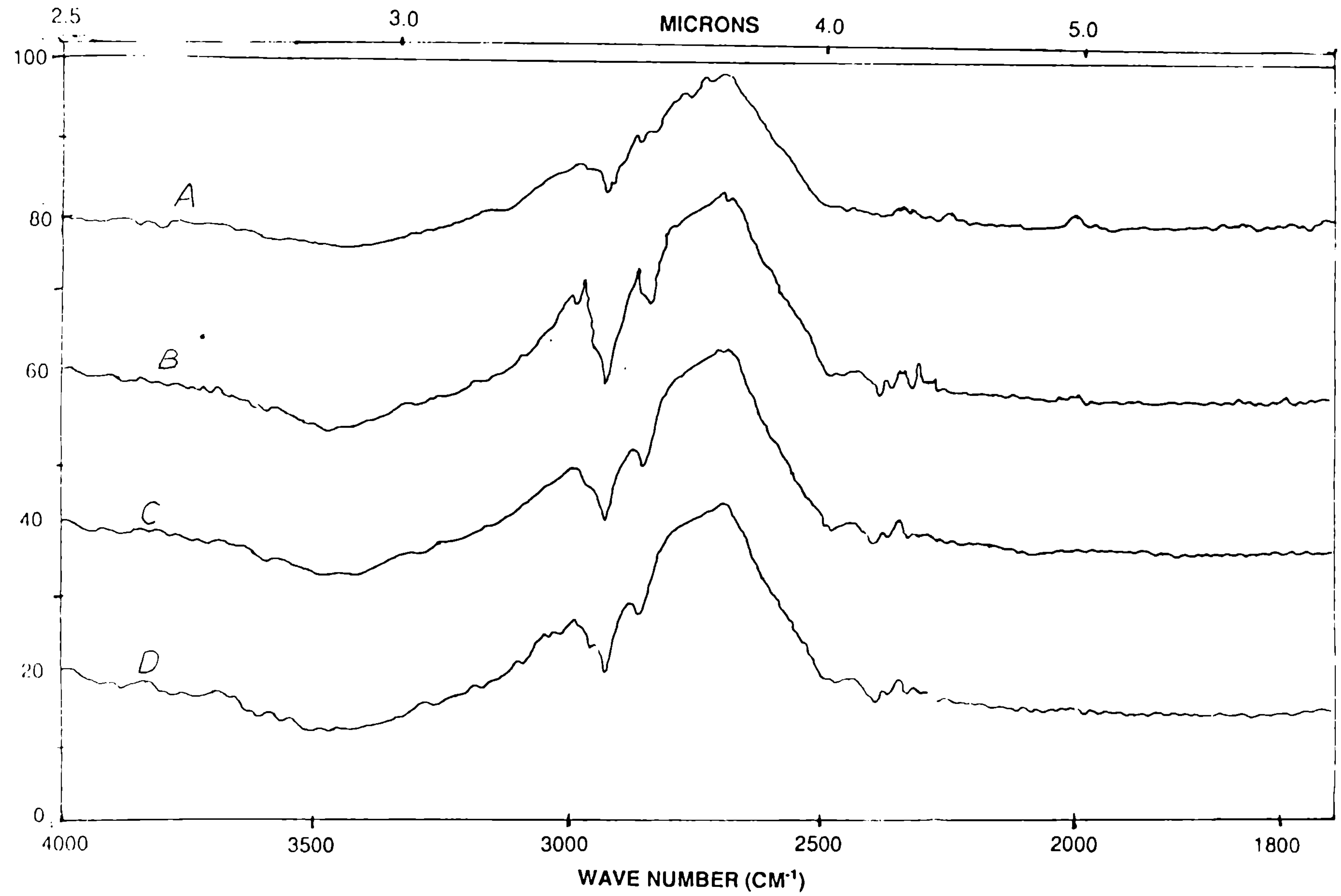


TABLE - 21

EFFECT OF ASPHALTENE CONTENT AND ITS MOLECULAR WEIGHT ON SOFTENING POINT - PENETRATION RELATIONSHIP

Bitumen Air-blown at 220 °C		Softening point °C	Penetration $\frac{1}{10}$ m.m.	Asphaltene content	Molecular weight of asphaltenes	
					Mw	Mn
COCHIN	with PVC alone	95	38	36.8	15600	8100
	with PVC and Iron powder	95	35	36.0	14900	7700
	with PVC and Manganese dioxide	95	33	35.4	14200	7310
HALDIA	with PVC alone	95	35	38.0	17500	9950
	with PVC and Iron powder	95	32	37.2	16300	9400
	with PVC and Manganese dioxide	95	30	36.6	15800	9000

FIG.9. GEL PEPMEATION CHROMATOGRAPHS OF THE ASPHALTENE FRACTIONS OF THE COCHIN AIR-BLOWN ASPHALTS.

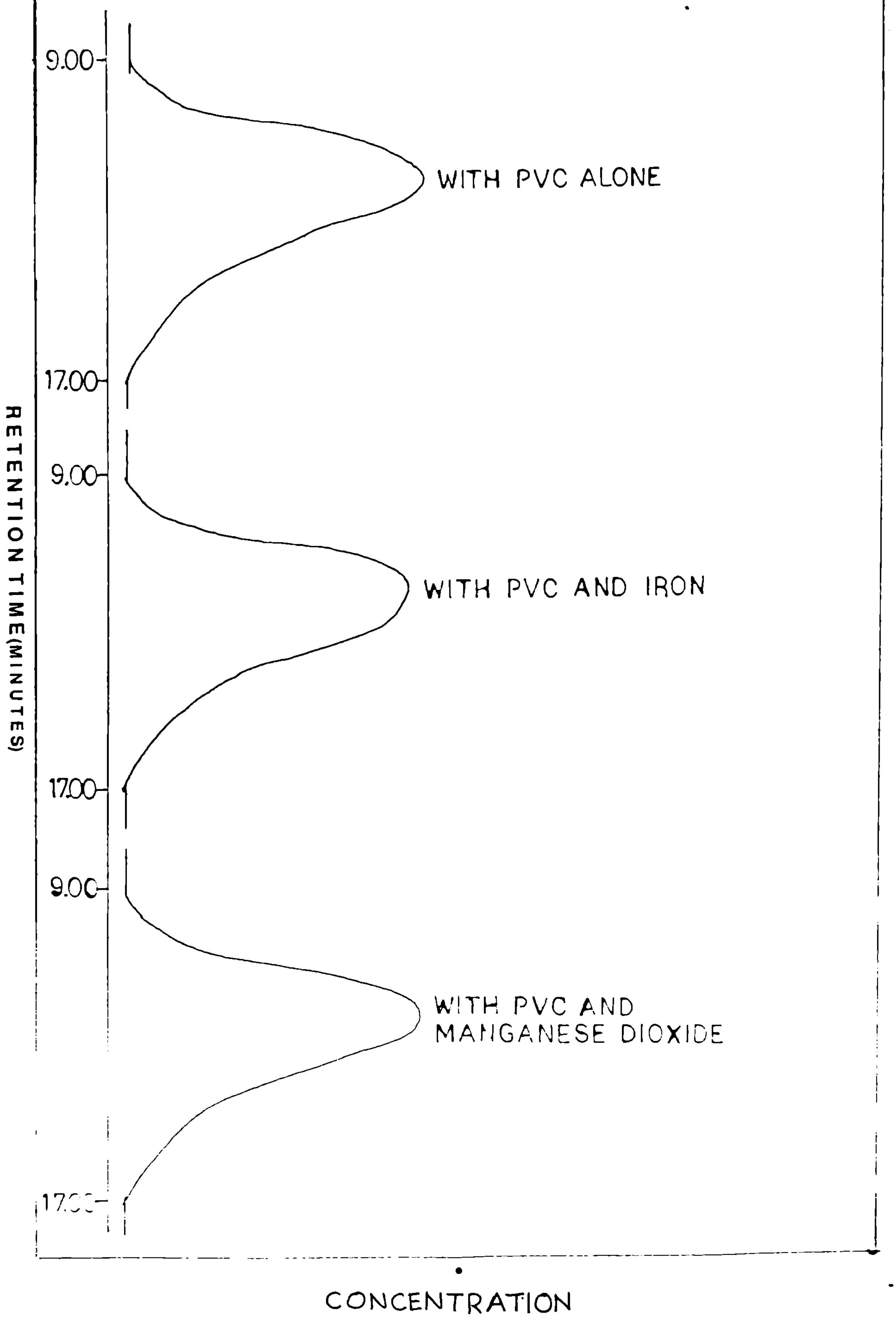
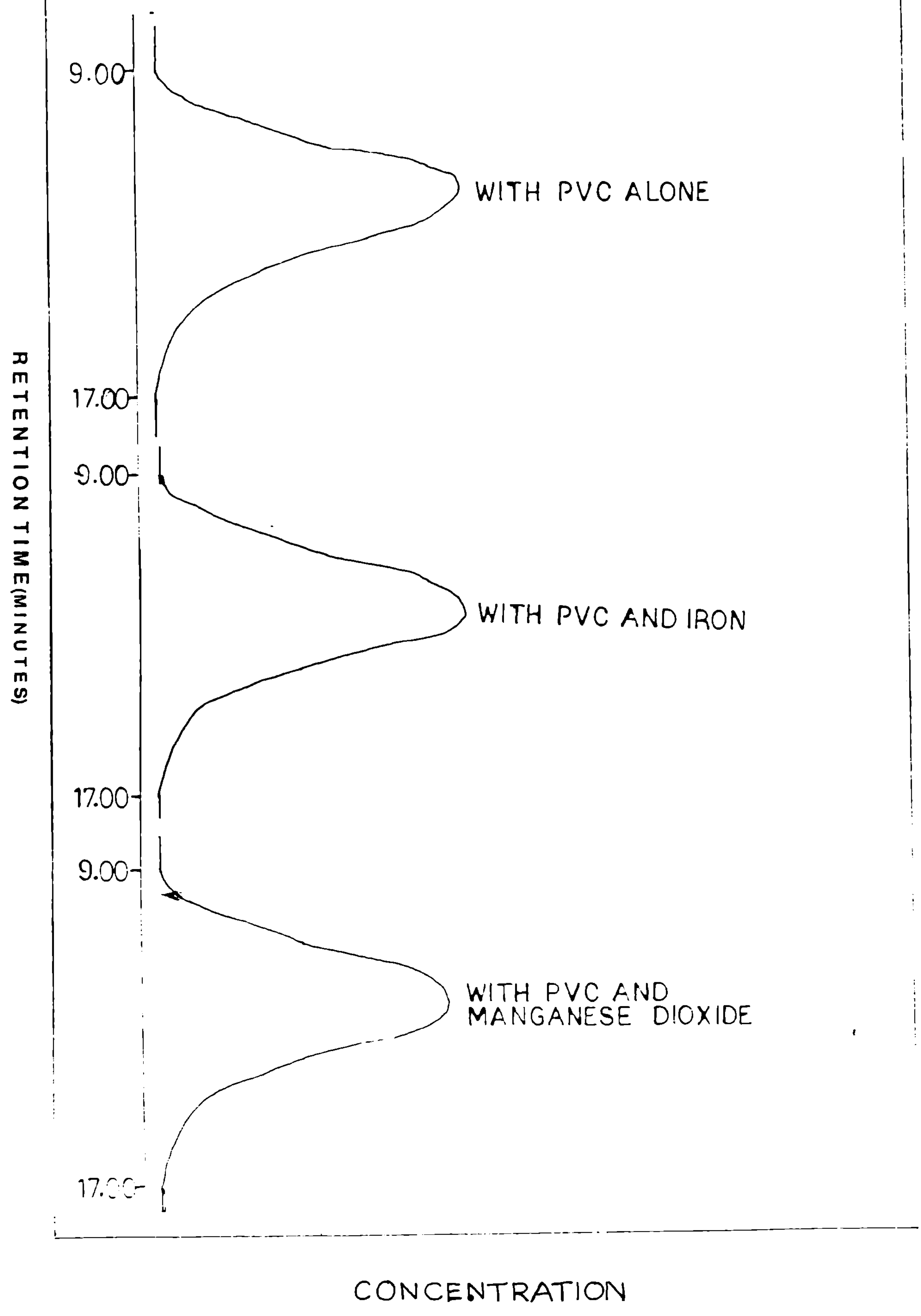


FIG.10. GEL PERMEATION CHROMATOGRAPHS OF THE ASPHALTENE FRACTIONS OF THE HALDIA AIR-BLOWN ASPHALTS.



From Table 21 it can be observed that when the air blown bitumen products possess high asphaltene contents of low molecular weights (softer asphaltenes), the softening point penetration relationship will be better. This is in agreement with the observations already made by Dark.[116]

V.b.3. EFFECT OF THE RAW MATERIAL ON THE SOFTENING POINT-PENETRATION RELATIONSHIP.

From Table 21 it can be seen that Cochin air-blown bitumen possess better softening point-penetration relationship compared to Haldia air-blown bitumen. This is attributed to the presence of high content of saturates in Cochin paving bitumen compared to that in Haldia paving bitumen. This is in accordance with the observations made in Chapter IV. However, our studies reveal that by suitably adjusting the temperature of the air-blowing process, it is possible to manufacture all the ten different grades of industrial bitumen as per IS 702-1961 from both the raw materials.

V.c KINETIC STUDIES ON BITUMEN AIR-BLOWING

V.c.1. BITUMEN AIR-BLOWN WITH PVC ALONE.

In order to find out the optimum concentration of waste PVC required for the process the raw materials

TABLE - 22

COCHIN PAVING BITUMEN AIR-BLOWN WITH DIFFERENT CONCENTRATIONS OF WASTE PVC AT 220°C

Concentration of waste PVC	Duration of blowing in hours	Softening point °C	First Order rate constant hour^{-1}
1%	1	57	0.21
	1.5	63	0.21
	2	69	0.20
	2.5	76	0.20
	3	85	0.20
2%	1	62	0.30
	1.5	72	0.30
	2	84	0.30
	2.5	98	0.30
	3	118	0.31
3%	1	64	0.33
	1.5	76	0.33
	2	89	0.33
	2.5	105	0.33
	3	125	0.33

TABLE - 23

HALDIA PAVING BITUMEN AIR-BLOWN WITH DIFFERENT CONCENTRATIONS OF WASTE PVC AT 220°C

Concentration of waste PVC	Duration of blowing in hours	Softening point °C	First Order rate constant $hour^{-1}$
1%	1	52	0.15
	1.5	55	0.15
	2.0	59	0.15
	2.5	64	0.15
	3.0	70	0.15
2%	1	55	0.22
	1.5	62	0.23
	2	68	0.22
	2.5	75	0.21
	3	85	0.22
3%	1	56	0.24
	1.5	63	0.24
	2	72	0.25
	2.5	80	0.24
	3.0	91	0.24

FIG.11 BITUMEN AIR-BLOWN AT 220°C WITH VARYING CONCENTRATIONS OF WASTE PVC.

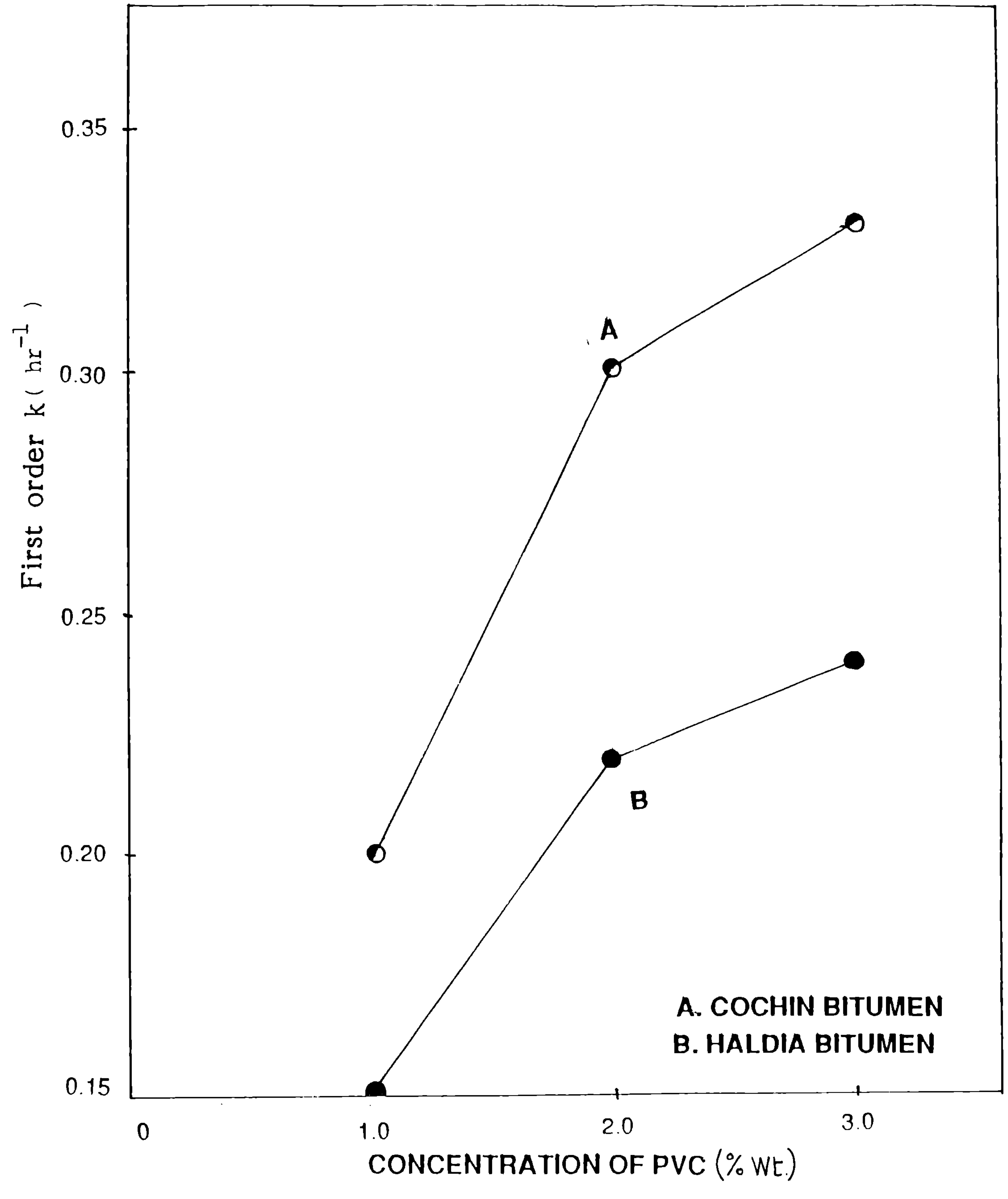


TABLE - 24

COCHIN BITUMEN AIR-BLOWN WITH 2% WASTE PVC AT VARYING TEMPERATURES, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1} 6
0	46	-	46	-	46	-
0.5	-	-	56	0.39	60	0.53
1	62	0.30	68	0.40	78	0.52
1.5	72	0.30	84	0.40	99	0.51
2	84	0.30	102	0.40	128	0.51
2.5	98	0.30	125	0.40	165	0.51
3	118	0.31	152	0.40	-	-

TABLE - 25

HALDIA BITUMEN AIR-BLOWN WITH 2% WASTE PVC AT VARYING TEMPERATURES, THE AIR-FLOW RATE BEING 5L/MIN/KG SAMPLE

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point °C	Ist order rate constant $hour^{-1}$	Softening point °C	Ist order rate constant $hour^{-1}$	Softening point °C	Ist order rate constant $hour^{-1}$
0	44	-	44	-	44	-
1	55	0.22	59	0.29	63	0.36
1.5	62	0.23	68	0.29	76	0.36
2	68	0.22	79	0.29	92	0.37
2.5	75	0.21	92	0.30	108	0.36
3	85	0.22	105	0.29	128	0.36

were air-blown with 5ℓ/min/kg of sample at 220°C in presence of varying concentrations of waste PVC. Samples were drawn at definite intervals of time and tested. The analytical data are presented in Tables 22 and 23. The first order rate constants were calculated from the rate data. From figure 11 it can be seen that the optimum concentration of PVC required for the process is 2.0%.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS

In order to determine the temperature coefficients of the reaction the process was carried out at varying temperatures keeping the concentration of waste PVC and rate of flow of air constant.

The results are presented in Tables 24 and 25. Arrhenius plot was made by ploting log of rate constants vs reciprocal of absolute temperature. From figures 14 and 15 it can be seen that the activation energies in k cal/mole for Cochin bitumen and Haldia bitumen are 7.04 and 6.50 respectively.

Based on the above experimental results, the following reaction mechanism is suggested :

1) formation of free radicals

$$RH + O_2 \longrightarrow R^{\bullet} + HOO^{\bullet}$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + HCl \longrightarrow ROOH + Cl^{\bullet}$$

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$RH + HOO^{\bullet} \longrightarrow R^{\bullet} + H_2O_2$$

$$H_2O_2 \longrightarrow 2\ OH^{\bullet}$$

$$RH + Cl^{\bullet} \longrightarrow R^{\bullet} + HCl$$

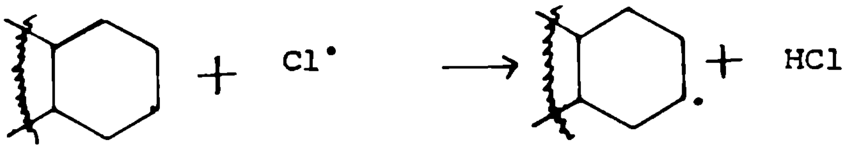
2) Polymerization by chain reaction

$$\overset{\bullet}{R} + \underset{\text{(Unsaturated compound)}}{R'H} \longrightarrow \overset{\bullet}{R}R'H$$

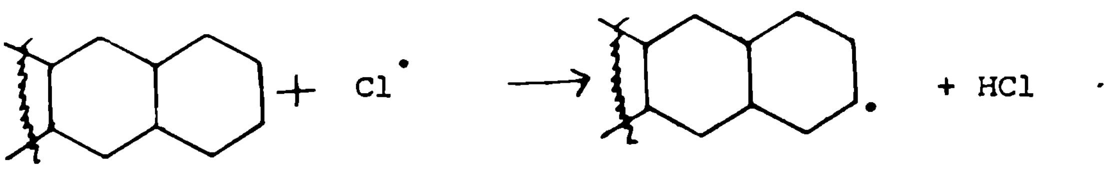
$$\overset{\bullet}{R}R'H + R''H \longrightarrow \overset{\bullet}{R}R'HR''H$$

$$\overset{\bullet}{R}R'HR''H \xrightarrow{\text{disproportionation}} \text{Stable products}$$

3) Cross linking



(Naphthenic compound)



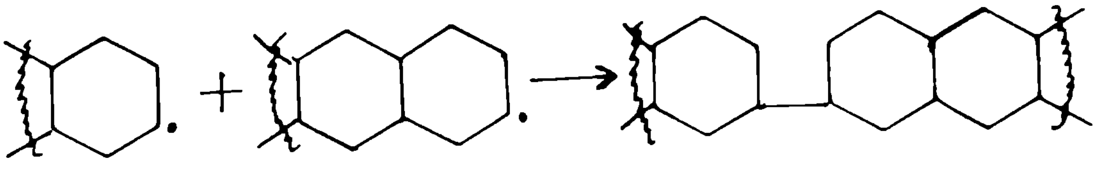


TABLE - 26

COCHIN PAVING BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF WASTE PVC AND IRON POWDER AT 220°C

Concentration of waste PVC and iron powder	Duration of blowing in hours	Softening point °C	1^{st} order rate constant $hour^{-1}$
1% waste PVC and 0.1% Iron powder	1	62	0.25
	1.5	67	0.25
	2	78	0.26
	2.5	87	0.25
	3	96	0.25
1% waste PVC and 0.3% Iron powder	1	64	0.33
	1.5	75	0.33
	2	88	0.32
	2.5	105	0.33
	3	125	0.33
1% waste PVC and 0.5% Iron powder	1	66	0.36
	1.5	78	0.35
	2	93	0.35
	2.5	114	0.36
	3	135	0.36

TABLE - 27

HALDIA BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF WASTE PVC AND IRON POWDER AT 220°C.

Concentration of waste PVC and Iron powder	Duration of blowing in hours	Softening point °C	1^{st} order rate constant $hour^{-1}$
1% waste PVC and 0.1% Iron powder	1	52	0.18
	1.5	57	0.17
	2	63	0.18
	2.5	69	0.18
	3	76	0.18
1% waste PVC and 0.3% Iron powder	1	57	0.26
	1.5	63	0.24
	2	72	0.25
	2.5	82	0.25
	3	92	0.25
1% waste PVC and 0.5% Iron powder	1	58	0.28
	1.5	67	0.28
	2	77	0.28
	2.5	88	0.28
	3	101	0.28

FIG.12 BITUMEN AIR-BLOWN AT 220°C WITH 1% WASTE PVC AND VARYING CONCENTRATIONS OF IRON POWDER.

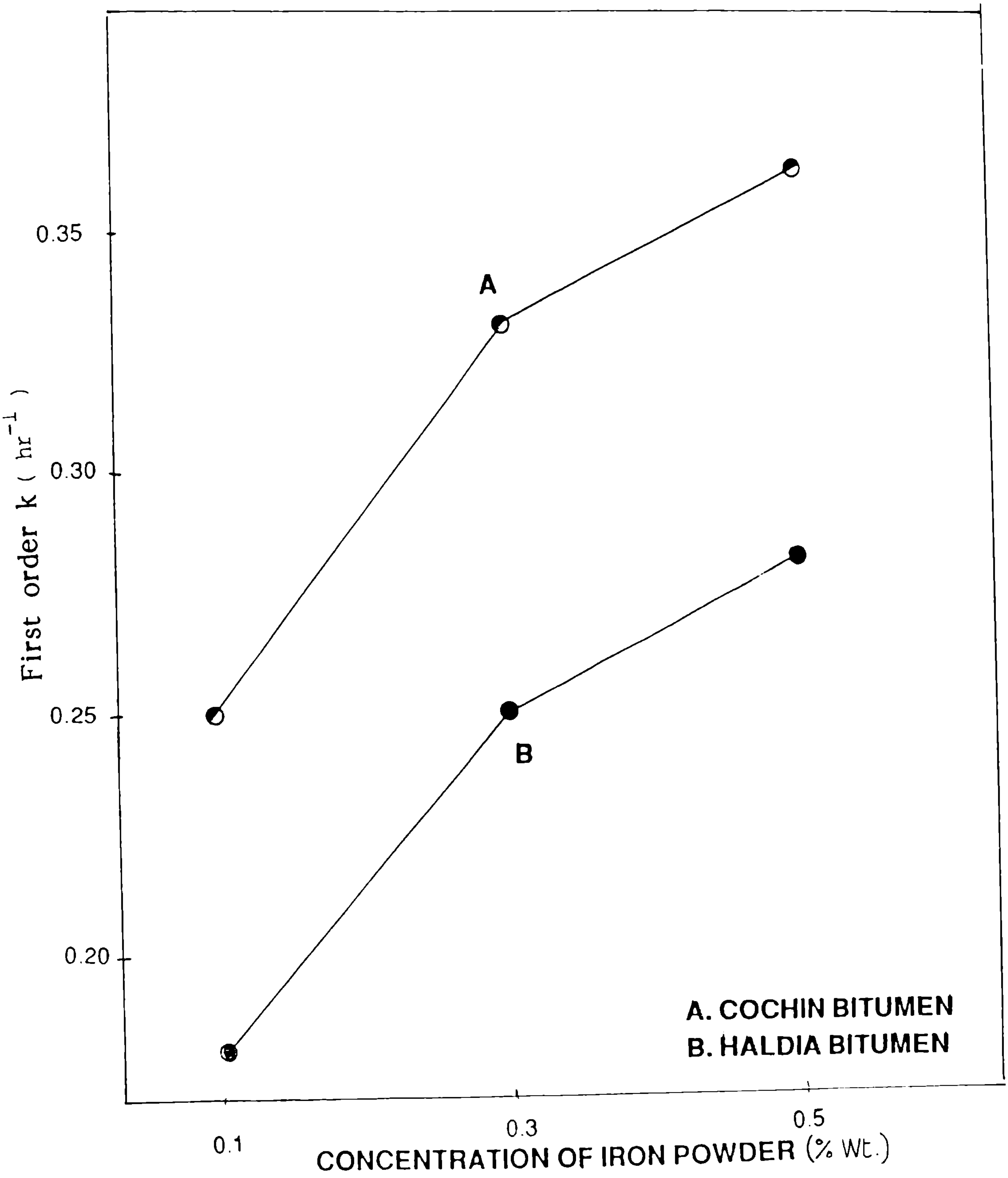


TABLE - 28

COCHIN BITUMEN AIR-BLOWN AT THE AIR-FLOW RATE OF 5L/MIN/KG SAMPLE WITH 1% WASTE PVC AND 0.3% IRON POWDER AT VARYING TEMPERATURES

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1}
0	46	-	46	-	46	-
0.5	54	0.32	58	0.46	60	0.53
1	64	0.33	72	0.45	80	0.55
1.5	75	0.33	90	0.45	104	0.54
2	88	0.32	110	0.44	135	0.54
2.5	105	0.33	138	0.44	178	0.54
3	125	0.33	170	0.44	-	-

TABLE - 29

HALDIA BITUMEN AIR-BLOWN AT THE AIR-FLOW RATE OF 5L/MIN/KG SAMPLE WITH 1% WASTE PVC AND 0.3% IRON POWDER AT VARYING TEMPERATURES

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point °C	Ist order rate constant hour^{-1}	Softening point °C	Ist order rate constant hour^{-1}	Softening point °C	Ist order rate constant hour^{-1}
0	44	-	44	-	44	-
1	57	0.26	61	0.33	66	0.41
1.5	63	0.24	71	0.32	79	0.39
2	72	0.25	83	0.32	96	0.39
2.5	82	0.25	98	0.32	118	0.39
3	92	0.25	114	0.32	140	0.39

Chlorine is reported to be more powerful than oxygen in the abstraction of hydrogen from hydrocarbons in bitumen.[138] The catalytic effect of PVC is attributed to the formation of chlorine radicals during the process.

V.c.2. BITUMEN AIR BLOWN WITH PVC AND IRON POWDER

In order to determine the optimum concentration of PVC and iron powder required for the process the raw materials were air-blown with 5ℓ/min/kg sample at 220°C in presence of varying concentrations of waste PVC and iron powder. Samples were drawn at definite intervals of time and analysed. The analytical data are presented in Tables 26 and 27. From figure 12 it can be observed that the optimum concentration of waste PVC and iron powder required is 1% and 0.3% respectively.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS

In order to find out the temperature coefficient of the reaction the process was carried out at varying temperatures, keeping the concentrations of PVC and iron powder 1% and 0.3% respectively at a constant flow rate of air 5ℓ/min/kg sample. Log.of the mean rare constants were plotted against the reciprocal of

TABLE - 30

COCHIN BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF WASTE PVC AND MANGANESE DIOXIDE AT 220°C.

Concentration of waste PVC and Manganese dioxide	Duration of blowing in hours	Softening point °C	1st order rate constant hour^{-1}
1% waste PVC and 0.1% Manganese dioxide	1	58	0.24
	1.5	66	0.24
	2	74	0.24
	2.5	84	0.24
	3	95	0.24
1% waste PVC and 0.3% Manganese dioxide	1	64	0.32
	1.5	73	0.31
	2	87	0.32
	2.5	102	0.32
	3	120	0.32
1% waste PVC and 0.5% Manganese dioxide	1	66	0.35
	1.5	78	0.35
	2	92	0.35
	2.5	110	0.35
	3	132	0.35

TABLE - 31

HALDIA BITUMEN AIR-BLOWN WITH VARYING CONCENTRATIONS OF WASTE PVC AND MANGANESE DIOXIDE AT 220°C.

Concentration of Waste PVC and Manganese dioxide	Duration of blowing in hours	Softening point °C	1st order rate constant hour^{-1}
1% waste PVC and 0.1% Manganese dioxide	1	52	0.17
	1.5	57	0.17
	2	62	0.17
	2.5	67	0.17
	3	73	0.17
1% waste PVC and 0.3% Manganese dioxide	1	56	0.24
	1.5	63	0.24
	2	70	0.23
	2.5	80	0.24
	3.0	90	0.24
1% waste PVC and 0.5% Manganese dioxide	1	58	0.28
	1.5	66	0.27
	2	76	0.27
	2.5	87	0.27
	3	99	0.27

FIG.13 BITUMEN AIR-BLOWN AT 220°C WITH 1% WASTE PVC AND VARYING CONCENTRATIONS OF MANGANESE DIOXIDE

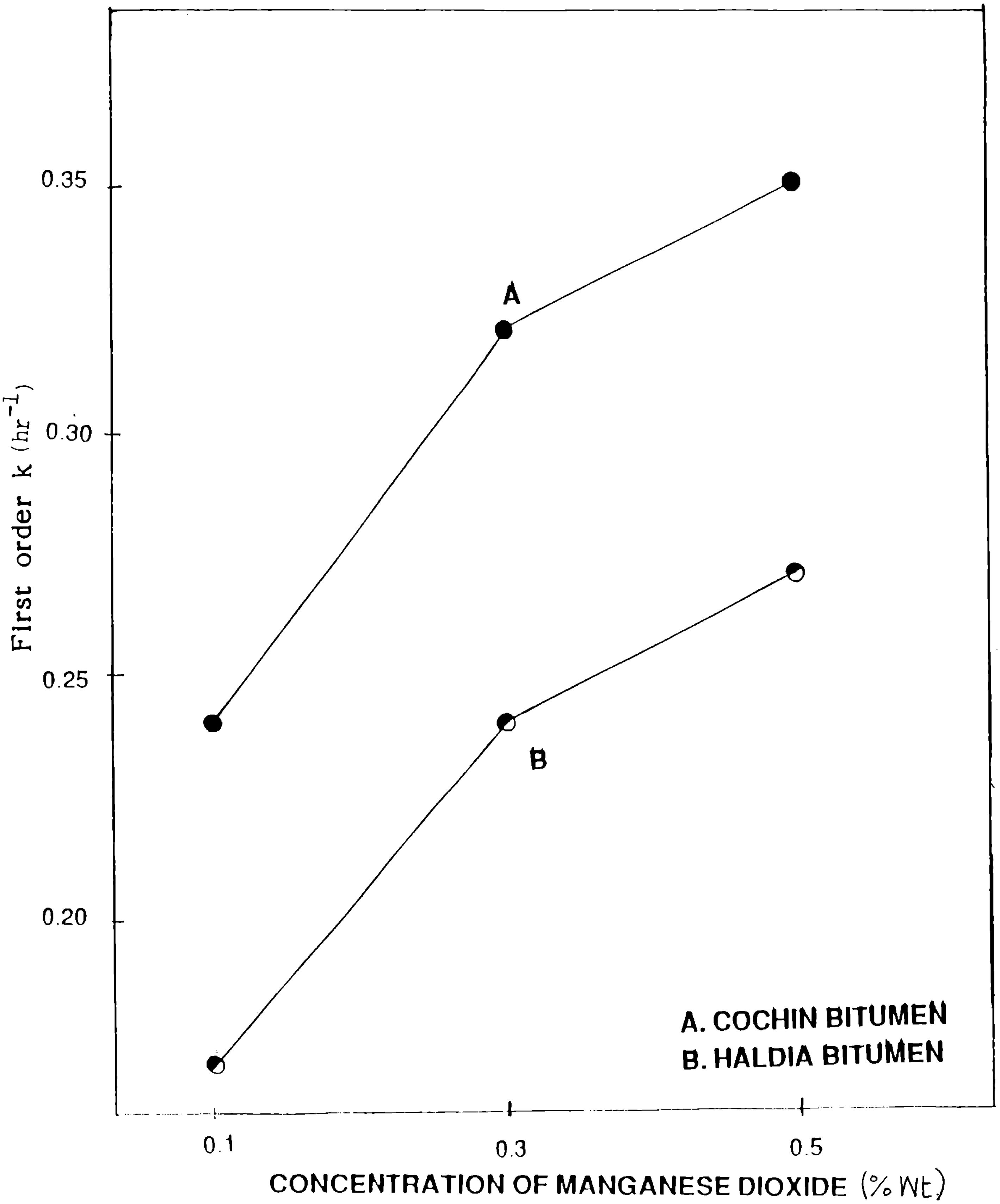


TABLE - 32

COCHIN BITUMEN AIR-BLOWN AT THE AIR FLOW RATE OF 5L/MIN/KG SAMPLE WITH 1% WASTE PVC AND 0.3% MANGANESE DIOXIDE AT VARYING TEMPERATURES

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1}	Softening point °C	1st order rate constant hour^{-1}
0	46	-	46	-	46	-
0.5	54	0.32	57	0.43	60	0.53
1	64	0.32	70	0.42	78	0.53
1.5	73	0.31	86	0.42	102	0.53
2	87	0.32	105	0.41	135	0.54
2.5	102	0.32	132	0.42	172	0.53
3	120	0.32	163	0.42	-	-

TABLE -33

HALDIA BITUMAN AIR-BLOWN AT THE AIR FLOW RATE OF 5L/MIN/KG SAMPLE WITH 1% WASTE PVC AND 0.3% MANGANESE DIOXIDE AT VARYING TEMPERATURES

Duration of blowing hours	at 220°C		at 240°C		at 260°C	
	Softening point°C	Ist order rate constant hour^{-1}	Softening point °C	Ist order rate constant hour^{-1}	Softening point °C	Ist order rate constant hour^{-1}
0	44	-	44	-	44	-
1	56	0.24	60	0.31	65	0.38
1.5	63	0.24	70	0.31	78	0.38
2	70	0.23	80	0.30	95	0.38
2.5	80	0.24	95	0.31	115	0.38
3	90	0.24	110	0.31	135	0.37

absolute temperatures as shown in figures 14 and 15. The activation energies in k cal/mole for Cochin bitumen and Haldia bitumen are found to be 6.50 and 6.00 respectively.

Based on the above experimental results the following reaction mechanism is suggested :

$$4\ \mathrm{Fe} + 12\ \mathrm{HCl} + 3\mathrm{O_2} \longrightarrow 4\ \mathrm{FeCl_3} + 6\ \mathrm{H_2O}$$

This is followed by the reaction scheme given in Chapter IV.C.4.

V.c.3. BITUMEN AIR-BLOWN WITH WASTE PVC AND MANGANESE DIOXIDE

The optimum concentration of waste PVC and manganese dioxide required for the process are found out by air-blowing the raw materials with 5ℓ/min/kg sample with varying concentrations of waste PVC and manganese dioxide. Samples were drawn at definite intervals of time and tested. The results are presented in Tables 30 and 31. From figure 13 it can be observed that the optimum concentration of waste PVC and manganese dioxide required are 1.0% and 0.3% respectively.

EFFECT OF TEMPERATURE ON THE VELOCITY CONSTANTS.

The temperature coefficients of the reaction were determined by running the process at varying temperatures with the air-flow rate of 5ℓ/min/kg sample, keeping the concentrations of waste PVC and manganese dioxide 1.0% and 0.3% respectively. Arrhenius plots were made as given in Figures 14 and 15. From the figures it can be observed that the activation energies in k cal/mole for Cochin bitumen and Haldia are 6.68 and 6.13 respectively.

Based on the above experimental results the following reaction mechanism is suggested :

$$2\,HCl + \tfrac{1}{2}\,MnO_2 \longrightarrow \tfrac{1}{2}\,MnCl_2 + H_2O + Cl^{\bullet}$$

This is followed by the reaction scheme given in chapter V.c.1.

Chlorine radicals are formed at a faster rate from hydrochloric acid in presence of manganese dioxide. The synergistic effect of waste PVC and manganese dioxide is attributed to the liberation of chlorine radicals at a faster rate in presence of manganese dioxide.

FIG.14 ARRHENIUS PLOTS OF AIR-BLOWN COCHIN BITUMEN

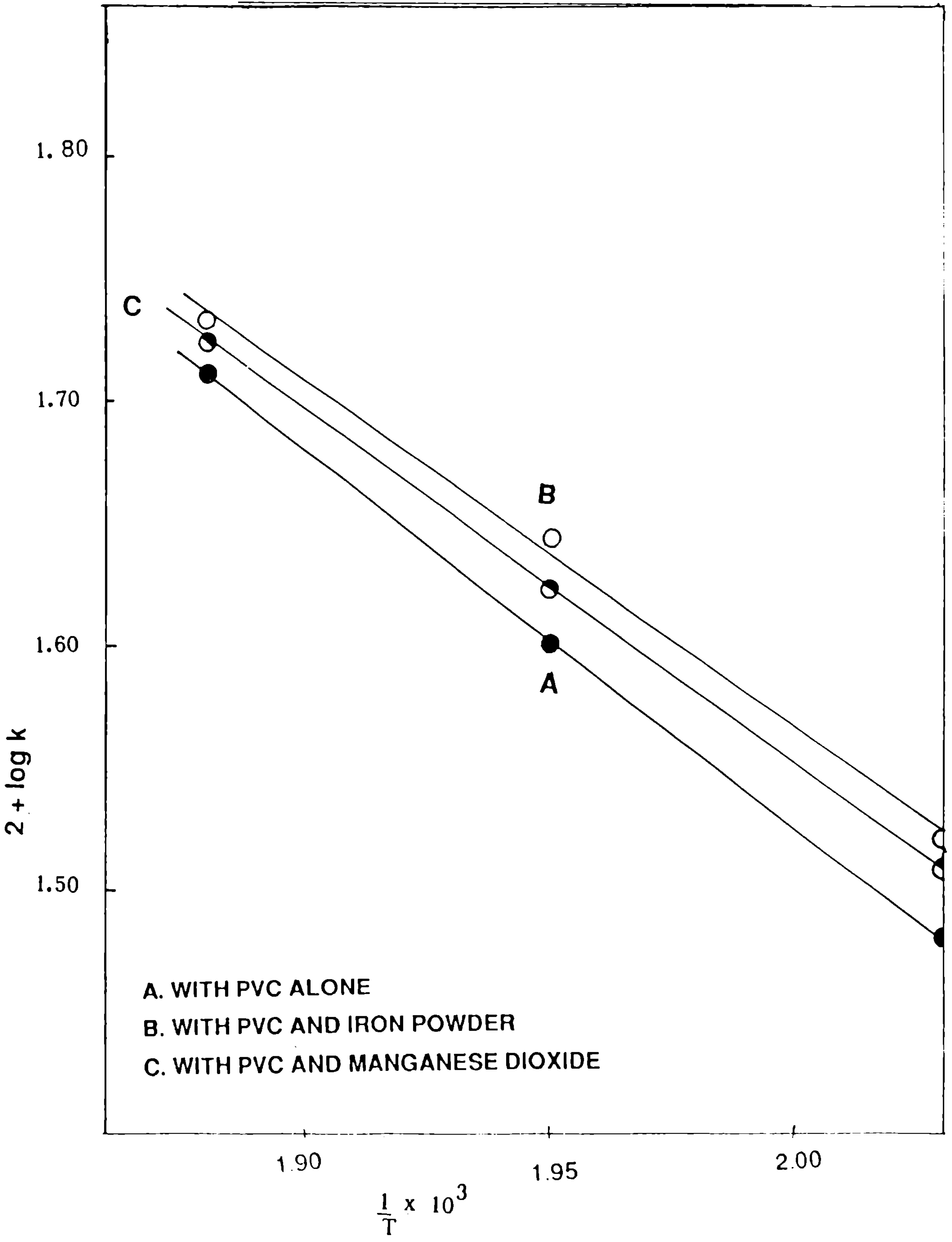
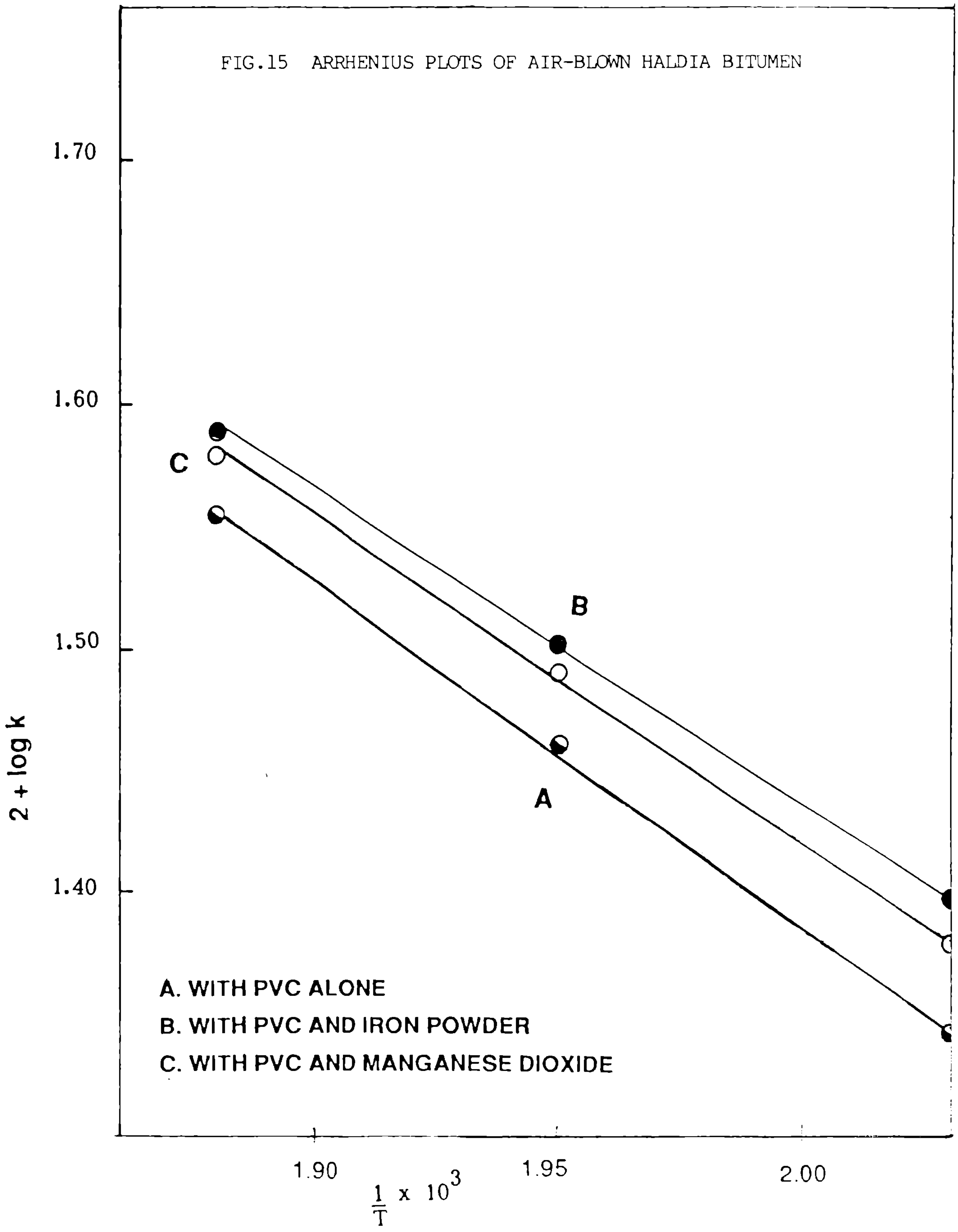


FIG.15 ARRHENIUS PLOTS OF AIR-BLOWN HALDIA BITUMEN



SUMMARY

In the polymerization of paving bitumen to manufacture Industrial bitumen, waste PVC was found to be effective. The products formed were found to be superior in quality compared to those manufactured by a conventional catalyst ferric chloride. It has the added advantage that it is a cheap material being a waste.

Iron powder alone was found to have no catalytic effect on the polymerization reaction. But it was found to be an excellent promotor for waste PVC. Manganese dioxide was found to be only a feeble catalyst for bitumen polymerization. But it was found to exhibit synergistic effect in presence of waste PVC.

Chapter 6

APPLICATION OF INDUSTRIAL BITUMEN FOR THE MANUFACTURE OF BITUMINOUS PAINTS

VI(a) INTRODUCTION

Paint has been used for more than 4000 years for decorative and protective purposes in our daily life. The yearly world paint consumption of about 21 million tonnes is strongly related to the standards of living and the industrial development in countries[139]. More than 50% of the consumption is related to houses. The foregoing chapters describe how the paving bitumen can be polymerised to obtain the various grades of industrial bitumen using some novel additives. Almost half of the industrial bitumen manufactured is used for the production of bituminous paints. So it is worthwhile to know the usefulness of these industrial bitumen towards their application for the manufacture of the bituminous paints. The present study also reveals how the Cashew nut shell liquid-formaldehyde resin can be incorporated to the bituminous paints to modify their properties for improved performance.

Petroleum asphalts have been used as protective coatings with or without filling materials for nearly half a century[140]. The inherent physical and protective properties of industrial bitumen along with their ready availability and low lost renders them very useful and desirable as economical utility bituminous paint coatings. Large volumes of such bituminous paints are used industrially. A limitation to their more extensive use is their dark colour but this is not a deterrent for many industrial coating requirements.

It was in the field of water proofing and protection against corrosion that industrial bitumen first gained recognition and importance many centuries ago in the limited construction and industrial pursuits of successive early civilization. Even in these days asphalt is used for applications involving continuous contact with fresh water and sea water as for example, the lining of water storages and public baths and the caulking of ships. These uses continued and increased so that today asphalt is accepted invariably and almost without limitations in water proofing, road building, roofing, industrial surface coatings, industrial flooring and long distance oil and water pipes line coatings[141]. Virtually all of which affirm and emphasise its high degree of resistance against water and water - borne corrosion and also against air-borne corrosion. Thus it may be fairly claimed that industrial bitumen coatings properly designed, formulated and applied provide very strong protection against common industrial chemicals in solutions and in gaseous forms and ofcourse against water itself. This is due to the virtual insolubility of bitumen in water and in solutions of these chemicals at concentrations usually found in industrial exposures and to its low degree of chemical reactivity with such corrosive solutions and atmosphere. Most of the severely corrosive industrial conditions which attack metal, concrete and masonary surfaces result from law concentrations of mineral acids and alkalies. Bitumenous coatings have given excellent service for many years on ships and docks, steel structures and underground tanks and pipe lines. A typical example is the performance of the bituminous paints on the dry dock of "The Dewey" which was built at Sparrows Point in 1915 and towed to the Philipines. Upon inspection before the fall of Manila in World War II when the dock was 35 years old, the enamel was reported to be in excellent condition[142].

VI(b) FORMULATION OF BITUMINOUS PAINTS

VI(b)(1) Formulation - I

Industrial bitumen of grade 115/15	=	30%
Petroleum heavy naphtha	=	70%

VI(b)(2) Formulation - II

PREPARATION OF CNSL-FORMALDEHYDE 'A' STAGE RESIN

The resole resin is prepared by carrying out the condensation, taking formaldehyde and cashew nut shell liquid in the ratio 1:4 by weight. 7.5 ml of 25% ammonia was used as the catalyst per 100 ml of CNSL. The mixture is shaken well and kept overnight for reaction to take place to the desired level. The resin is vaccum distilled to remove the water of condensation.

COMPOSITION OF POT A

CNSL - formaldehyde A stage resin = 20%
Carbon black = 20%
Toluene = 60%

COMPOSITION OF POT B

Industrial bitumen grade 155/5 = 20%
Hexamethylene tetramine = 3%
Petroleum heavy naphtha = 77%

VI(c) METHOD OF APPLICATION

The application of the paints having formulations I can be accomplished by any of the usual methods in the industry - brushing or spraying. In the case of paints with formulation II equal quantities of Pot A and Pot B are mixed together prior to application. Hot air is then supplied to cause the thermosetting reactions of the CNSL - formaldehyde resin. These are generally applied as moderate to heavy coatings $2^{1}/2$ gallons or more per 100 Sq.ft. depending upon the service conditions to be encountered. In order to ensure high degree of protection generally expected of these products, they should be applied in two or more layers.

VI(d) RESULT AND DISCUSSION

From tables V and VII it can be observed that bituminous paints made using formulation I is meeting

TABLE - I

CHARACTERISTICS OF INDUSTRIAL BITUMEN OF GRADE 115/15

DERIVED FROM COCHIN PAVING BITUMEN

(AIR-BLOWN AT 240°C)

	Characteristics	$FeCl_3$	Na_2S	PVC	PVC+Fe	PVC+MnO_2
1.	Softening point C	115	115	115	115	115
2.	Penetration 1/10mm.	13	11	19	17	15
3.	Ductility cm	7	5.5	13	11	9
4.	Flash point °C	>300	>300	>300	>300	>300
5.	Loss on heating % wt.	$<.01$	$<.01$	$<.01$	$<.01$	$<.01$

TABLE - II

CHARACTERISTICS OF INDUSTRIAL BITUMEN OF GRADE 155/6 DERIVED FROM COCHIN PAVING BITUMEN

	Characteristics	* $FeCl_3$	* Na_2S	** PVC	** PVC+Fe	** PVC+MnO_2
1.	Soft point C	155	155	155	155	155
2.	Penetration 1/10mm	8	6	4	3	2
3.	Ductility cms	4	3	2	1.5	1
4.	Flash point °C	>300	>300	>300	>300	>300
5.	Loss on heating % wt.	$<.01$	$<.01$	$<.01$	$<.01$	$<.01$

* Air blown at 220°C

** Air blown at 240°C

TABLE - III

CHARACTERISTICS OF INDUSTRIAL BITUMEN OF GRADE 115/15

DERIVED FROM HALDIA PAVING BITUMEN

(Air-blown at 240 ^{o}C)

	Characteristics	$Fecl_3$	Na_2S	PVC	PVC+Fe	PVC+MnO_2
1.	Soft Point ^{o}C	115	115	115	115	115
2.	Penetration 1/10mm	10	8	17	14	12
3.	Ductility Cm	4	3	7	6	5
4.	Flash point ^{o}C	>300	>300	>300	>300	>300
5.	Loss on heating % wt.	$<.01$	$<.01$	$<.01$	$<.01$	$<.01$

TABLE - IV

CHARACTERISTICS OF INDUSTRIAL BITUMEN OF GRADE 155/5

DERIVED FROM HALDIA PAVING BITUMEN

	Characteristics	* Fecl$_3$	* Na$_2$S	** PVC	* PVC+Fe	* PVC+MnO$_2$
1.	Soft point ^{o}C	155	155	155	155	155
2.	Penetration 1/10mm	5	2	3	9	7
3.	Ductility cm	2	1	1.5	3.5	2.5
4.	Flash point ^{o}C	$>$300	$>$300	$>$300	$>$300	$>$300
5.	Loss on heating % wt.	$<$.01	$<$.01	$<$.01	$<$.01	$<$.01

* Air-blown at 220^{o}C

** Air-blown at 240^{o}C

TABLE - V

CHARACTERISTICS OF BITUMINOUS PAINTS MADE FROM COCHIN INDUSTRIAL BITUMEN HAVING FORMULATION I

Characteristics Method of Test	$FeCl_3$	Na_2S	PVC	PVC+Fe	PVC+MnO_2
(1)	(2)	(3)	(4)	(5)	(6)
1. Drying time	5 Hrs.	5 Hrs.	5 Hrs.	5 Hrs.	5 Hrs.
2. Consistancy	Smooth & Uniform	Smooth & Uniform	Smooth & Uniform	Smooth & Uniform	Smooth Uniform
3. Finish	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy
4. Colour	Black	Black	Shining black	Shining black	Shining black
5. Flah point °C	>30	>30	>30	>30	>30
6. Protection against corrosion under conditions of condensation.	------------ No sign of corrosion ----------------				
7. Stripping test	------------ Scratches free from jagged edges ---------				
8. Flexibility & adhesion	---------- No visible change or detachment of the film ----------				

CONTD....

(ii)

(1)	(2)	(3)	(4)	(5)	(6)
9. Keeping properties	----------------------	More than one year			-------------------
10. Resistance to water.	-------	Paint film is firmly adherent and imparts no undesirable odour or taste to water.			-----
11. Resistance to acid	-------	Paint film shows no sign of softening, dulling, blistering or cracking or change of colour.			-----
12. Resistance to alkali		"	"	"	"
13. Resistance to chlorine.		"	"	"	"
14. Heat resistance	---------------		Paint film softens		---------------

TABLE - VI

CHARACTERISTICS OF BITUMINOUS PAINTS MADE FROM COCHIN INDUSTRIAL BITUMEN HAVING FORMULATION II

	Characteristics	$FeCl_3$	Na_2S	PVC	PVC + Fe	PVC + MnO_2
	(1)	(2)	(3)	(4)	(5)	(6)
1.	Drying time	4 Hrs.	4 Hrs.	4 Hrs.	4 Hrs.	4 Hrs.
2.	Consistancy	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform
3.	Finish	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy
4.	Colour	Black	Black	Shining black	Shining black	Shining black
5.	Flash point °C	>30	>30	>30	>30	>30
6.	Protection against corrosion under conditions of condensation.	-------------- No sign of corrosion -------------				

contd....

(ii)

(1)	(2)	(3)	(4)	(5)	(6)
7. Stripping test	---------------	scratches free from jagged edges			-----------
8. Flexibility & adhesion	---- No visible change or detachment of the film --------				
9. Keeping properties	-------------	More than one year		-----------	
10. Resistance to water	------	Paint film is firmly adherent and imparts no undesirable odour or taste to water.			------
11. Resistance to acid	------	Paint film shows no sign of softening, dulling, blistering or cracking or change of colour.			------
12. Resistance to alkaly.	"	"	"	"	
13. Resistance to chlorine.	"	"	"	"	
14. Resistance to heat	-------	The film remains firmly adherent and shows no sign of cracking or blistering.		-------	

TABLE - VII

CHARACTERISTICS OF BITUMINOUS PAINTS MADE FROM HALDIA INDUSTRIAL BITUMEN HAVING FORMULATION I

Characteristics	$FeCl_3$	Na_2S	PVC	PVC + Fe	PVC + MnO_2
1. Drying time	5 Hrs.	5 Hrs	5 Hrs.	5 Hrs.	5 Hrs.
2. Consistancy	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform
3. Finish	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy
4. Colour	Black	Black	Shining black	Shining black	Shining black
5. Flash point ^{o}C	>30	>30	>30	>30	>30
6. Protection against corrosion under conditions of condensation.	----------- No sign of corrosion -----------				
7. Stripping test	----------- Scratches free from jagged edges -----------				

contd...

(ii)

(1)	(2)	(3)	(4)	(5)	(6)
8. Flexibility & adhesion	No visible change or detachment of the film				
9. Keeping properties	More than one year				
10. Resistance to water	Paint film is firmly adherent and imparts no undesirable odour or taste to water.				
11. Resistance to acid	Paint film shows no sign of softening, dulling, blistering or cracking or change of colour				
12. Resistance to alkaly		"	"	"	"
13. Resistance to chlorine		"	"	"	"
14. Heat resistance	Paint film softens				

TABLE - VIII

CHARACTERISTICS OF BITUMINOUS PAINTS MADE FROM HALDIA INDUSTRIAL BITUMEN HAVING FORMULATION II

Characteristics	$Fecl_3$	Na_2S	PVC	PVC + Fe	PVC + MnO_2
(1)	(2)	(3)	(4)	(5)	(6)
1. Drying time	4 Hrs.	4 Hrs.	4 Hrs.	4 Hrs.	4 Hrs.
2. Consistancy	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform	Smooth & uniform
3. Finish	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy	Smooth & glossy
4. Colour	black	black	Shining black	Shining black	Shining black
5. Flash point °C	>30	>30	>30	>30	>30
6. Protection against corrosion under conditions of condensation	No sign of corrosion				
7. Stripping test	Scratches free from jagged edges				

(ii)

(1)	(2)	(3)	(4)	(5)	(6)
8. Flexibility & adhesion	-------- No visible change or detachment of the film --------				
9. Keeping properties	---------- More than one year ----------				
10. Resistance to water	--------	Paint film is firmly adherent and imparts no undesirable odour or taste to water.			--------
11. Resistance to acid	--------	Paint film shows no sign of softening, dulling, blistering or cracking or change of colour.			--------
12. Resistance to alkali	"	"	"	"	
13. Resistance to chlorine	"	"	"	"	
14. Resistance to heat	--------	The film remains firmly adherent and shows no sign of cracking or blistering.			--------

the requirements of acid, alkali and water resistant bituminous paints as per IS 158-1968. But it can be seen that formulation I doesn't posses the property of resistance to heat. For high temperature applications as for industrial chimneys and boilers etc. it is essential that the paint coatings should be resistant to heat. Table VI and VIII show how CNSL-formaldehyde resin can be incorporated to bituminous paints to impart heat resistance properties. It is advantageous since CNSL is a cheaply available product.

SUMMARY

The study shows that acid, alkali and water resistant bituminous paints can be manufactured using the Industrial bitumen produced using the novel additives. The study also reveals that heat resistant bituminous paints can be manufactured by suitably incorporating cashew nut shell liquid-formaldehyde resin. Cashew nut shell liquid is a by-product of Cashew industry and its utilization will reduce the cost of production of bituminous paints.

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Chapter 7

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The main findings of the present investigation on the manufacture and application of Industrial Bitumen, are summarised below.

A pilot plant to carry out studies on the air-blowing process of bitumen was designed and fabricated. It had the provision for drawing samples at any desired time for kinetic studies.

Petroleum refinery caustic wash waste has been shown to be an efficient additive for the manufacture of Industrial bitumen for the first time. It is economical, since it reduces the air-blowing time. The air-blowing time is directly related to the cost of production. It improves the softening point-penetration relationship and makes possible the manufacture of good quality industrial bitumen. By air-blowing without any additive, it was found to be impossible to manufacture the various grades of industrial bitumen according to specifications. The conventional additives used for the manufacture of industrial bitumen viz. ferric chloride, phosphorous pentoxide are costly and hence the high cost of production of industrial bitumen. In petroleum refineries caustic washing process is used for the removal of hydrogen sulphide from the liquified petroleum gas and naphtha fractions and the waste so formed is disposed to the inland waters. It is highly hazardous to the aquatic organisms. Petroleum refinery caustic wash is a waste material and its utilisation will lead to better pollution control. A comparative study with ferric chloride shows that it is equally effective.

Another significant finding of the study is that waste PVC is capable of functioning as an effective additive in bitumen polymerization process. Hydrochloric acid formed by the degradation of PVC is found to catalyse the reaction. The polyolefins formed are found to improve the softening point - penetration relationship of the air-blown products. A comparative study of the air-blown products with ferric chloride shows that the quality of the air-blown products with waste PVC are much superior. The softening point - penetration relationship of the air-blown products with waste PVC are much better ie. they possess high penetration for a given softening point. This will impart increased flexibility in the products made out of them. The catalytic effect of waste PVC is attributed to the formation of chlorine radicals during the process.

The effect of iron powder as a promoter for waste PVC catalyst is investigated. Iron alone is found to have no effect in the polymerization of bitumen. But it was observed that the effect of waste PVC on bitumen polymerization is highly improved in presence of iron powder. The promoting effect of iron is attributed to the formation of ferric chloride. The utilization of iron as a promoter will reduce the consumption of the catalyst.

The synergistic effect of manganese dioxide and waste PVC is investigated. Manganese dioxide alone is found to be only a feeble catalyst for bitumen polymerization. But when bitumen is air-blown in presence of both manganese dioxide and waste PVC, the rate of the reaction is found to be more than the sum of their individual rates. The synergistic effect of manganese dioxide and waste PVC is attributed to the effect of manganese dioxide to liberate chlorine radicals at a faster rate.

The study also reveals that the quality of industrial bitumen ie. the softening point - penetration relationship made with different additives depends on the content and molecular weight of the asphaltene fraction. The higher the asphaltene content and the lower the molecular weight of the asphaltenes, the better the softening point - penetration relationship .

Our observation shows that the industrial bitumen manufactured from Haldia propane deasphalted bitumen is inferior in quality to that manufactured from vaccum distillation bitumen of Cochin Refineries. This is attributed to the presence of lower saturate content. However, it is found to be possible to improve the softening point-penetration relationship and to manufacture the products as per the specifications by lowering the process temperature.

For the planning of operations as well as for the design of plants for bitumen air-blowing in presence of the novel additives it is essential to know the kinetics of the reactions involved in the process. Bitumen air-blowing polymerization reaction is found to be first order with respect to the hydrocarbon reactants in bitumen . The possible mechanism of the reactions involved is suggested. This type of kinetic analysis gives a middle - of - the road basis for plant design and control of operations.

Bituminous paints have been developed using the different industrial bitumen made with the novel additives. Two grades of bituminous paints (1) water, acid, alkali and chlorine resistant and (2) Heat resistant were made. The performance of the above bituminous paints were compared with those made with a conventional additive ferric chloride. The studies reveal that the industrial bitumen made with the novel additives can be applied for the manufacture of bituminous paints and they are capable of replacing the industrial bitumen made with the conventional additives. The study also reveals that cashew nut shell liquid-formaldehyde resin can be incorporated into bituminous paints in order to improve heat resistance. CNSL is cheap being the by-product of cashew nut industry and its utilization will improve the properties of bituminous paints and make them cheaper.

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