THE OXIDATIVE DEGRADATION OF PETROLEUM FRACTIONS

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by

GORDHANBHAI MOTIBHAI PATEL

Chemical Technology Section,
Department of Pure and Applied Chemistry,
The University of Strathclyde,
GLASGOW, C.1

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SUMMARY

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Under weathering conditions bitumen surfacings deteriorate, largely due to oxidation by atmospheric oxygen. The ageing of the exposed surface can be attributed to the effect of photo-oxidation whereas the inner layers are subjected to slow oxidation in the dark, i.e. thermal oxidation. It is known that petroleum bitumens when used as binders in dense road surfacings may produce smooth surfaces of low skid resistance while Trinidad Lake Asphalt is likely to give a rougher texture. This can be attributed to the fact that Trinidad Lake Asphalt is more susceptible to oxidation than petroleum bitumens and, therefore, prone to slight surface abrasion.

In view of the importance of skid resistance in modern high-speed motorways, it is of interest to study the difference in behaviour of Trinidad Lake Asphalt and petroleum bitumens during oxidation and a study of the particular components of Trinidad Lake Asphalt responsible for its better performance as a road binder in rolled asphalt. With this purpose the investigation has been designed on the following basis:-

(1) Bitumen fractionation and characterisation.

(2) Thermal oxidation of bitumens and fractions.

(3) Photo-oxidation of bitumens and fractions.

A.1 – Bitumen fractionation and characterisation

Petroleum bitumens from Middle East, Venezuelan and mixed base crudes and Trinidad Lake Asphalt were first separated into asphaltenes and maltene fractions by precipitating asphaltenes with petroleum spirit (B.P. 30–40°C). Maltene fractions were further separated into white oils, dark oils and resins by chromatographic adsorption in a silica gel-alumina column using petroleum spirit, methylene chloride and methylethyl ketone as eluents. Trinidad Lake Asphalt produced large amounts of asphaltenes (57%) and low amounts of white oil (5%). Petroleum bitumens, on the other hand, only gave about one third of this amount of asphaltenes (20%) with proportionally greater amounts of other fractions. This clearly shows one initial composition difference between the naturally occurring bitumen and the residual materials.

Bitumen fractions were further characterised by nuclear magnetic resonance spectroscopy. White oil fractions of all bitumens were found to be paraffinic-naphthenic in character. Dark oil and resin fractions were highly aromatic. Asphaltenes could not be analysed by this method due to their paramagnetic properties.

Infra-red spectra of bitumens showed that petroleum bitumens were aromatic with long paraffinic chains whereas Trinidad Lake Asphalt was slightly less aromatic with short but heavily branched paraffinic chains. The other major difference was that Lake Asphalt contained larger amounts of oxygen containing functional groups such as carbonyl (acids, aldehydes, esters and/or ketones) and C–O, S=O or Si–O groups whereas petroleum bitumens had these groups in small amounts. White oil fractions of both types of bitumen showed a paraffinic-naphthenic character with or without a trace of aromatic content. Dark oil and resin fractions of all bitumens were highly aromatic in character with large amounts of carbonyl, C–O, S=O or Si–O, OH and NH groups. Asphaltenes were also highly aromatic with carbonyl, hydroxyl and/or NH groups, while the fraction from T.L.A., in addition to these groups, showed a high amount of C–O, S=O or Si–O groups.

Sulphur in all bitumens and fractions was determined using a modified bomb method. Average values showed asphaltenes contained large amounts of sulphur (5.47%) with white oil giving the lowest figures (1.44%). Dark oil had a higher average sulphur (4.33%) than resins (3.68%). Trinidad Lake Asphalt showed higher sulphur content (4.73%) than the petroleum bitumens (3.86%).

A.2 – Thermal oxidation of bitumens and fractions

An oxidation apparatus was designed on a semi-micro scale. Problems which had to be considered during the design of an apparatus for oxidation in the dark were:

(i) The formation of skin on sample surfaces reducing the rate of oxygen diffusion.

(ii) The effect of viscosity on oxygen diffusion due to fractions varying from mobile, low-viscosity oils to solid asphaltene particles. It was important to eliminate this variable.

(iii) The formation of gaseous oxidation products such as carbon dioxide and water vapour. These materials may have influenced the oxidation reaction.

The above problems were solved to a large extent by oxidising the samples in xylene solution. Xylene did not oxidise under the conditions used. In addition, the sample container was vibrated continually to break the liquid surface. To absorb the water vapour and carbon dioxide formed potassium hydroxide soaked papers were suspended inside the flasks on platinum wire.

Measurements were made (at known temperatures in the range 30-60°C) of the rate of oxygen uptake by three petroleum bitumens from different sources and Trinidad Lake Asphalt. Their fractions were also oxidised in the same temperature range. Trinidad Lake Asphalt showed higher rate of oxygen absorption than petroleum bitumens. The oxygen absorption of bitumen fractions was found to decrease in the order; asphaltenes, resins, dark oils and white oil in all cases. The overall activation energy of all bitumens and fractions was calculated. The activation energy of T.L.A. was found to be 13.97 k.cals/mole and for the petroleum bitumens 14.85-17.60 k.cals/mole.

In order to study the effect of asphaltenes on the rate of bitumen oxidation, several synthetic bitumens were prepared with varying amounts of asphaltenes. Bitumens with a high amount of asphaltenes showed high rates of oxygen uptake. This confirms that asphaltene fractions oxidise most readily while the oils are more resistant. T.L.A. has more than twice the asphaltene content of the petroleum bitumens and this may contribute to the susceptibility of T.L.A. to oxidation. It was shown that for every 10°C rise in reaction temperature the reaction rate doubled.

A.3 - Photo-oxidation of bitumens and fractions

A photo-oxidation apparatus was constructed using an ultra-violet medium-pressure mercury arc lamp with a light intensity stabiliser. In this investigation, bitumens, fractions, synthetic bitumens with varying amount of asphaltenes and bitumens modified with photo-sensitising chemicals were photo-oxidised in thin films. The rates of oxygen absorption and of formation of water soluble degradation products were measured in each case. The type of skin formed on exposure to u.v. radiation was also studied.

Petroleum bitumen from the Middle East mixed base crude was found to be more reactive than Venezuelan bitumen, with Trinidad Lake Asphalt the most reactive of the bitumens studied. In each case the white oil fractions were most reactive with dark oils least reactive. Martin(144) has suggested that hydrocarbons with aromatic groups, branched chain structures, oxygenated groups and cycloparaffins are likely to be more reactive with atmospheric oxygen. I.R. analysis of bitumens has shown that T.L.A. is slightly less aromatic with a high amount of carbonyl groups and high amount of other oxygen functional groups such as C-O, S=O and Si-O with short but heavily branched paraffinic chains than petroleum bitumens. This may be one of the reasons why T.L.A. is more reactive than petroleum bitumens.

In the case of the synthetic bitumens produced by adding varying amounts of asphaltenes to the corresponding maltene fractions it was shown that reactivity increased in all cases with increasing asphaltene content. However, a maximum reactivity was reached at an asphaltene content below the 'natural' content for each bitumen. The petroleum bitumen had a maximum activity at about 15% asphaltenes and decreased in activity on addition of more asphaltenes. For the Lake Asphalt the maximum was at about 45% against the natural content of 55%. These apparently anomalous results may be caused by the rate of oxygen diffusion rather than by any inherent changes in actual reactivity.

Bitumens containing small amounts of photo-sensitising chemicals such as anthracene, anthracene oil, anethole, eugenol, safrole and di-tert.butyl peroxide showed increased rates of oxygen uptake and water soluble production, proportional to the amounts of these chemicals present in the bitumen. The decreasing order of reactivity was found to be di-tert.butyl peroxide, anthracene, anethole, eugenol, safrole and anthracene oil. The skin formed on oxidation in the presence of these materials varied from bright-smooth to dull-rough depending on the amount of photo-sensitiser used. With 5% of these chemicals, the bitumen films produced dull and rough surfaces similar to those produced by Trinidad Lake Asphalt.

The changes resulting from the thermal and photo-oxidation of bitumens and their fractions were also examined by infra-red spectroscopy. The changes on oxidation were generally related to hydroxyl, carbonyl, C-O, S=O, Si-O, aromatic, cycloparaffins, aromatic substitution and paraffinic chains.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Petroleum fractions such as gasolines, kerosenes, transformer oils, lubricating oils, residual bitumens, etc., deteriorate on storage, and in service, by action of atmospheric oxygen. Oxidation of gasoline is undesirable as it may lead to formation of deposits in engines and can reduce the octane number of gasoline through the formation of peroxides(1,2,3). Transformer oil forms sludges, acids, water and other oxidation products, while lubricating oil on oxidation forms corrosive acids, lacquer and sludge.

While a great deal of work has been directed at the understanding of the deterioration of gasolines, transformer oil and lubricating oil by oxygen, rather less effort has been made where heavier fractions are concerned.

A major use of petroleum bitumen is its capacity to act as a binder for aggregate in road surfacings. With skid-resistant surface textures becoming more important as high-speed motorways are being built more information is required on the function that bitumen plays in imparting skid-resistance to such surfaces.

1.1 - Purpose of research

With the above points in mind the present work has concentrated on various aspects of oxidation of bitumen and bitumen fractions. The purpose of this investigation can be summarised as follows:-

(a) Fractionation of selected bitumens to provide samples for oxidation and to give also, initial characterisation of the various bitumens.

(b) Thermal oxidation of bitumens and fractions in an attempt to elucidate the particular component responsible for differences in the reactivity of bitumens during oxidation in the 'dark'.

(c) Photo-oxidation of the same fractions, this study being more directly related to the effect of sunlight on bitumens and taking into account the well-known characteristics of natural asphalts, e.g. Trinidad Lake Asphalt.

1.2 - Bitumen designation and nomenclature

The expression 'bitumen' originated in the Sanskrit, where the words 'jatu' meaning 'pitch' or 'native asphalt'; sila-jatu meaning 'rock asphalt' and 'jatu-krit' meaning 'pitch creating', 'pitch producing' (referring to coniferous or resinous trees). The Latin equivalent is 'gwitumen' (pertaining to pitch) and 'pixtumens' (exuding or bubbling pitch) which was subsequently shortened to 'bitumen'.(4)

Bitumen is a generic term applied to native substances of variable colour, hardness and volatility; composed principally of hydrocarbons, substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being fusible and largely soluble in carbon disulphide, yielding water-insoluble sulphonation products(4). Bitumen is also defined as a mixture of hydrocarbons of natural or pyrogonous origin, or a combination of both, frequently accompanied by non-metallic derivatives which may be gaseous, liquid, semi-solid or solid and which are completely soluble in carbon disulphide(5). The word 'asphalt' is also used in the American sense to designate the residual material obtained by the distillation of asphaltic-based petroleum and also includes native and rock asphalts(6).

Bitumen is sometimes called 'residual bitumen', (i.e. residue on distillation of petroleum) in order to distinguish it from those which occur naturally. It is often termed 'straight run' when the viscosity, or composition, of the bitumen has not been adjusted by blending or by softening with fluxing or cut-back oil. The term cut-back bitumen is also used for bitumen the viscosity of which has been reduced by the addition of a volatile diluent(7).

Deposits of bituminous materials in large quantities are distributed over the earth. These have been formed by natural processes as the result of geological forces and this asphalt is generally found in intimate association with mineral aggregate in a natural form. Bitumens may be classified as follows(6):-

I Petroleum bitumen: from asphaltic base crude oils, (i.e. 'refinery bitumen'),

II Native asphalts: solid, or semi-solid:-
- (a) nearly pure bitumens, e.g. Bermudez Lake Asphalt (Venezuela)
- (b) associated with mineral matter, (i) Lake Asphalt, e.g. Trinidad Lake Asphalt and (ii) Rock Asphalt, e.g. Uvalde (Texas)

III Asphaltites: hard materials, Gilsonite (Utah and Colorado).

1.3 - History of bitumen

Bitumen was the first petroleum derivative used extensively by man. Abraham(4) cites many examples of bitumen utilisation prior to the time of Christ.

Bitumen was used as early as 3800 B.C. as a binder and waterproofing by the civilians along the Euphrates river. About 3000 B.C. an ancient civilisation in the Indus Valley in India used bitumen in the construction of a large public bath at Mohenjo Daro. Egyptians (2500-1500 B.C.) were using natural asphalt in the preparation of mummies. Babylonians (2500- 538 B.C.) in Iraq used bitumen to build roadways, retaining walls to impound waters of the Euphrates and as a paint on walls. The Assyrians (1400- 607 B.C.) recommended the use of asphalt for medical purposes, when mixed with sulphur as a fumigant, mixed with oil for soothing the eyes, mixed with beer as a sedative for the stomach, and dropsy was supposed to be cured by standing on bitumen.

In the Bronze Age (1000 B.C.) dwellings were constructed on piles in lakes close to the shore. This offered some protection to the inhabitants from the ravages of wild animals and attacks from other marauders. Excavations have shown that the wooden piles were preserved from decay by coating with asphalt.

The ancients coated their bronze monuments with bitumen and about A.D.750 the early Italians are claimed to have been the first to employ asphalt as a colour in paintings. In 1498, Christopher Columbus on his third voyage to America discovered the island of Trinidad; in 1595, Sir Walter Raleigh visited Trinidad and gave an account of the so-called pitch lake and used the pitch to caulk his ship.

This early use of bitumen was normally from naturally occurring surface deposits and refining was only developed to the extent of evaporating the lighter petroleum components by natural means. By the last two decades of the 19th century a considerable amount of natural bitumen from Venezuela and Trinidad had been for road building and other purposes associated with construction engineering.

1.4 - Production of bitumen

Native asphalts which usually contain a percentage of water and mineral matter require only to be dehydrated by heating to about 160°C before use; in some cases, however, where the percentage of mineral matter is higher, the asphalt is solvent-extracted and the solvent removed by distillation.

Three main processes are used to produce bitumen from petroleum crudes(5), viz:-

(i) - Distillation

Temperatures and residence times are kept low enough to prevent cracking using vacuum or steam distillation at temperatures up to 625°F. Distillate fractions are removed leaving an asphaltic residue. This process is generally carried out in two stages, the crude oil being 'topped' by a primary atmospheric distillation to remove the more volatile distillates and the 'topped' crude distilled under vacuum to give a bitumen residue.

(ii) - Precipitation or solvent extraction

In this process the feed may be treated with liquid propane, propane-butane or butane under pressure (400-650 psi) at 120-250°F temperature by countercurrent flow through an extraction tower - the reduced crude charge entering the top and the solvent at the bottom. The paraffinic components are preferentially dissolved in the solvent and withdrawn from the top, whilst the bitumen which can be expected to pass through chemically unchanged is withdrawn from the bottom.

(iii) - Air blowing

The process of oxidising the residue obtained from crude oil has been known for a long time. The process is basically simple and consists of intimately contacting the residuum with air in a vessel at a suitable temperature until a product of the desired consistency is obtained. The residuum so treated markedly changes in physical characteristics (becoming more 'rubbery') and changing in hardness, gravity, ductility and softening point. The process of air blowing produces changes in bitumen by means of chemical reactions. It has been observed, at high temperatures (480°F), that these reactions are primarily dehydrogenation followed by condensation and polymerisation.

Air blowing is carried out both as batch and continuous processes. Catalysts may be used in air blowing for product modification and reduction of the blowing time. The most widely used catalysts are stable phosphorous compounds, (phosphorous pentoxide) and metallic salts (ferric chloride).

As mentioned, the chief virtue of air blowing is the effect on the rheological properties of the bitumen. Blown bitumens are not used for road purposes but are used widely for other coating purposes.

1.5 - Uses of bitumen

Bitumen is a thermoplastic with good adhesion properties which can be produced in a range of consistences. It is resistant to attack by many industrial chemicals and solutions and its properties may be modified through processing and/or the addition of fillers and additives. Some of the main uses of bitumen are as follows:-

(i) Highway construction.
(ii) Roofing construction.
(iii) Protective coatings.
(iv) Hydraulic engineering.
(v) Waterproof paper goods.
(vi) Adhesive compositions.
(vii) Caulking compounds.

Asphaltic products for use as roofing materials, pipe coatings and certain other applications must be highly weather-resistant, have a high softening point and remain ductile at low temperatures. Bitumen produced from blowing operations is generally used for these applications.

Bitumen for road purposes is generally straight-run bitumen (i.e. petroleum bitumen) either as obtained from the distillation process or, fluxed with volatile oils, i.e. cut-back bitumens.Viscosities and other general specifications are covered in British Standard BS.3690.

Skid-resistance in wet conditions is normally only a problem with hot rolled asphalt (British Standard 594), an expensive but long-lasting dense material used on major roads. Bitumen used in this material is always 'penetration grade' and ranges from 30-80 penetration.

1.6 - Composition of bitumen

Bitumen is a complex mixture of hydrocarbons containing sulphur and nitrogen in small amounts and frequently associated with mineral matter in varying amounts. Bitumen is a homogeneous or heterogeneous mixture of chemical substances associated as a simple solution of liquids, or solids in liquids, or in the form of a colloidal solution. These constituents may contain structures of the following four basic types(8):-

(i) Paraffinic.
(ii) Naphthenic (cycloparaffinic).
(iii) Aromatic.
(iv) Olefinic.

This last type is rarely found in bitumens.

Bitumens may be divided into the following three main fractions:-

(i) Carbenes - fraction insoluble in carbon tetrachloride.
(ii) Asphaltenes - fraction insoluble in n-pentane (or a similar low molecular weight paraffin).
(iii) Maltenes - fraction soluble in n-pentane.

Nellensteyn(9) suggested the presence of three principle groups of components in colloidal bitumen as follows:- (i) the medium (maltenes or oil constituents), (ii) the lyophilic portion or protective bodies (asphaltic resins) and (iii) the lyophobic portion, composed of elementary carbon.

Asphaltic resins and carbon form a disperse phase called the asphaltic micelles (asphaltenes). Asphaltenes, resins and oily constituents are believed to form a colloidal system in which asphaltenes are dispersed in the oil constituents and the resin fraction stabilises the solution by acting as a protective colloid thus, the properties of the bitumen depend upon the concentration of the disperse phase and the properties of the medium.

On the basis of the flow properties bitumen can be divided into two groups:-

(i) A sol-type where there is little interaction between the micelles,

or

(ii) A gel-type where the quantity and association of the micelles are great enough to form a loose structure.

The type of structure depends on the chemical nature of the maltene fraction.

Road bitumens are invariably of the sol-type, i.e. straight-run and the blown or gel-type bitumen is used for roof coatings, etc.

1.7 - Weathering of bitumen

The influence exerted by weather (heat, cold, air, light, moisture) on bituminous surfaces is an important factor determining the lifetime of bituminous coatings and constructions. The changes brought about in the physical and chemical properties of bitumen by weather is often referred to as 'weathering' and the extent to which it resists these influences is called its durability. Bitumens, under the influence of weather, are affected by temperature changes, oxygen of the air, sunlight and moisture. Oxidation in the presence of ultra-violet radiation, i.e. sunlight, is well known to have a marked effect on bitumens. This photo-oxidation(14,33,37), however, is confined to a thin surface layer and oxidation of bitumen beneath this surface must occur by a thermal oxidation mechanism. Both photo-oxidation and thermal oxidation processes play an important role in the weathering of bitumen.

The most important effect of both aging and weathering from the practical point of view is an increase in hardness, which is attributed largely to oxidative condensation reactions which are greatly accelerated by heat and light(10). Hardening of bitumen from any cause is undesirable due to loss of plasticity leading to reduction in adhesive properties and durability in service. While in service, bituminous materials on road or roof will be subjected to temperature changes causing stresses which may cause thin bitumen films to crack so destroying the original weatherproof character of the coating. It has been suggested that moisture may act to dissolve oxidised species from the surface, causing erosion(19).

In certain circumstances a bitumen with too high a resistance to weathering may not be desirable. For example, in a dense road surfacing, bitumen which is resistant to weathering will tend to remain on the surface of the road as a smooth film giving, in wet weather, a slippery surface. On the other hand a more reactive bitumen may produce a skid-resistant surface. The use of refinery bitumen (i.e. from a crude oil source) has been shown, in full-scale road experiments, to produce smooth surfaces of low skid resistance, whereas surfacings containing Trinidad Lake Asphalt have a rougher texture(13,14,15,33,37). Under traffic compaction the bitumen binder tends to concentrate at the surface, producing a smooth film. Improvements in skid resistance with Trinidad Lake Asphalt have been attributed to the more rapid hardening of this film on weathering and subsequent exposure of fine aggregate by traffic abrasion. This aspect of weathering led Lee and Dickenson(14) to suggest that the addition of coal tar pitch to refinery bitumen would increase the rate of oxidation of the exposed binder, producing a rougher texture with improved skidding resistance. This was proved to be the case in a full-scale experiment(15) in which pitch-bitumen was compared with Trinidad Lake Asphalt and a straightrun Venezuelan bitumen in hot-rolled asphalt surfacings.

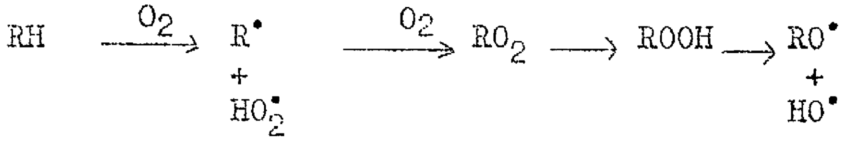
The various factors contributing to the durability of bitumens are reviewed briefly below. Since bitumens vary in composition it is not feasible to list the causes in any strict order of importance.

(i) Oxidation and polymerisation.
(ii) Volatilisation.
(iii) Age hardening.

1.7.1 - Oxidation and polymerisation

The action of oxygen is one of the principal factors responsible for the occurrence of aging phenomena. When bitumen is exposed to atmospheric oxygen slow auto-oxidation occurs and progresses more rapidly at high temperatures(16). Weathering of bitumen is attributable to oxy-polymerisation which produces acids with extremely surface-active alkaline salts(17). The effect of oxidation is two-fold and involves the direct union of oxygen with bitumens as well as the elimination of hydrogen or carbon in the form of water and carbon dioxide. These reactions are accelerated by actinic light rays.

An exact mechanism for oxidative polymerisation is not possible due to the complicated nature of bitumen. Hughes(19) in studies on bitumen oxidation kinetics suggested the following reaction mechanism:



$$RH \xrightarrow{O_2} \begin{array}{c} R^\bullet \\ + \\ HO_2^\bullet \end{array} \xrightarrow{O_2} RO_2 \longrightarrow ROOH \longrightarrow \begin{array}{c} RO^\bullet \\ + \\ HO^\bullet \end{array}$$

He maintained that the radicals (excepting $HO_2^{\bullet}$) may then initiate olefinic polymerisation in the bitumen. In addition, more olefins may be formed by dehydrogenation of the $R^{\bullet}$ radicals. The amount of oxygen in the polymer will depend on the relative rates of initiation by the oxygen-containing radicals and the other radicals. He concluded that if the process of oxidation is slow, polymerisation will take place and result in hardening and cracking, if initiation is rapid, peroxides and other oxidised species will dissolve in moisture, causing erosion.

A similar type of mechanism was advanced by Bolland and Ten Have(20), and Kennerly and Patterson(21) as follows:

Initiation:

$$ROOH \longrightarrow R\dot{O} + H\dot{O} \quad \ldots \quad \ldots \quad \ldots \qquad (1)$$

$$RO(H\dot{O}, H\dot{O}_2) + RH \rightarrow ROH(H_2O, H_2O_2) + \dot{R} \qquad (2)$$

$$AH + O_2 \rightarrow A^{\bullet} + HO_2^{\bullet} \quad \ldots \quad \ldots \quad \ldots \qquad (3)$$

Propagation:

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad \ldots \quad \ldots \quad \ldots \qquad (4)$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad \ldots \quad \ldots \qquad (5)$$

Termination:

$$2RO_2^{\bullet} \longrightarrow X \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (6)$$

Kennerly and Patterson(21) explained the above equations as follows. Peroxides, which are present, or are formed, in the hydrocarbons, initially cleave into free radicals when supplied with energy in the form of heat or ultra-violet light (1). Hydrocarbon molecules react with these radicals and form alkyl radicals (2). This initiation stage is followed by a chain reaction where more hydrocarbon reacts (4) (5). The chain process can terminate with the dimerisation of two peroxy radicals to form an inactive product (6). Beitchman(22) further studied the effects of antioxidants on bitumen durability using phenothiazine as a peroxide decomposer and explained the inhibiting reaction as follows:

Inhibition:

$$RO_2^{\bullet}(RO^{\bullet},HO^{\bullet},HO_2^{\bullet}) + AH \rightarrow ROOH(ROH,H_2O,H_2O_2) + A^{\bullet} \qquad (a)$$

$$RO_2^{\bullet}\ (RO^{\bullet},HO^{\bullet},HO_2^{\bullet}) + A^{\bullet} \rightarrow Y \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (b)$$

The function of antioxidant is to intercept radicals which would propagate the chain reactions (a) (b). The inhibitor can contribute to initiation (3) and the rate of this reaction is directly proportional to inhibitor concentration. He condluded that asphaltic degradation during accelerated weathering involves a free radical oxidation and this also takes place in natural weathering. Similar work was carried out by Greenfeld(23) in studies of the effect of mineral additives on the durability of blown bitumens.

More recently Martin(24) has shown that the resistance to oxidative hardening of blown bitumens can be improved by using antioxidants of a 'peroxide-decomposer' type or a 'free radical trap' type. The effect of temperature and humidity on the oxidation of blown bitumen was studied by Campbell, Wright and Bowman(29). They concluded, in general, that bitumen durability varies inversely with both temperature and relative humidity and that their effect on bitumen oxidation rates may be due to the formation and subsequent decomposition of a bitumen-oxygen-water complex. Heithaus(30) conducted tests of bituminous material in a weatherometer. He showed that bitumens with maltenes of high viscosity were most resistant and postulated that the rates of the reactions involved in the hardening of bitumen coatings are largely diffusion controlled. A high viscosity intermicellar liquid provides greater hindrance to oxygen diffusion, slowing down the hardening process.

Blokker and Van Hoorn(31) took the view that oxidation in light is due to the ultra-violet part of the spectrum and that hardening is limited to a depth of about four microns; in the dark hardening may occur to a depth of three millimetres.

Martin(32) proposed three different tests for evaluating the durability of roofing bitumens, namely, heat stability (kettle stability), dark oxidation and photo-oxidation. He concluded that coal tar pitches are definitely more reactive to oxidation than asphaltic bitumens but from the viewpoint of overall durability surface oxidation is not necessarily harmful and, in fact, may protect the main film from further oxidation. Exposure stimulates particular conditions under which hardening proceeds by different mechanisms and the extent of hardening indicates the relative durabilities. One important characteristic of bitumen deterioration is cracking, due to slow hardening of the bitumen until a condition is reached when external stresses in excess of the breaking strength may develop.

The absorption of oxygen by thin films of bituminous road binders were studied by Dickinson, Nicholas and Boas-Traube(33). They showed that bitumen oxidation in the absence of light at temperatures normally encountered on the road was a diffusion-controlled reaction. The rate of absorption of oxygen per unit weight of binder depended on the binder viscosity and film thickness. Irradiation of the film with light in the wavelength range 3000-5000 Å was found to produce a marked acceleration of the reaction. Greenfeld(34) studied the chemical changes occurring during the weathering of two blown bitumens in an accelerated weathering machine and on outdoor exposure. He decided that when bituminous surfaces are exposed to light, heat and water, numerous and complex chemical changes take place. Oxidation occurs and results in the formation of volatile and water-soluble degradation products. More than one-third of these weight losses are accounted for by the formation of carbon dioxide and water. Another third of the losses are due to water-soluble material which is highly acidic. A fourth reaction product, insoluble in both water and n-pentane, remains on the surface of the coatings.

A durability test for bitumen called 'the microfilm durability test' has been developed by Griffin, Miles and Penther(35). A very thin film of bitumen (5 µ) is spread on a glass plate and heated in an oven at 107.2°C for 2 hours. The increase of viscosity is measured by a sliding plate microviscometer and the ratio of the final viscosity to initial viscosity, known as the aging index, has been shown by Heithaus and Johnson(36) to be related to the lifetime of bituminous surfacings on the road after three or more years. A pressure oxidation test(37) devised by the Road Research Laboratory of the Ministry of Transport consists essentially in exposing tar films 7 mm thick to oxygen at 3000 lb/sq.in. in a steel bomb held at 65°C for a period of 64 hours. The changes produced are either measured as Frass Breaking Point or the increase in equiviscous temperature(37). Blokker and Van Hoorn(31) used similar tests for bitumens in which oxygen at high pressure (20 atmospheres) and at temperatures of 50 to 60°C were used. They concluded that under these conditions, one day's aging in the bomb is equivalent to half a year on the road.

Volkova(39) studied the effects of oxidants and antioxidants on weathering of bitumen. Retarding effects, on oxidation, were found with small amounts of sulphur, tannin, naphthol, sulphanilamide, sulphapyridine, pyrocatechin and alizarin. Accelerating effects were found with carbamide, phenyl-β-naphthylamine and 'Ferronapht No.1'. Sparlin(40) in his studies of the effect of u.v. light on viscosity of thin films of bitumen showed that u.v. energy is capable of producing measurable increases in the viscosity of bitumen films sealed from the atmosphere.

Kinnaird(41) showed a definite relationship between the penetration and softening point of bitumens obtained by oxidation from the same stock. Wright, Campbell and Fridinger(42) studied the effect of carbon arc intensities on two air-blown bitumens, by measuring the changes of the carbonyl band in the infra-red spectrum. The bitumen oxidation rate increased with the intensity of carbon-arc.

Exposure of bitumens to ultra-violet light in the presence of oxygen has been shown to produce water-soluble materials. Strieter and Snoke(10) were the first to report the formation of water-soluble materials in the presence of sunlight or artificial light and concluded that both light and oxygen were necessary to form these products. More recently, however, Gallaway(45) has shown that bitumen films exposed to artificial light in the absence of oxygen had a higher viscosity than unexposed samples.

1.7.2 - Volatilisation

Cut-back bitumens and tars contain a certain amount of volatile oils which are lost by evaporation on exposure on road or roof. This causes an increase in the viscosity of oil constituents by slow evaporation. The low molecular weight components of road tar are considered to be more volatile than those in straight run bitumens and thus tars are more prone to rapid hardening. Sabrou et al.(46) suggested that the increase in viscosity by evaporation was more important than that due to oxidation. This view was also supported by other workers, including Leaute(47), Batta(48) and Mitchell et al.(49). Mitchell(50) proposed a mechanism for the loss of oil by evaporation and showed that the initial rate of loss in the dark under thermostatic conditions was controlled by the rate of diffusion of oil to the surface, which depends on the viscosity of the binder. The development of a tough surface skin of hardened binder by the influence of u.v. light, stops further evaporation. Griffin, Simpson and Miles(51) showed that no material above a mol. wt. of 400 is lost from bitumen even at a temperature of 107°C.

The full scale road experiments carried out by the Road Research Laboratory(7), led to the conclusion that, even under conditions where an evaporation loss is most likely, i.e. in open-textured macadam, this factor cannot be considered as the most important factor in the deleterious hardening. The Laboratory has, therefore, concentrated its experimental research on binder oxidation studies.

1.7.3 - Age hardening

The phenomenon of age hardening concerns the hardening of a binder by slow change in the internal structure while in service. Lee and Dickinson(37) showed that coke-oven tars gave poor road performance mainly due to formation of internal structures, partly due to crystallisation of aromatic hydrocarbon components at low temperatures and partly to a change in colloidal structure. It has also been found that both heat and traffic movement destroy the internal structure formed by age hardening. Cracking or disintegration due to this age hardening is most likely to occur in the life of surfacings under very light traffic and cool weather conditions.

CHAPTER 2

ANALYSIS

2.1 - Analysis of bitumen and fractions

2.2 - The characterisation of bitumens and their components by infra-red spectroscopy

2.3 - The characterisation of bitumens and their fractions by nuclear magnetic resonance spectrometry

2.4 - Sulphur determination in bitumens and their fractions

2. ANALYSIS

2.1 - Analysis of bitumen and fractions

The composition of bitumen is very complex and has presented a great challenge to chemists. Fortunately, in recent years, new techniques and tools have been developed for the fractionation and analysis of bituminous materials. Several methods used for fractionation of bitumens are solvent-extraction, selective-adsorption-chromatography (column chromatography, paper chromatography), thermal diffusion, urea adduction, electrical deposition and various combinations of these.

2.1.1 - Solvent extraction

Traxler and Schweyer(53) developed a method based on the solvent action of n-butanol and acetone to separate bituminous material into (1) asphaltics, (2) paraffinic oils and (3) cyclic oils. According to this method the higher molecular weight materials like asphaltics are precipitated with hot n-butanol. The butanol-soluble oils are then fractionated by means of cold acetone which dissolves the cyclic compounds and precipitates paraffinic material. A similar method was used by Grant and Hoiberg(52).

2.1.2 - Selective adsorption

(a) Column chromatography

Separation by adsorption of certain bitumen components on solid surfaces followed by selective solvents to elute various fractions has been studied by many workers. In these studies, investigators have used chromatographic columns with different adsorbents such as fuller's earth, anhydrous alumina, silica-gel and a combination of the last two. Marcusson and co-workers(54) as early as 1916 developed a method for the fractionation of bitumens using fuller's earth as adsorbent and selective solvents. Hubbard and Stanfield(55) fractionated bitumen into three components; asphaltenes were precipitated by n-pentane and pentane-soluble maltenes were fractionated into oils and resins by adsorbing the last on anhydrous alumina.

O'Donnell(56) developed a procedure which involved molecular distillation to give separation by size, silica gel chromatography to separate saturates, aromatics and resins; solvent dewaxing of the saturates to determine wax content; urea complex formation to separate long chain paraffins; alumina chromatography to separate mono-cyclic aromatics; peroxide oxidation followed by chromatography to remove thiophene analogues and thermal diffusion in the liquid state to segregate naphthenes on the basis of ring number.

Kleinschmidt(57) used a chromatographic separation method using fuller's earth as adsorbent and n-pentane, methylene chloride, methylethyl ketone and a chloroform-acetone-water mixture as selective desorbing solvents. After removal of pentane insoluble asphaltenes, the pentane soluble maltene fraction was percolated through the adsorbent column using the desorbing solvents mentioned. The fractions obtained were termed white oil, dark oil, asphaltic resins and an acetone-chloroform desorbed fraction. Corbett and Swarbrick(58) used a chromatographic column of activated 'Porocel'. Alternatively, they suggested four inches alumina on silica gel. With the column maintained at 150°F, they could separate bitumen into asphaltenes, paraffins + naphthenes and aromatics using n-hexane, iso-octane and pyridine as desorbing solvents.

Chelton and Traxler(59) separated bitumen into 32 fractions by chromatography and liquid thermal diffusion after separating pentane insoluble asphaltenes. Middleton(60) fractionated bitumens into five fractions; asphaltenes were precipitated using n-pentane and the pentane soluble material was purified by treating with Attapulgus clay and passed through an activated alumina column and the adsorbed material eluted with n-pentane, cyclohexane-carbon tetrachloride and methanol-benzene.

(b) Paper chromatography

Wetzel and Peter(61) separated bituminous materials into asphaltenes, petroleum resins and mineral oil types by paper chromatography, observations being made with the aid of ultra-violet light.

2.1.3 - Thermal diffusion

O'Donnell(56) used thermal diffusion to segregate naphthenes present in the bitumen. He used a column consisting of three concentric glass tubes. Steam was passed through the centre tube and cooling water circulated through the outer annulus. Samples were removed from time to time from five reservoirs to determine refractive index in order to ascertain the equilibrium stage. Fractions from the top of the column contained most hydrogen.

Gardner, Hardman and Jones(62) employed a similar method to separate n-pentane soluble material into several fractions.

Chelton and Traxler(59) fractionated bituminous material after removal of asphaltenes, using chromatography and thermal diffusion. The thermal diffusion apparatus was a concentric metal column 6 feet in length with a temperature differential of 60°C. After 200 hours at these conditions the fractions were removed from the column from top to bottom. Several days were required for emptying because of the viscosity of the lower fractions.

2.1.4 - Electrical precipitation

Electrical deposition of asphaltic particles from crude oil was investigated by Preckshott and co-workers(63). Csanyi and Bassi(64) fractionated bitumen by electrical precipitation using different solvent combinations such as methanol-carbon tetrachloride, methanol-benzene and acetic acid-pyridine-carbon tetrachloride. With one exception deposition was at the negative electrode.

2.1.5.- Urea complex formation

This method was employed by O'Donnell(56) to separate long chain paraffins from branched molecules of bitumen. Calderbank and Nikalov(65) used this method to fractionate bituminous fractions. Solid complexes are formed between urea and adductable substances which can be filtered from the matrix and washed free from other oils. Heating or treating with water is commonly used to decompose the complex and recover the hydrocarbon.

2.1.6 - Experimental

Since the work envisaged was thermal and photo-oxidation of bitumens and their fractions a suitable fractionation method was necessary. It has been seen in the foregoing sections of this Chapter that many methods exist along with others too numerable to mention.

It was decided that a relatively simple method providing a few fractions only would suffice since the emphasis of the work was to be on oxidation rather than on fractional composition.

Throughout this work the same four bitumens were chosen. It was essential that one of these should be Trinidad Lake Asphalt since this material is, in a sense, the standard with which other bitumens are compared with respect to non-skid hot rolled asphalt.

The four bitumens are described in Table I showing, where possible, their sources and method of manufacture. It may be noted that penetrations in the normal asphalt range of 40-60 were chosen.

The following three methods of fractionation were tried.

(a) n-Butanol-acetone solvent method(53): Bitumen was dissolved in n-butanol and insoluble asphaltics were removed by centrifuging. The n-butanol soluble fraction was concentrated by distillation. The viscous portion was then dissolved in warm acetone and chilled at -10°F using solid carbon dioxide. It did not liberate any insoluble matter. This method was found to be tedious and the fractionation obtained not very distinct.

TABLE 1

SOURCE OF BITUMENS USED

		VISCOSITY	
tumen	Source	Penetration	S.Pt.°C (R and B)
1	Blended Venezuelan and Middle East Crudes (vacuum distillation of topped crude)	43	55
2	Venezuelan crude (Langunillas) (vacuum distillation of topped crude)	60	49
3	Trinidad Lake Asphalt (filler removed and fluxed with Trinflux)	40	52
4	Blended South American and Middle East crudes (vacuum distillation of topped crude)	44	55

(b) Kleinschmidt method(57) of fractionation by adsorption in fuller's earth: After removal of asphaltenes the maltene fraction was eluted through a fuller's earth column. Elution was very slow, the first fraction taking 20 hours to pass through the column. The chromatographic column was, therefore, modified as described in method (c).

(c) Modified Kleinschmidt method of fractionation:

A diagram summarising the modified fractionation method is shown in Figure 1. In the case of bitumen 3 (Trinidad Lake Asphalt) the mineral filler was removed by dissolving the bitumen in methylene chloride, centrifuging and subsequently removing solvent. This filler-free bitumen and the other three petroleum bitumens were then subjected to fractionation.

The asphaltenes were separated by dissolving bitumen in 100 volumes of petroleum spirit (b.p. 30-40°C) and the solution left for two hours. Asphaltenes were precipitated, removed by centrifuging and washed with an additional 50 volumes of petroleum spirit. The petroleum spirit from the asphaltene fraction was removed by evaporation in an oven at 60°C. This fraction was weighed as asphaltenes. The petroleum-soluble portion of bitumen was concentrated by distillation under reduced pressure and classed as maltenes in the usual way.

Several chromatographic columns were made from 1 inch diameter pyrex glass as in Figure 2. The overall

FIG 1

SUMMARY DIAGRAM OF FRACTIONATION METHOD

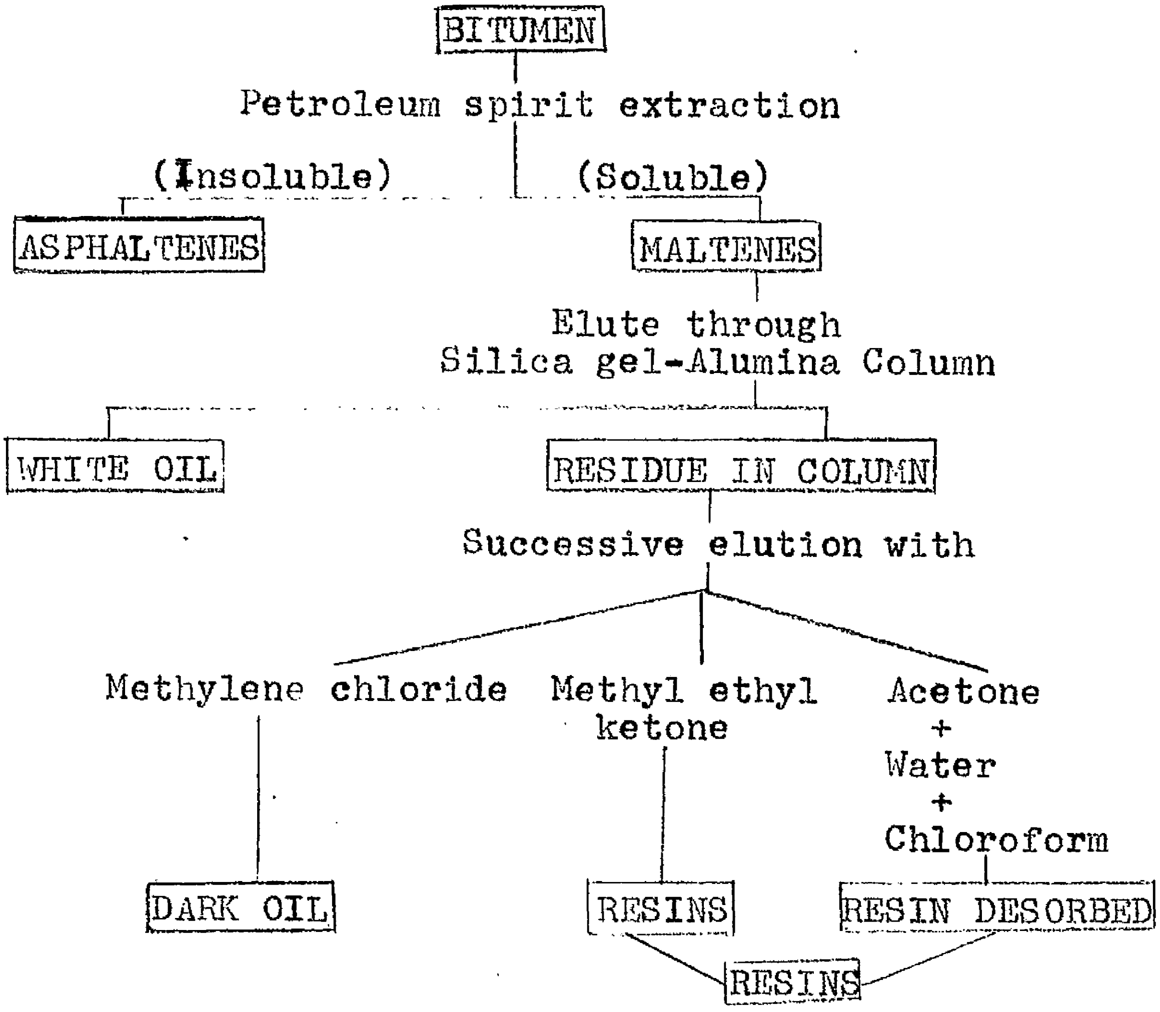
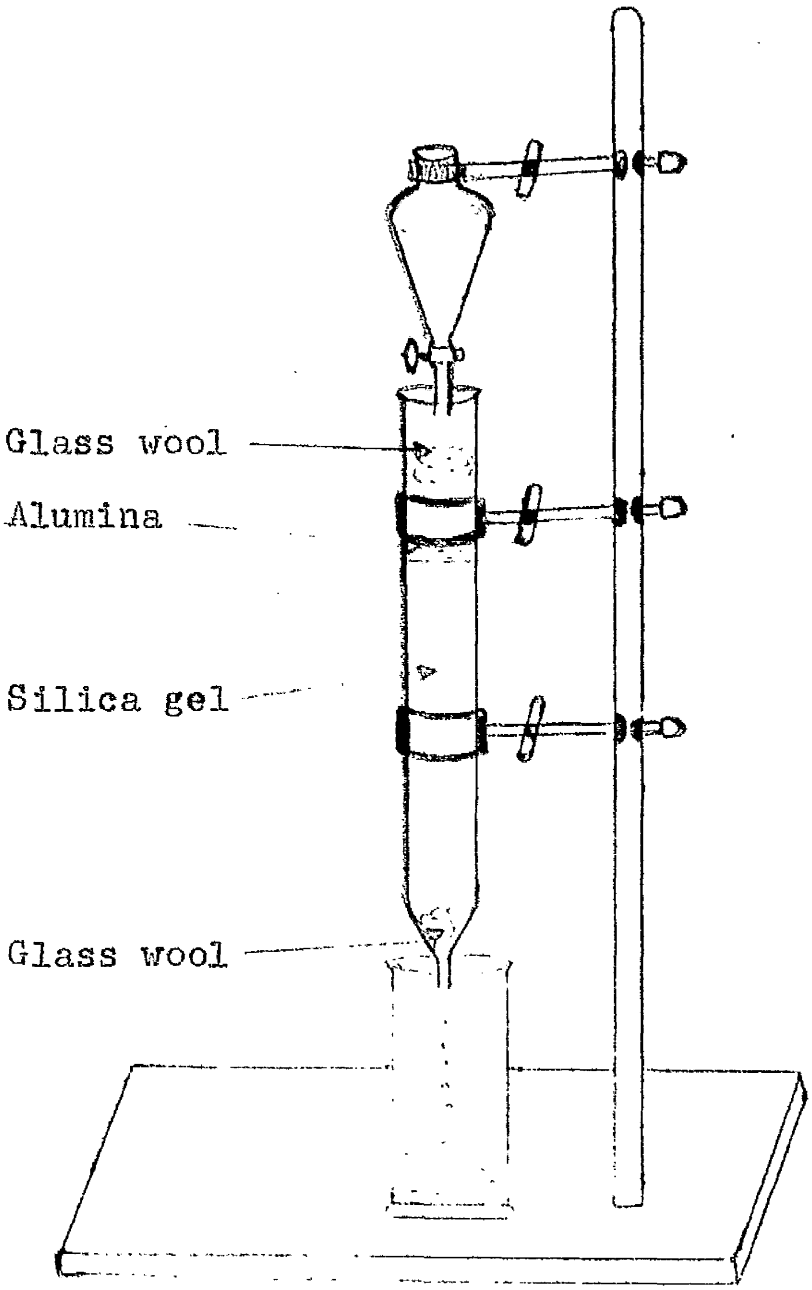


FIG. 2.

CHROMATOGRAPHIC COLUMN ASSEMBLY



lengths were 24 inches and the orifice at the tapered end approximately 2 mm i.d.

The column was packed with 3 parts by weight of activated silica gel and 1 part of activated alumina on top (both heated at 120°C for 8 hours). Glass wool plugs were inserted top and bottom and close packing ensured by vibrating.

Columns were first wetted with petroleum spirit (b.p. 30-40°C) and the maltene solution fed into the column at 5 ml/min. The solution leaving the column was collected and several washings of petroleum spirit passed through until the elute left no oil stain on filter paper. Solvent was removed from this first fraction by vacuum distillation and final traces removed in a vacuum oven until a constant weight was obtained. This fraction was called WHITE OIL.

The material adsorbed by the silica gel/alumina was eluted using, successively, methylene chloride and methylethyl ketone to give DARK OIL and ASPHALTIC RESINS respectively.

Final elution was made with a 10:90 mixture of water acetone followed by chloroform and this acetone-chloroform desorbed material added to the RESIN fraction.

2.1.7 - Description of bitumen fractionated components

The four fractions collected were:-

(i)	Asphaltenes:	Charcoal grey powder.
(ii)	White oil:	Water-white oil of medium viscosity. Occasionally a very pale straw colour.
(iii)	Dark oil:	Black liquid of high viscosity.

and

(iv)	Resins:	Black semi-solid material of very high viscosity.

A schematic diagram of the fractionation procedure is shown in Figure 1. The percentage fractions obtained from the four different bitumens are represented in Table 2. The chemical-type distribution of bitumen fractions are represented diagrammatically in Figure 3.

2.1.8 - Discussion of results

Reference to Table 2 and Figure 3 indicates that the four bitumens selected differ considerably in fractional composition and so should behave differently during oxidation studies.

Bitumen 3 (T.L.A.) has the highest percentage of asphaltenes, more than twice the other bitumens but contains a correspondingly lower amount of the other fractions.

The petroleum bitumens are fairly alike in general fractional composition with bitumen 2 having a large percentage of dark oil but less white oil than the others. The only

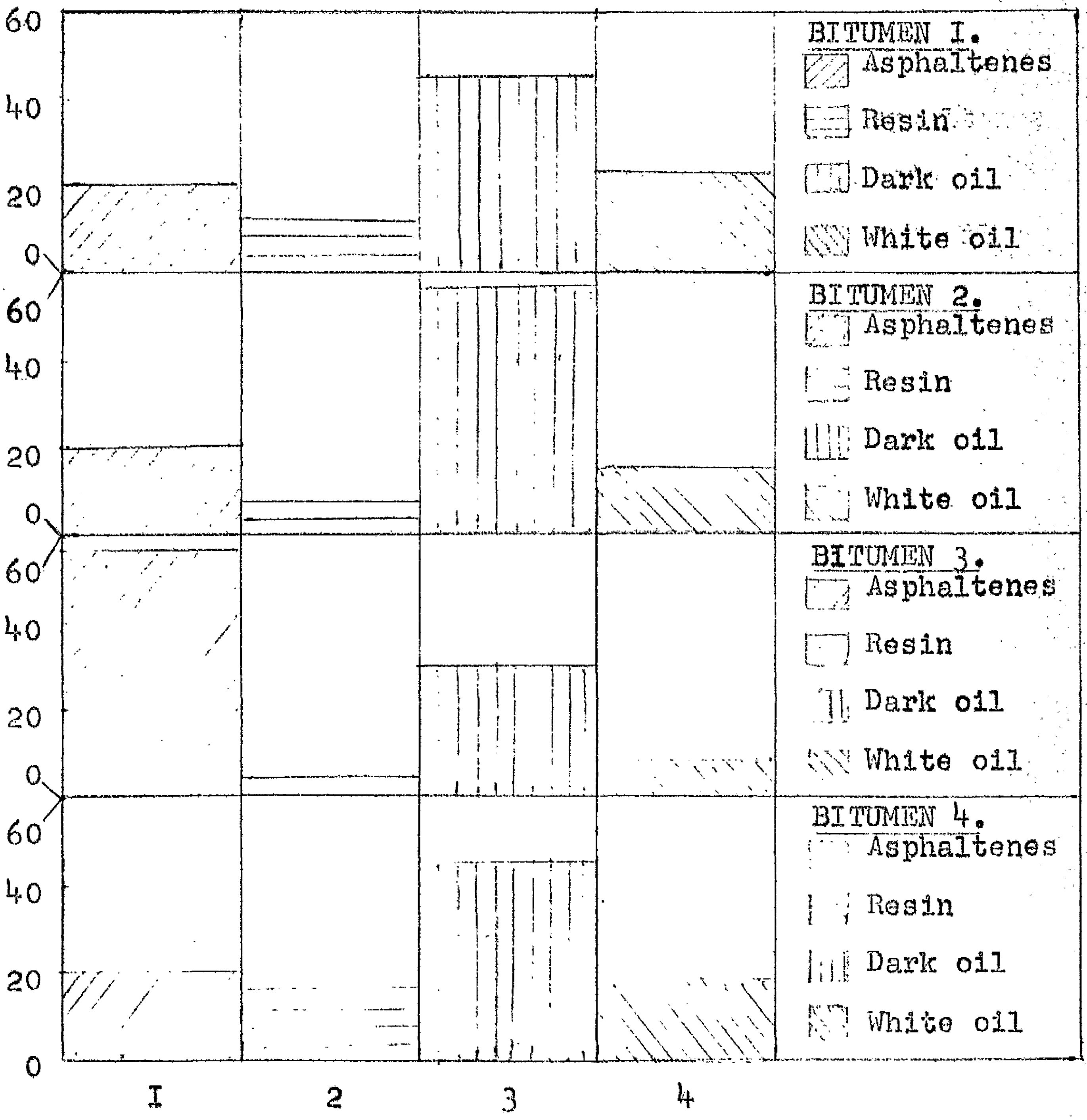
TABLE 2

DISTRIBUTION OF FRACTIONATED COMPONENTS OF FOUR BITUMENS FROM DIFFERENT SOURCES

Bitumen No.	Asphaltenes %	White Oil %	Dark Oil %	Resin %	Recovery %
1	19.85	22.78	44.82	12.36	99.81
1	20.20	23.00	45.05	12.00	100.25
Average	20.025	22.89	44.935	12.18	100.03
Deviation	± 0.175	± 0.11	± 0.115	± 0.18	± 0.22
2	19.30	15.81	56.85	7.70	99.65
2	19.02	14.24	57.60	7.66	99.42
Average	19.61	15.025	57.225	7.68	99.535
Deviation	± 0.31	± 0.785	± 0.375	±0.02	± 0.115
3	56.06	8.10	31.01	5.05	100.22
3	57.00	7.96	30.80	4.96	100.72
Average	56.53	8.03	30.905	5.005	100.47
Deviation	± 0.47	± 0.07	± 0.105	± 0.045	± 0.25
4	20.50	18.35	45.48	15.72	100.05
4	20.00	18.02	46.12	15.97	100.11
Average	20.25	18.185	45.80	15.835	100.08
Deviation	± 0.25	± 0.165	± 0.32	± 0.135	± 0.03

FIG. 3

CHEMICAL TYPE DISTRIBUTION OF BITUMEN FRACTIONS



Fractions

other notable difference is in bitumen 4 where the resin fraction was nearly twice as great as bitumen 2 and three times as great as bitumen 3.

2.2 - The characterisation of bitumens and their components by infra-red spectroscopy

Infra-red spectroscopy has been used in this work in an attempt to define (a) the functional groups of bitumens and components to provide information about the chemical constitution before and after oxidation and (b) the differences between refinery bitumens and Trinidad Lake Asphalt, since these behave very differently when used in dense road surfacings.

2.2.1 - Experimental

Infra-red spectra of the different bitumens described in Table 1 and their chromatographically separated fractions were scanned on a Perkin-Elmer Infra-Cord Spectrophotometer Model 174 using various techniques as follows:

(i) Solvent method

Bitumens, dark oils and resin, being very viscous, were best studied by a solvent method. A solution of 50 mg of sample in carbon tetrachloride was placed in the solution cell with pure solvent in a reference cell of equal path length for compensation.

(ii) - Liquid-film method

The white oil fraction was fluid enough for this technique. 10 mg of white oil was spread uniformly in the form of a thin film between two rock salt discs. Two other discs were taken as a reference cell and the spectrum scanned.

(iii) - Disc method

The asphaltene fraction was a powder, so a disc was prepared by pressing 2 mg of finely ground powder mixed with 200 mg of potassium chloride using a metal die.

2.2.2 - Spectra and their interpretation

Figures of these spectra with their interpretation are given in Appendix , along with spectra of thermally oxidised and photo-oxidised samples which are referred to in later chapters and discussed in detail there.

2.3 - The characterisation of bitumens and their fractions by nuclear magnetic resonance spectrometry

Nuclear magnetic resonance (NMR) spectroscopy is the most modern technique used for rapid and accurate determination of molecular structure, geometry of structure, quantitative analysis and the conformational analysis of hydrocarbons for either pure compounds or mixture of compounds. This technique is also used to characterise hydrocarbon mixtures. In this work NMR spectroscopy is employed in an attempt to elucidate functional groups in bitumens and fractions using chemical shifts of hydrogen nuclei present in these groups.

The chemical shifts (the absorption band location) - τ value - give a clue to the chemical nature of hydrogens and their structural environment. The band intensities are directly proportional to the number of protons responsible (66,67). The band multiplicities produced by spin-spin interaction provide structural and often stereochemical information.

Williams(68) used NMR for study of petroleum fractions. He characterised saturates by a 'Branchiness Index' (BI), which is defined as the ratio of the heights of signals due to methyl and methylene groups respectively. He devised a scheme for aromatic analysis which provides determinations of alkyl and aromatic ring carbon, alkyl group substitution on aromatic rings, the average number of aromatic rings per molecule and the number of carbons per alkyl group. He also devised a group characterisation scheme for olefin fractions in the same manner as for aromatics.

Winniford et al(69) studied the structure of petroleum asphaltenes using proton magnetic resonance. They measured four classes of hydrogens, viz. aromatic, benzylic, methylene and methyl protons. Gardner(62) studied 10 thermal diffusion fractions from the maltene fraction of bitumen, using an NMR technique. Chamberlain(70) studied many pure hydrocarbons and mixtures by NMR spectroscopic analysis. He produced summary charts of the chemical shifts of various hydrogen containing functional groups suitable for identifying chemically different types of hydrogen present in the molecule. Yen and Erdman(71) employed NMR analysis to study the structure of asphaltenes and resins . They employed this technique to distinguish between hydrogens in different structural environments within a molecule and gave some information regarding the shape of the aromatic rings, the extent of aromatic substitution naphthenic groups and the location of methyl groups relative to the condensed ring systems.

Sternhell(72) in his paper on high-resolution nuclear magnetic resonance spectroscopy showed the importance of NMR in structural studies of coal by giving typical chemical shifts and their assignment representing different types of protons. Friedel(73) studied the structure of asphaltenes, obtained from coal hydrogenation using NMR technique. He concluded that asphaltenes contain large molecules with many tetralin-type structures but with few polynuclear condensed aromatics and a few bonds easily broken to form free radicals.

Brown et al(74,75) employed NMR spectroscopic analysis in the study of hydrogen distribution in coals and with few assumptions they estimated aromaticity, degree of substitution and ring size. Ladner and Stacey(80) studied the hydrogen distribution in coals and soluble fractions of coal using a proton magnetic resonance technique. They estimated the ratio of aliphatic hydrogen in CH_3^- and CH^- groups to that in CH_2^- groups making a few assumptions. Dewalt and Morgan(76) employed NMR technique to study the structure of tars, pitches and asphalts. Durie, Shewchyk and Sternhell(77) recently studied the hydrogen distribution in the vitrains and their solvent extracts from some Australian bituminous coals using NMR technique. They have given a chemical shift assignment for aromatic hydrogen, hydrogen on carbon atoms α to the aromatic ring (benzylic) and aliphatic hydrogen at 8.4-6.5 δ ; 3.5-1.9 and less than 1.9 δ regions respectively.

2.3.1 - Experimental

NMR spectra of the two bitumens and their fractions were scanned on a Perkin Elmer NMR spectrometer which operates at a frequency of 40 Mc/s. The radio frequency was Kept at 2 mV. The internal reference was tetramethylsilane (TMS) which gave a signal at 10 τ . Carbon tetrachloride which gives no signal was used as a solvent so the signals only arise from the dissolved compound. The electronic integrator was employed to get integral of the absorption signals (chemical shifts) and this helps in assessing the significance of various signals. The vertical displacement of each plateau from the preceding one is proportional to the area under the absorption band integrated.

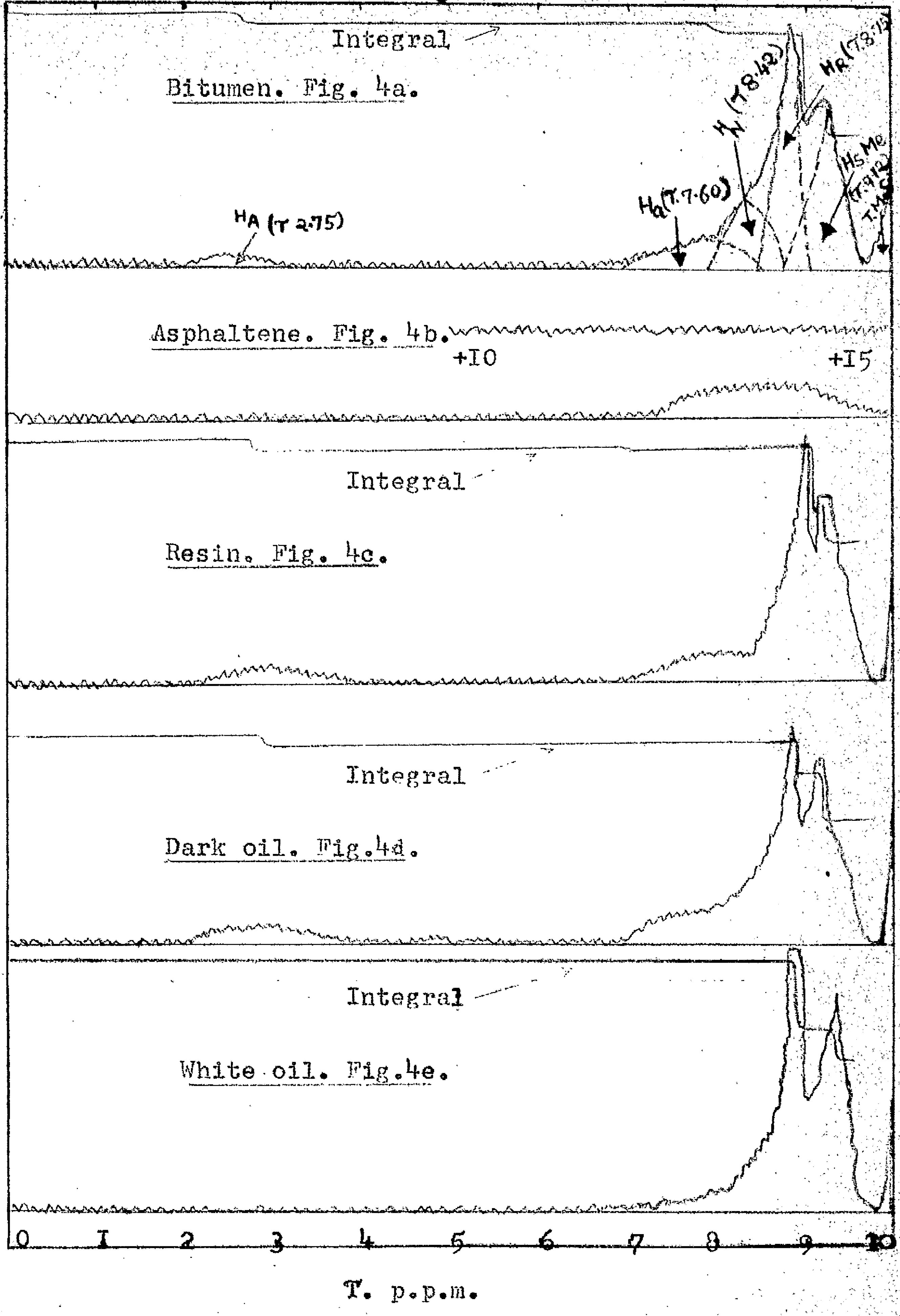
It was most difficult to obtain NMR spectrum of the asphaltenes due to the very high molecular weight and the paramagnetic properties which broaden the absorption bands even in relatively dilute solutions.

2.3.2 - Spectra and their intepretation(74,75,78,79)

The procedure suggested by Brown and Ladner(74,75) and employed by Yen and Erdman(71) was used in marking five regions between 1 and 10 τ in each spectrum to show five different types of protons (Fig.4a). The characteristic of these hydrogen types and their respective band locations relative to each other are given in Table 3. The breadth of all the absorption bands in the spectrum being very much greater than obtained for simple compounds is probably due to the molecular complexity of bitumen.

FIG. 4

N.M.R. SPECTRA OF BITUMEN 3 & ITS COMPONENTS



The NMR spectra of resin (Fig.4c) and dark oil (Fig.4d) fractions are similar to those of bitumen except for the variation in absorption band areas. They all show aromatic, benzylic, naphthenic, aliphatic methylene and aliphatic methyl protons in different proportions. NMR spectra of white oil fractions (Fig.4d) show the presence of naphthenic, aliphatic methylene and aliphatic methyl protons. White oil does not show any signal at 2.75 and 7.60 region suggesting the absence of aromatic and benzylic protons. NMR spectra of white oil, dark oil, resins and bitumen show no signal in the region of 3.5 to 5.0 τ suggesting the absence of olefinic protons. This indicates some agreement with the results obtained by infra-red analysis.

2.3.3 - Quantitative measurement of hydrogen distribution

The signals observed in NMR spectrum are very useful in distinguishing hydrogen atoms in aromatics and saturates. The integrated intensities of the different signals in NMR spectrum under suitable experimental conditions are directly proportional to the number of nuclei involved. The hydrogen distribution could also be obtained from these signals by measuring areas of these peaks by either counting squares or by cutting tracings on paper and weighing. The percentage of different types of hydrogen distribution was calculated by counting squares under the area within respective τ values. These results are represented in Tables 4 and 5.

2.3.4 - Discussion

The hydrogen distribution in petroleum bitumen (2) and Trinidad Lake Asphalt (3) and their components is represented in Tables 4 and 5. It can be seen from these tables that both petroleum bitumen and Trinidad Lake Asphalt show little difference in hydrogen distribution. In addition, there is a marked similarity fraction for fraction.

The paraffinic character of both white oils is confirmed by the absence of aromatic hydrogen. The high percentage of methyl groups present in this fraction suggests the presence of heavily branched paraffinic chains. This characteristic is comparatively more prominent in the white oil fraction of T.L.A. than that of petroleum bitumen.

Dark oil and resin fractions show the presence of aromatic hydrogen and benzylic protons suggesting substituted aromatic rings. In both bitumens the dark oil fraction would appear to have slightly more aromatic hydrogen than the resin fraction.

Asphaltene fraction did not show prominent signals in the spectrum (Fig. 4b) due to its para-magnetic properties, hence the hydrogen determination was not possible in that fraction.

Only two bitumens and their fractions were studied using NMR techniques since it was felt that, while interesting, no information leading to a significant characterisation of the fractions was obtained.

TABLE 3

TYPICAL CHEMICAL SHIFTS

Symbol	BAND CENTRE POSITION δ	τ	Multiplicity	Assignment
H_A	7.25	2.75	Broad band	Aromatic proton Ph-$\underline{H}$
H_a	2.40	7.60	Broad band	Benzylic proton Ph-C$\underline{H}_3$, Ph-C$\underline{H}_2$-CH$_3$
H_N	1.58	8.42	Broad region	Naphthenic proton
H_R	1.25	8.75	Singlet	Aliphatic methylene CH$_3$-C$\underline{H}_2$-CH$_3$
H_{SMe}	0.88	9.12	Singlet	Aliphatic methyl C$\underline{H}_3$-CH$_2$-C$\underline{H}_3$

HYDROGEN DISTRIBUTION IN BITUMEN 2 (VENEZUELAN) AND FRACTIONS

Type of hydrogen and band location	Bitumen % hydrogen	White oil % hydrogen	Dark oil % hydrogen	Resins % hydrogen
H_A (τ 2.75)	11.7	-	10.0	7.3
H_a (τ 7.60)	15.0	-	16.7	18.2
H_N (τ 8.42)	14.2	15.0	15.0	15.5
H_R (τ 8.75)	38.3	52.5	37.5	36.5
H_{SMe} (τ 9.12)	20.8	32.5	20.8	22.5
TOTAL	100.0	100.0	100.0	100.0

TABLE 5

HYDROGEN DISTRIBUTION IN BITUMEN 3 (TLA) and FRACTIONS

Type of hydrogen and band location	Bitumen % hydrogen	White oil % hydrogen	Dark oil % hydrogen	Resins % hydrogen
H_A (τ 2.75)	10.0	-	6.2	5.5
H_a (τ 7.60)	20.0	-	16.4	17.6
H_N (τ 8.42)	14.6	14.6	16.4	15.1
H_R (τ 8.75	34.0	46.4	41.0	38.8
H_{SMe} (τ 9.12)	21.4	39.0	20.0	23.0
TOTAL	100.0	100.0	100.0	100.0

2.4 - Sulphur determination in bitumen and their fractions

Determination of sulphur in petroleum and products by the bomb method is described under IP.61 (81). In this method the sample is oxidised by combustion in oxygen under pressure in a bomb containing 5 ml of 5% sodium carbonate solution. Sulphur is determined gravimetrically as barium sulphate by precipitating the oxidised contents of the bomb with barium chloride. This gravimetric method of determining sulphur is lengthy and tedious and it was decided to modify the method using a titration technique in which the bomb contents after ignition are titrated against standardised 0.005 M barium perchlorate using thoron as indicator. This method was employed by James, Fritz and Yamamura (82) for the determination of low concentrations of sulphate in water. A flask combustion method was employed for the determination of sulphur in petroleum and its products by Lidell (83) who used a glass flask filled with oxygen at atmospheric pressure. In this method complete combustion of the sample was difficult so the modified bomb method was employed.

2.4.1 - Modified bomb method: experimental

(a) Reagents used:

1. Sodium carbonate solution: 50 g/litre sodium carbonate solution (135 g of $Na_2CO_3.10H_2O$ in a litre of water).
2. Cation-exchange resin (Amberlite resin CG-120 B.D.H)
3. 0.005 M barium perchlorate solution: 2 g of barium perchlorate trihydrate in 200 ml of water and 500 ml of ethyl alcohol. The pH was adjusted to approximately 3.5 using perchloric acid and the entire solution was diluted to one litre with ethyl alcohol. This was then standardised against standard 0.005 M H_2SO_4 using bromophenol blue as an indicator.
4. Thoron indicator: thoron powder (Thoronol) B.D. Products. 1-(0-Aroono-phenyl-azo)-2 naphthol-3:6-disulphonic acid. 0.2% solution in water.
5. Ethyl alcohol: Commercial grade.

(b) Procedure:

About 0.3 g of the bituminous sample was weighed accurately in a silica crucible and ignited under oxygen pressure in the bomb containing 5 ml of 5% sodium carbonate solution as described under ASTM.D.129-IP.61. The contents were removed and were diluted to 250 ml with distilled water, 10 ml of this solution was taken and was passed through the cation exchange resin column to remove the cations of the solution and was washed with 25 ml of ethyl alcohol. Every ten readings the cation-exchange resin column was regenerated with 5N HCl. This was then washed with distilled water until the eluate was free from chloride and it was ready for further use. To the previously eluted solution and washings in a beaker, two drops of thorin indicator were added. This was then titrated against previously standardised 0.0045 M barium perchlorate solution. The end point was noted by the change in colour from red to pink. Readings were taken into duplicates and their mean was used for calculating the percentage of sulphur. A specimen calculation is shown below.

(c) Calculations:

Bitumen 1 Mean litre 3.8 ml

$$M_1 = \frac{V_2 \times M_2}{V_1}$$

$$= \frac{3.8 \times 0.0045}{10 \times 4} \times 98 \quad = \quad 0.0421$$

$$\therefore \text{ sulphur} \quad = \quad \frac{0.0421 \times 32}{98} \quad = \quad 0.0138 \text{ g}$$

The percentage of sulphur was calculated as follows:

$$\% S = \frac{S \times 100}{w} = \frac{0.0138 \times 100}{0.3424} = 4.03$$

where

M_1 = molality of oxidised sample solution

M_2 = molality of barium perchlorate

V_1 = volume of solution of oxidised sample taken

V_2 = volume of barium perchlorate solution required (burette reading)

S = g of sulphur calculated in the given sample

w = g of sample taken.

Sulphur was determined in all bitumens and their fractions and the results obtained are represented in Table 6.

2.4.2 - Discussion

The determination of sulphur is important from two points of view, viz. (1) as an aid in the characterisation of bitumens and their fractions and (ii) to study its effect on the weathering. It has been suggested that sulphur has a retarding effect on the rate of oxidation(82), hence its determination is necessary. The effect of sulphur on thermal and photo-oxidation is described in the relative sections.

From Table 6 it can be seen that the highest percentage of sulphur is present in asphaltenes and the lowest in white oils. Dark oils and resins also show quite high sulphur contents. Of all the bitumens, Trinidad Lake Asphalt contained the highest percentage of sulphur.

SULPHUR DISTRIBUTION IN BITUMENS AND THEIR FRACTIONS

Bitumen description	Sample description	% Sulphur
Bitumen 1 and Fractions	Bitumen	4.03
	White oil	1.53
	Dark oil	4.53
	Resins	4.10
	Asphaltenes	5.55
	Bitumen (calculated)	3.99
Bitumen 2 and Fractions	Bitumen	3.76
	White oil	1.63
	Dark oil	4.04
	Resins	3.12
	Asphaltenes	5.11
	Bitumen (calculated)	3 78
Bitumen 3 and Fractions (Filler free)	Bitumen	4.73
	White oil	1.08
	Dark oil	4.76
	Resins	4.44
	Asphaltenes	5.62
	Bitumen (calculated)	4.88
Bitumen 4 and Fractions	Bitumen	3.80
	White oil	1.52
	Dark oil	4.01
	Resins	3.05
	Asphaltenes	5.60
	Bitumen (calculated)	3.83

CHAPTER 3

THE THERMAL OXIDATION OF BITUMENS AND THEIR FRACTIONS AT DIFFERENT TEMPERATURES

3. THE THERMAL OXIDATION OF BITUMENS AND THEIR FRACTIONS AT DIFFERENT TEMPERATURES

The long-term durability of bitumen coatings is very important from the viewpoint of commercial application. The durability of bitumens depends on the influence of weather, including air, light, moisture, heat etc. The action of atmospheric oxygen is one of the principal factors responsible for the deterioration of bituminous coatings, producing slow autoxidation the rate depending on temperature. At normal atmospheric temperatures bitumen oxidised slowly. Oxidation of the outer surface is accelerated by sunlight and the inner oxidation is thermal. The aging of exposed bitumen is thus affected by the presence or absence of sunlight and so this study has involved both thermal and photochemical oxidation.

Thurston and Knowles(25) were pioneers in the study of thermal oxidation of bitumens and their components. They used a static oxidation method and concluded that the solid constituents (asphaltenes) oxidised most readily and the oils least. Ebberts(27) employed potassium permanganate and sulphuric acid in oxidising thin films of bitumen. Erdman and Ramsey(16) devised a rapid semi-automatic procedure for the determination of the oxidation rate of natural bitumens and asphaltenes using alkaline potassium permanganate.

Lewis and Welborn(84,85,86) developed a thin film oxidation test for bitumens. In this test a 3175 μ thick film of bitumen is oxidised for 5 hours at 325 °F. The changes in penetration, softening point and ductility are then determined. Traxler(87) employed this technique for oxidation of bituminous films for 5, 10 and 15 hours and measured the changes in viscosity. He used the factor (D) (the ratio of the original viscosity to viscosity after oxidation) to give the degree of hardness.

Griffin et al(35,51) developed a Shell thin-film test in which thin films of bitumen of five microns thickness were oxidised for two hours at 225 °F. They used the ratio of the final viscosity to the original viscosity as an aging index to express the durability of the material. They also used the ratio of the air aging index to the nitrogen aging index as a measure of the hardening due to oxidation. The durability of bitumen measured by its hardening in the dark was investigated by van Oort(28). He concluded that experimental conditions simulate normal practice if bitumen films five microns thick are examined. He used a microviscometer to measure changes in viscosity after oxidation.

Martin(32) studied thermal oxidation of bitumens in thin films of 40 microns under 300 psi pressure at 65 °C using a stainless steel vessel. He studied the rate of increase in viscosity as a suitable means of expressing increase of hardness, critical viscosity at rupture and oxidation resistance. Hughes(38) employed a thin film oven oxidation test and air blowing of bitumens to study the rate of oxygen and the effects of temperature and time on the rate of reaction. He suggested that conversion of resins to asphaltenes and asphaltenes to insoluble polymeric materials took place.

Huet(88) in his oxidation experiments in absence of light concluded that aging of bitumen is caused by the diffusion of oxygen in the material, accompanied by oxidation and polymerisation reactions, bitumens containing a high percentage of sulphur appear to be more resistant to oxidation than those with a low sulphur content.

3.1 - Chemistry of hydrocarbon oxidation

Bitumens are largely composed of hydrocarbons including three main groups, namely, aliphatics, naphthenics and aromatics. Olefins are generally absent. The oxidisability of bitumen is closely related to the composition of the molecules, the presence of different types of hydrocarbon in a mixture and the influence of the oxidisability of each of the components, therefore, a study of the literature on the oxidation of pure hydrocarbons and various hydrocarbon mixtures is pertinent to this work.

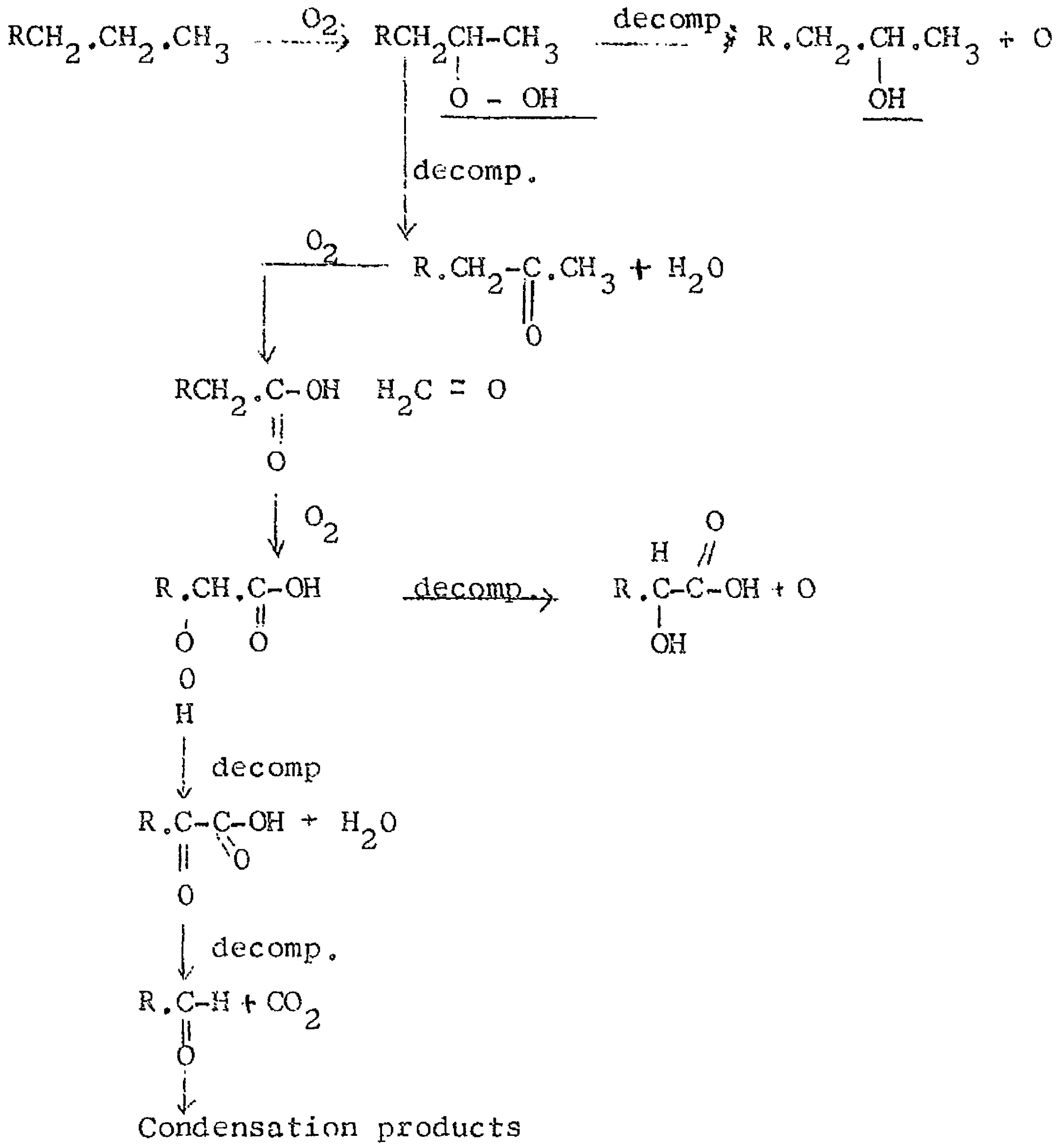
Lundberg(89) in his study of the oxidation of pure hydrocarbons concluded that compounds having olefinic double bonds are generally oxidised at a substantially higher rate than the saturates or highly aromatic hydrocarbons. Benzene derivatives with long side chains or a number of alkyl substituents come next, followed by naphthenes, paraffins and benzene structure with short side chains with condensed benzene ring structures being most stable. Jezl(90) studying mineral oil and its fractions concluded that mononuclear aromatics were the most readily oxidised and saturates were nearly as readily attacked. Dinuclear aromatics were more stable and trinuclear aromatics were most stable of all. He also showed that, for mixtures, blends of saturates and trinuclear aromatics were stable, followed by a blend of saturates, di- and trinuclear aromatics.

Chernozhukov and Krein (91) studied oxidation of pure hydrocarbons and various hydrocarbon mixtures at 150°C and 15 kg/sq.cm oxygen pressure. They showed that aromatics with side chains are more easily oxidised than aromatics without side chains. Aromatics with short side chains gave resins and asphaltenes as the main oxidation products while with increasing chain length the formation of resins and asphaltenes decreased and products of more acidic character were formed. The oxidisability of naphthenes increased with increase in molecular weight and with increasing side chains. Oxidation of paraffin-naphthene mixtures was inhibited by the presence of small amounts of aromatics without sidechains. This effect became more pronounced with an increased number of aromatic rings in the molecule but weakened in the presence of side chains to the aromatic rings. Aromatic rings with long chains may even promote the oxidisability of naphthenes.

Von Fuchs and Diamond (92) showed that maximum resistance to oxidation is obtained with hydrocarbon mixtures having an optimum aromaticity. They concluded that aromatics can possibly act in a twofold capacity, i.e. both as inhibitors and retardants. Larsen et al.(93) concluded that the rate at which oil absorbed oxygen cannot be explained simply on the basis of aromaticity and that the presence of natural inhibitors produced on oxidation is an important factor. Berry et al.(94) showed the importance of composition on the rate of oxygen attack.

Lundberg(89) indicated that when methylnaphthalene was blended with white oil, the antioxidant effect was not as potent as with aromatic fractions extracted from lubricating oils. This might be due to the absence of sulphur compounds in the synthetic blend. Leonardi et al.(95) confirmed the above results and showed that aromatic hydroperoxides decomposed phenolic inhibitors by the action of acids derived from the oxidation of natural sulphur compounds.

The following diagram summarises the possible oxidation products of hydrocarbons(96,97,98)



3.2 - Purpose of thermal oxidation work

Thermal oxidation of bitumens was studied because most of the bitumen in road surfacings is in a dark environment and protected from light by aggregate particles. The surface layer only is exposed to sunlight and may undergo photo-oxidation whereas lower levels can only be oxidised thermally. Another object was to compare the reactivity of bitumen components from different bitumens in order to assess the significance of fractional composition in the behaviour of bitumens under dark oxidation conditions. A major point in this study was the inclusion of Trinidad Lake Asphalt which appears to behave very differently from petroleum bitumens under road conditions.

3.3 - Development of an oxidation method

Different methods for measuring the rate of oxidation of bitumens and bitumen fractions can be employed depending on the physical properties of the material, the amount of substance available and the information required. Oxidation of bitumens with potassium permanganate solution was employed by several workers(16,27). The drawback in this method is probably lack of correlation with practical conditions. Changes in the physical properties(51,84) of thin films of bitumen on oxidation have also been measured, oxidation normally being assessed by the degree of hardening with subsequent correlation to durability. This method could not be easily employed due to the large variation in viscosity of the fractions and the difficulty of preparing films of defined thickness. Similar problems are met in considering the pressure oxidation test(37). With all these difficulties in mind it was decided to develop a micro- or semi-micro technique. Oxidation temperatures were chosen to be in keeping with temperatures in actual road service and oxidation was carried out at 30,45 and 60°C. Oxygen uptake was measured by a direct manometric method and was considered to be most suitable in this case.

A similar method was employed by Jezl (90) to study oxidation stability of oil components.

Some probable difficulties which had first to be overcome were:-

(1) Skin formation affecting the subsequent rate of oxidation.

(2) The rate of diffusion dominating the rate of reaction.

(3) Variation in reactivity due to viscosity differences (i.e. solid and liquid fractions).

These problems were eliminated to a large extent by dissolving the component in a small amount of xylene which is inert to oxidation and by vibrating a flask containing ballotini (20 mesh), which would bounce up and down constantly breaking the surface of the solution.

3.4 - Development of apparatus

Apparatus requirements

(1) Water bath:	A water bath fitted with immersion heater, thermostat, thermoregulator and stirrer was required.
(2) Vibrator:	It was necessary to make a device for vibrating the flasks in the water bath.
(3) Flasks:	Flasks had to be of small volume, since the pressure differences were expected to be small.

(4) Absorbents;	Absorbents for absorbing carbon dioxide and water vapour. This was essential if true oxidation rates were to be determined in view of the method used.
(5) Manometer;	A manometer sufficiently accurate to register very small differences in pressure.
(6) Water bath;	A thermostatically controlled water bath to give a constant temperature of 25 °C as a datum temperature for all the pressure measurements.

3.4.1 - Water bath

A bath was constructed from a glass tank (12 inches diameter and 18 inches high) covered with $1\frac{1}{2}$ inches thick glass wool as an insulating material. Other accessories fitted to this water bath for complete control were a Sunvic thermostat, heating element, heating lamp, stirrer with speed controller, thermometer and a Regavolt rheostat.

3.4.2 - Vibrator

Shaking was essential to ensure that all the sample was exposed to the oxygen and to eliminate the effect of diffusion on the reaction rate. This problem was solved by modifying a Proctor air pump.

Figure 5 shows the inverted pump with the necessary modifications to vibrate ballotini in the flasks. The bolt in the centre of the diaphragm was extended and onto this was attached the cradle which could hold four flasks. Adjustments were made during trial runs to obtain maximum vibration when the flasks were immersed in the water. This method seemed to give an adequate vertical vibrating amplitude to keep the surface of the solvent in the flasks disturbed by the bouncing ballotini.

3.4.3 - Design of the cradle

A platform had to be constructed to hold flasks in the water bath during the oxidation. For this purpose, the cradle shown in Fig. 5 was constructed.

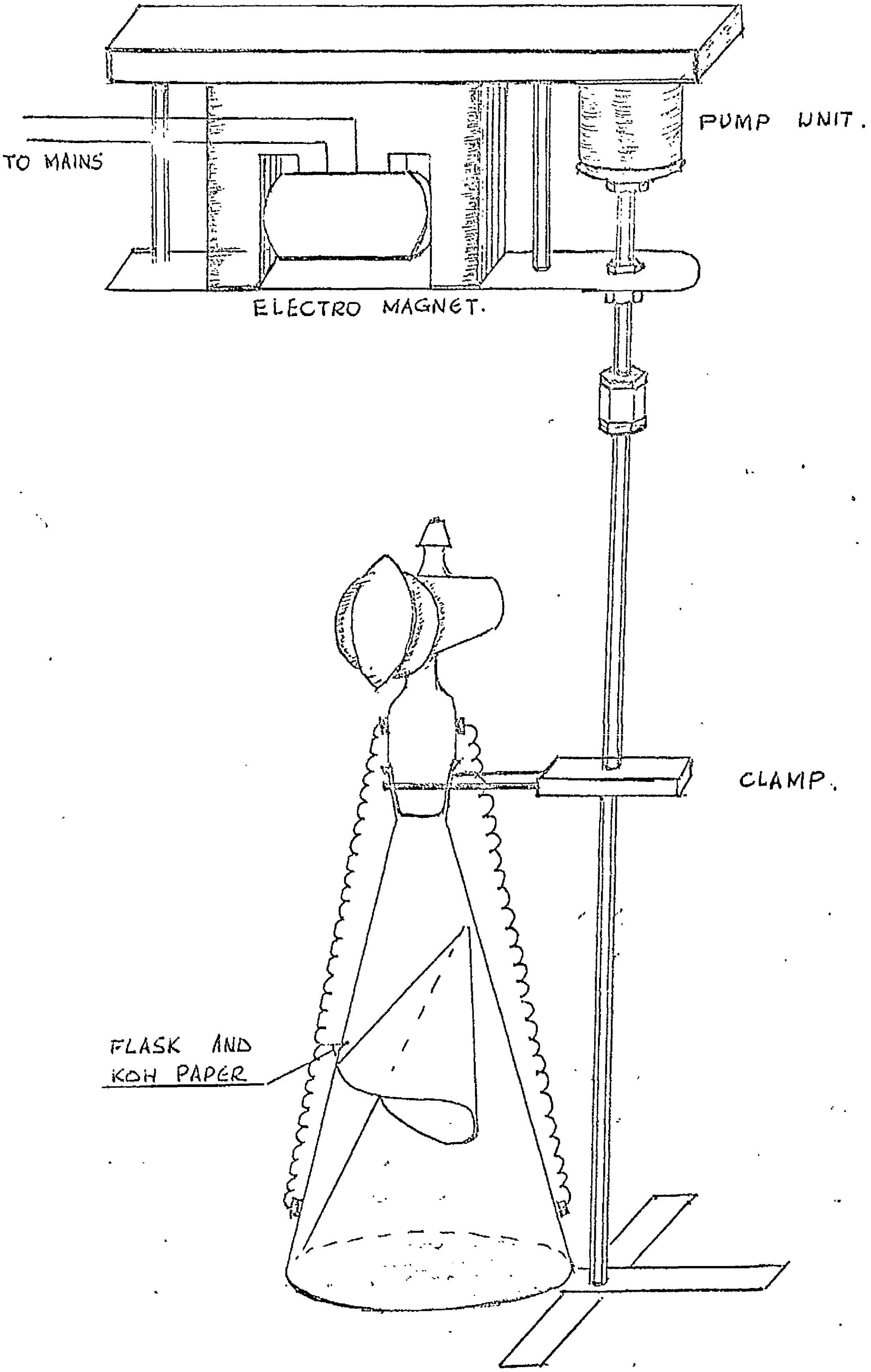
3.4.4 - Reaction flasks

The flasks used were 50 ml conical flasks with ground glass necks, fitted with Quickfit stopcocks, with the stopcocks held on firmly by springs. All the flasks were calibrated by determining accurately their volume at 25 °C.

3.4.5 - Solvents

The solvents considered as 'bitumen carriers' were xylene and pyridine. The boiling point of xylene is about 140°C and that of pyridine about 115 °C. Using pyridine alone, experiments showed some absorption of oxygen during an oxidation run. Xylene was found to be a suitable solvent, since it did not absorb an appreciable amount of oxygen.

FIG. 5.



VIBRATOR & CRADLE.

3.4.6 - Absorbent

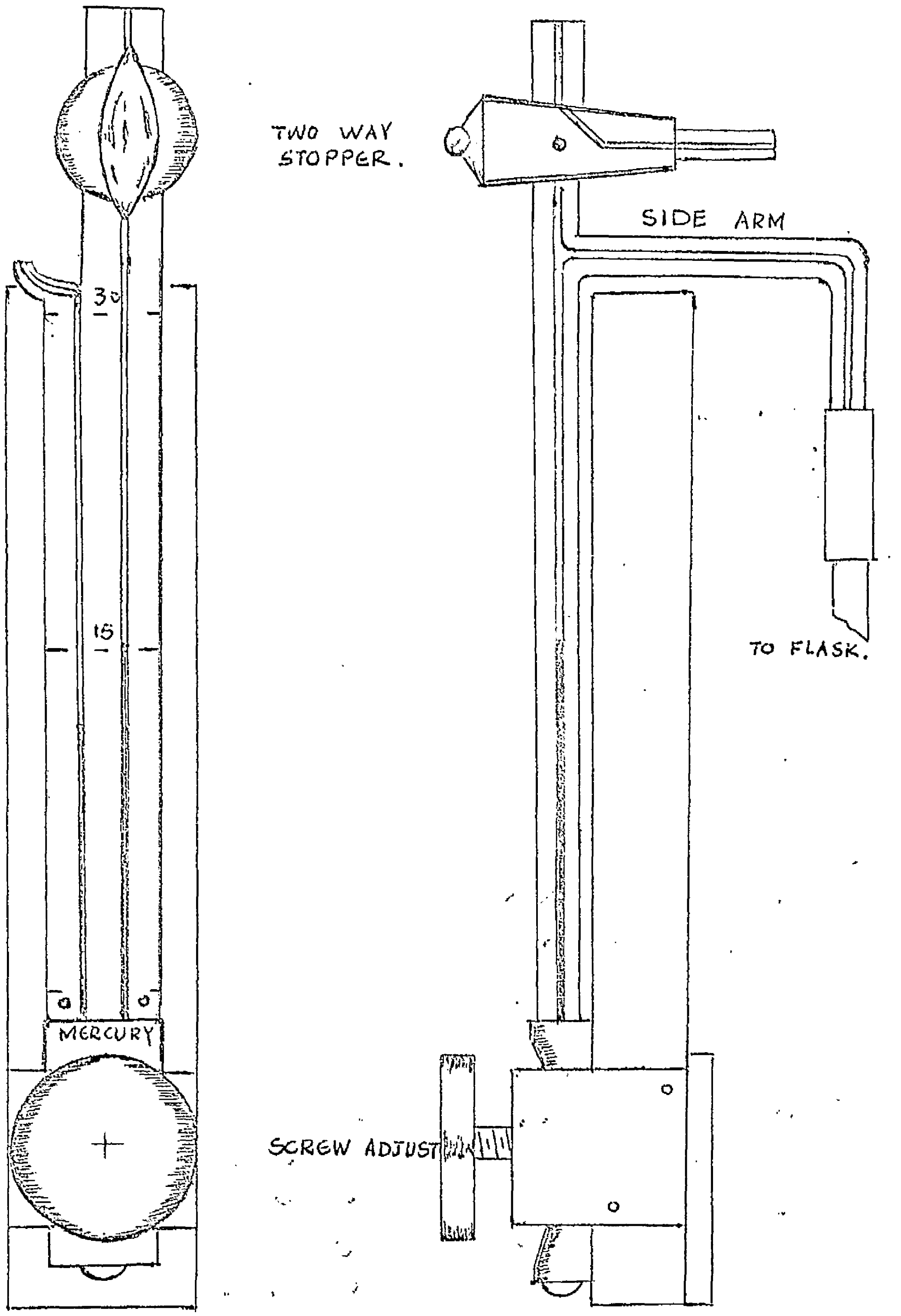
Silica gel and soda asbestos were first tried. They were bound in a nylon net and were hung from the hook of a small glass rod inside the reaction flasks. This did not work well so potassium hydroxide beads were fused onto a platinum wire and placed in the reaction flask. This also was not very satisfactory, possibly due to the formation of excessive amounts of carbon dioxide and water vapour which could not be completely absorbed by the small surface area of potassium hydroxide beads. To give a larger area, folded filter paper saturated in 40% potassium hydroxide solution was dried in a vacuum oven and suspended on a platinum wire being placed in the flasks as shown in Fig.5. Experiments carried out using these potassium hydroxide papers were very satisfactory and this method was adopted.

3.4.7 - Manometer

It was most important to find a suitable manometer to measure accurately the smallest change of oxygen pressure. A simple U-tube manometer, filled with liquid paraffin was tried but this was found not to be sufficiently sensitive. To improve the accuracy of the readings a Warburg Manometer filled with Brodie's solution was used but this solution was found to be of too low a density; however, mercury in this Warburg manometer was found to be very satisfactory.

Fig. 6 shows the construction of the manometer which was a constant pressure type. It consisted of a glass rod about 30 cms long with two narrow bores running the

FIG. 6.



WARBURG MANOMETER.

length of the glass rod. These capillaries were accurately graduated in mm. Onto one end of this glass cylinder was fitted a rubber tube reservoir and a screw clamp arrangement by which the level of the mercury in the tube could be adjusted so that the measured volume was always constant. One capillary was open to the atmosphere while the other carried a tube to which the oxidation flask could be attached by means of rubber tubing. Pressure in the flask and side arm could be brought to atmospheric by turning the ground glass stopper.

3.5 - Theory of the Warburg Manometer(99)

The amount of oxygen finally absorbed in the flasks was calculated from the following equation:-

$$x = h \frac{\left(Vg.\frac{273}{T} - Vf\alpha\right)}{P_o}$$

$$= hk$$

where x = amount of gas absorbed in ml at N.T.P.

h = observed change in the manometer (on the open side arm) in ml.

k = flask constant

Vg = volume of gas phase in the flask including connecting tubes down to the zero point.

Vf = volume of luid in vessel

P_o = 760 mm mercury (standard pressure) expressed in terms of manometric fluid

$$P_o = \frac{760 \times 13.60}{\text{Sp.gr. of manometric fluid}}$$

T = temperature of bath in degrees centrigrade absolute

α = solubility in liquid of the gas involved.

3.6 - The thermobarometer(99)

In the determination of the flask constant k, the value of P was assumed to remain constant from the beginning to the end of the given period. The atmospheric pressure and to a certain extent the temperature of the bath were likely to change, however, these changes were corrected by means of a thermobarometer. The thermobarometer consisted merely of a Warburg Manometer using mercury and with a flask containing water attached. The volume of the water was not critical.

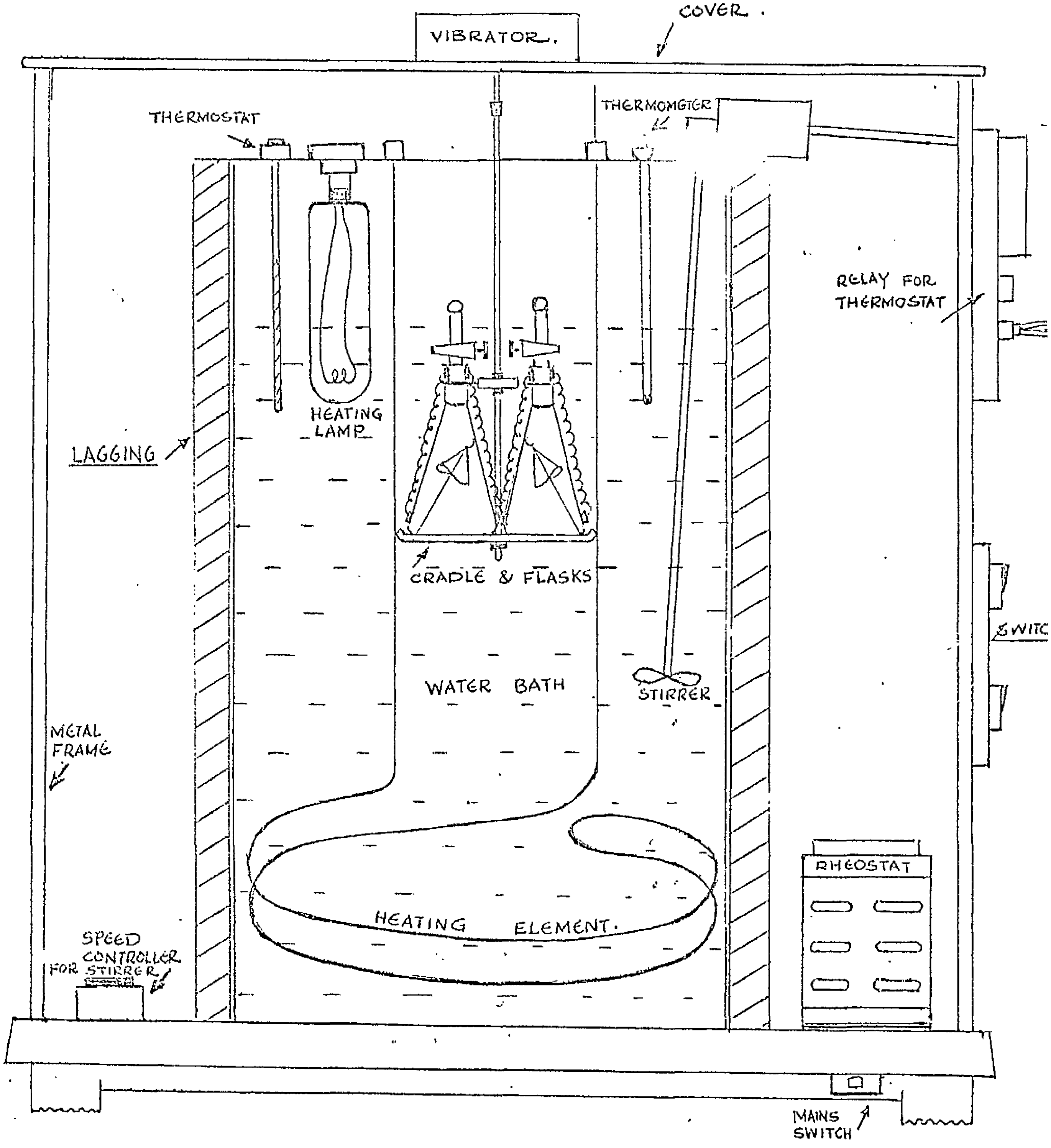
If the level of liquid in the open arm of the thermobarometer rose this suggested either a decrease in atmospheric pressure or an increase in the bath temperature. For reaction flasks which register a drop in pressure, the observed decrease was smaller than the actual decrease by the amount by which the thermobarometer fluid had risen and an additional correction was required and vice versa.

3.7 - Experimental technique and details

The thermal oxidation apparatus was designed as shown in Figure 7. Bitumens and their fractions were weighed exactly in quantities of 0.5 g into the 50 ml conical flasks. Each sample was dissolved in 2 ml of xylene and 2 g of ballotini were added into them. Whatman filter paper No.1 (7 cm diameter) was impregnated with 40% potassium hydroxide solution and dried at 60°C in the vacuum oven. Each filter paper was folded radially and was hung on a hooked platinum wire and placed vertically in the

FIG. 7.

THERMAL OXIDATION APPARATUS.



reaction flask. This kept the filter paper in an umbrella-shape giving a larger area for carbon dioxide and water vapour absorption.

3.7.1 - Method of filling the flasks

The reaction flasks were flushed with oxygen for five minutes and the cocks put on and closed. These flasks were again swept twice with pure oxygen from a cylinder for two minutes at 2 psig to ensure that the flasks were completely filled with pure oxygen. The stopcocks were held firmly in position by springs and the flasks placed in a water bath maintained at 25 °C for 15 minutes before the stopcocks were vented to air to bring the pressure in the flasks to atmospheric.

3.7.2 - Method of measuring oxygen absorption

These four flasks were then placed on the cradle and were put into the water bath kept at the oxidation temperature and the cradle rod bolted to the plunger rod of the vibrator by a locking nut. With the oxidation reaction under way oxygen uptake was measured every 10 hours for a period of 60 hours.

Every 10 hours the reaction flasks were taken from the water bath for measuring oxygen uptake. The flasks were fitted to the manometer, keeping the stopcock of the side arm in a vertical position. The mercury levels in both capillaries were adjusted to read 15 cms by means of the screw adjustment. The stopcock on the side arm was closed and the stopcock of the reaction flask opened giving a difference in mercury levels. The mercury level in the closed limb was re-adjusted to 15 cms and the reading of the mercury in the open limb was taken. From these readings the pressure drop was obtained.

Another Warburg Manometer was used as a thermo-barometer as described in Section 3.6.

After each 10 hourly measurement the flasks were refilled with pure oxygen and the oxidation continued. Oxygen uptake was calculated from manometer readings as described below.

3.7.3 - Determination of flask constants

For calculating flask constants the following formula was used.

$$KO_2 = \frac{Vg.\frac{273}{T} + V_f \alpha}{P_o}$$

Where KO_2 = flask constant for oxygen. (The other factors are as in 3.5). The solubility of oxygen in the solvent was taken as zero and so the equation simplified to:

$$KO_2 = \frac{Vg.\frac{273}{T}}{P_o}$$

where Vg = volume of gas space in the flask and in the side arm of the manometer.

A typical calculation is as follows:

$$Vg = \text{volume of flask} + \text{volume of side arm} - \text{volume of contents of flask}$$

$$= 72.7\text{ml} + 4\text{ ml} - 5.1\text{ ml}$$

$$= 71.6\text{ ml}$$

$$T = 273 + 25 = 298$$

$$P_o = 76 \text{ cms.}$$

Now KO_2 of the first flask can be calculated as follows:-

$$KO_2 = \frac{71.6 \times \frac{273}{298}}{76} = 0.86$$

The O_2 used up in the oxidation reaction can be calculated by multiplying this flask constant ($KO_2 = 0.86$) with the difference in pressure (h) in cm observed in the manometric reading after the thermobarometer correction.

3.8 - Experimental results and discussion

Four experiments were carried out first to study the effect of variations in the amount of xylene on the rate of oxidation at 60°C of four different bitumens. The observed results are given in Table 7. It can be seen that changes in the bitumen concentration has little effect on the thermal oxidation rate of different bitumens. These results also show good repeatabilities in oxygen uptake and so it was decided that this method could be used satisfactorily for determining rates of oxidation.

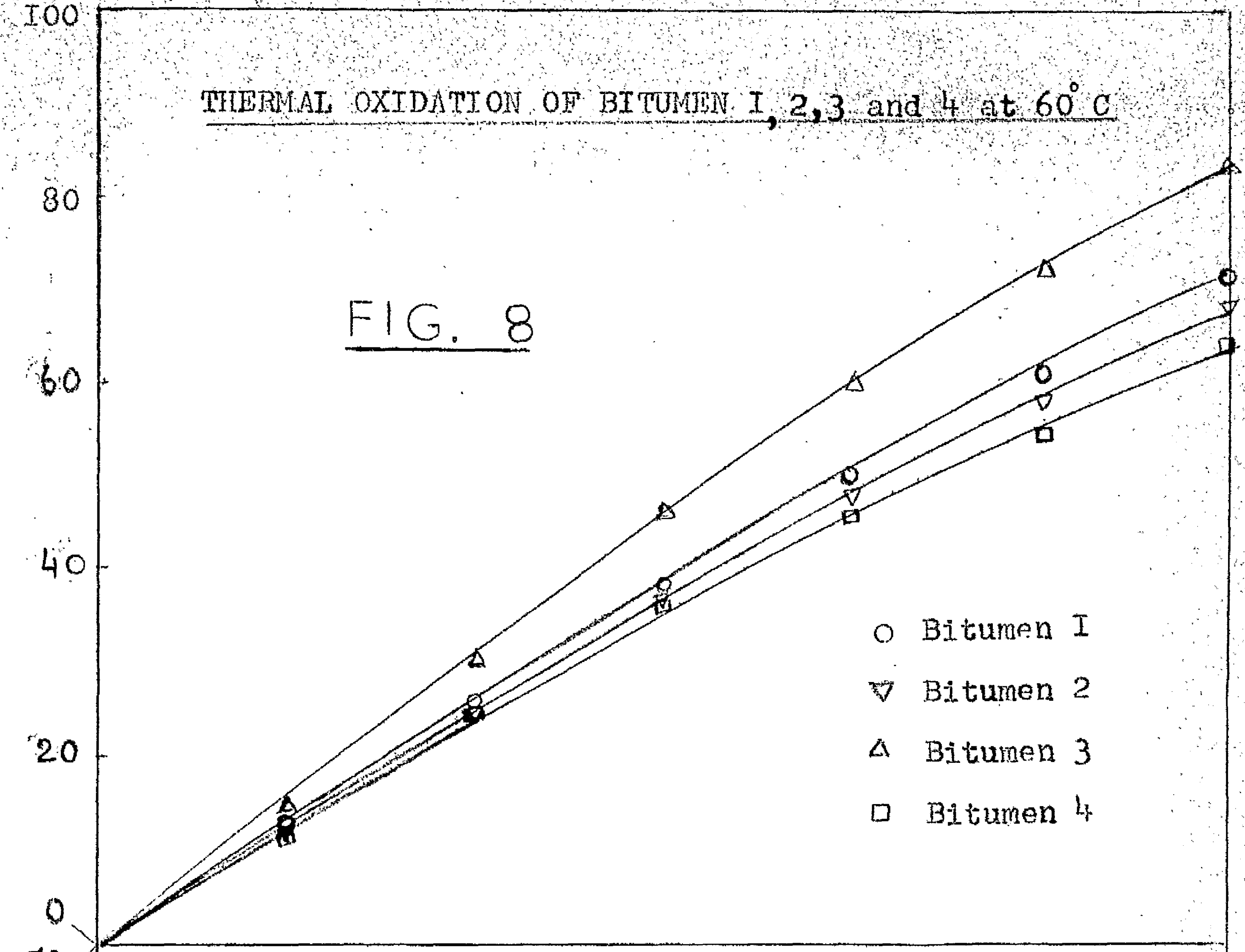
Four bitumens (Table 1) and their fractions were oxidised at 60°, 45° and 30°C as described in the experimental procedure. This resulted in 60 individual oxidations each 60 hours duration. Oxygen uptake at each stage was calculated as described and comparative reactivities of the fractions obtained plotting oxygen uptake (cc/g sample) against time. Similarly shaped reaction curves were obtained throughout and these are shown in Figures 8 to 22.

Figures 8, 9 and 10 show the curves obtained for

TABLE 7

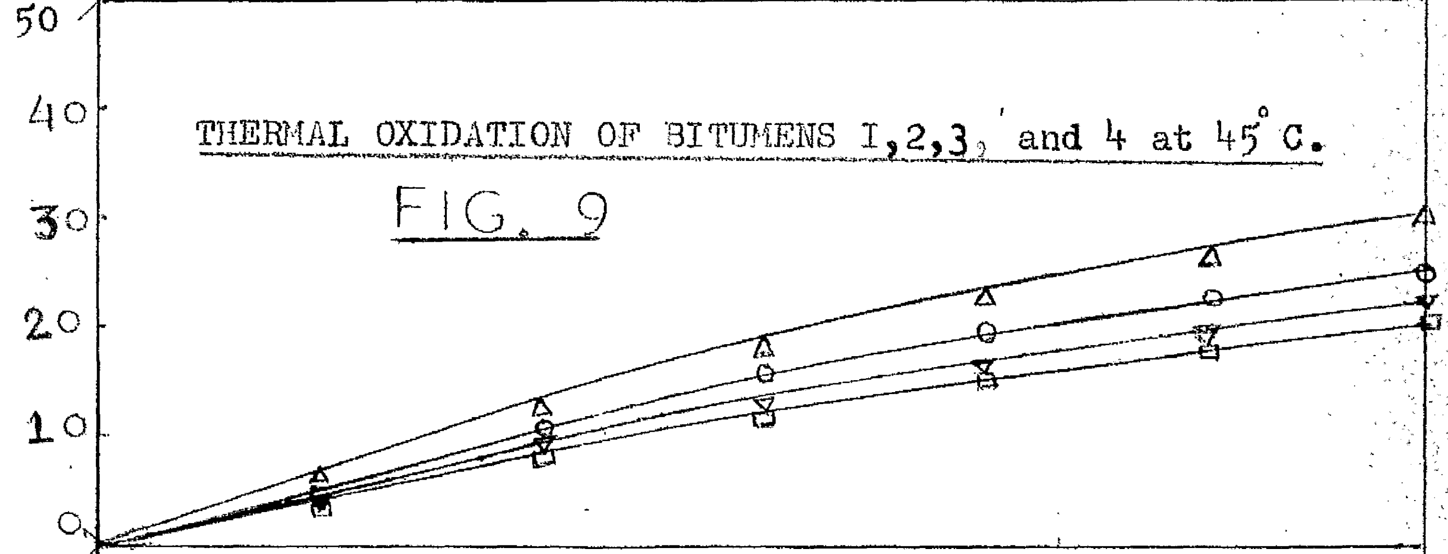
THE EFFECT OF PRESENCE OF XYLENE SOLVENT IN VARYING RATIOS ON THE RATE OF OXIDATION OF DIFFERENT BITUMENS AT 60 °C

Material	Wt of Material in mg	Ratio of Material to solvent	Rate of Oxidation cc/g/hr
Bitumen 1	500	1 : 1	1.2
Bitumen 2	"	"	1.3
Bitumen 3	"	"	1.6
Bitumen 4	"	"	1.2
Bitumen 1	500	1 : 2	1.3
Bitumen 2	"	"	1.3
Bitumen 3	"	"	1.7
Bitumen 4	"	"	1.2
Bitumen 1	500	1 : 3	1.4
Bitumen 2	"	"	1.4
Bitumen 3	"	"	1.6
Bitumen 4	"	"	1.3
Bitumen 1	500	1 : 4	1.4
Bitumen 2	"	"	1.3
Bitumen 3	"	"	1.7
Bitumen 4	"	"	1.2



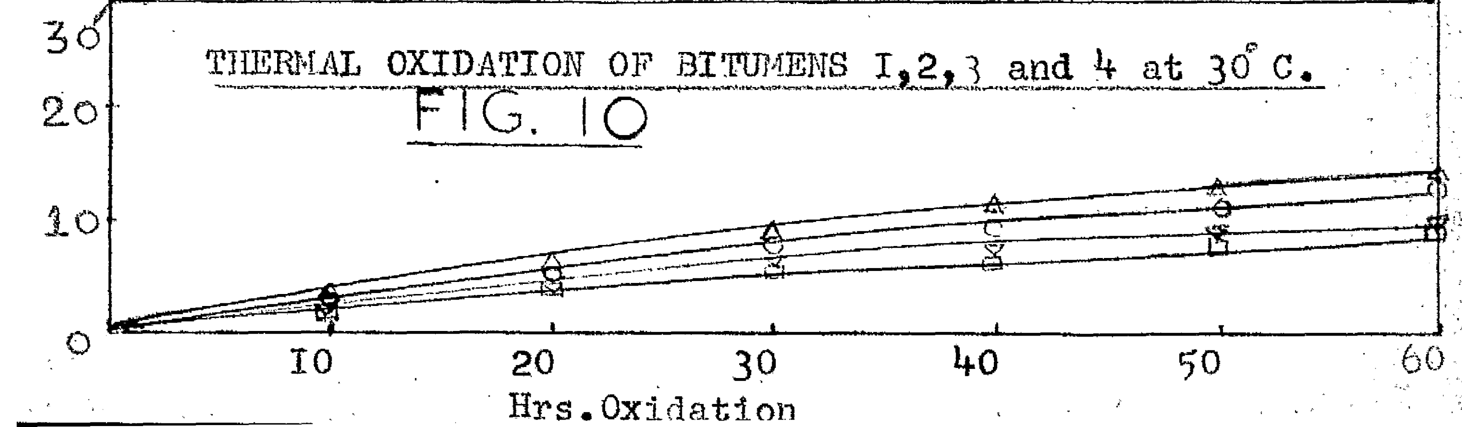
THERMAL OXIDATION OF BITUMEN I, 2, 3 and 4 at 60° C

FIG. 8



THERMAL OXIDATION OF BITUMENS I, 2, 3, and 4 at 45° C.

FIG. 9



THERMAL OXIDATION OF BITUMENS I, 2, 3 and 4 at 30° C.

FIG. 10

the four original bitumens at 60°C, 45°C and 30°C respectively. These curves are auto-retardent in character, i.e. the rate of absorption decreases with time. At the three oxidation temperatures Bitumen 3 (T.L.A.) shows a higher rate of oxygen uptake than the petroleum bitumens. Figure 11 shows the curves obtained for Bitumen 1 and its fractions on oxidation at 60°C. The curves are generally of the same shape but show variation in oxygen uptake. The order of reactivity is asphaltene, resins, dark oil and white oil in descending order. This indicates that the most reactive fraction is asphaltenes and the least reactive white oil. Similarly, the types of oxidation curves for Bitumen 2, 3 and 4 and their fractions at 60°C are represented in Figures 12, 13 and 14 respectively. These figures suggest similar reactivities for the various fractions of different bitumens.

Figures 15 - 18 show the types of curves observed on oxidation of the four bitumens and their fractions at 45°C. The type of curve is, in general, as before but, as expected, reactivities have diminished. Similar patterns are shown in Figures 19 - 22 for oxidation at 30°C again with a corresponding lowering of oxygen absorption.

Taking into account the reaction rates of each bitumen fraction and the fractional composition of the bitumens, theoretical oxygen uptake curves were plotted for each bitumen on the basis that bitumen could be represented by the sum of their component parts. These rates are shown in Figures 11 - 22 and are seen to be with the exception of Bitumen 1 close

FIG. 11

THERMAL OXIDATION OF BITUMEN I & ITS FRACTIONS AT60°C.

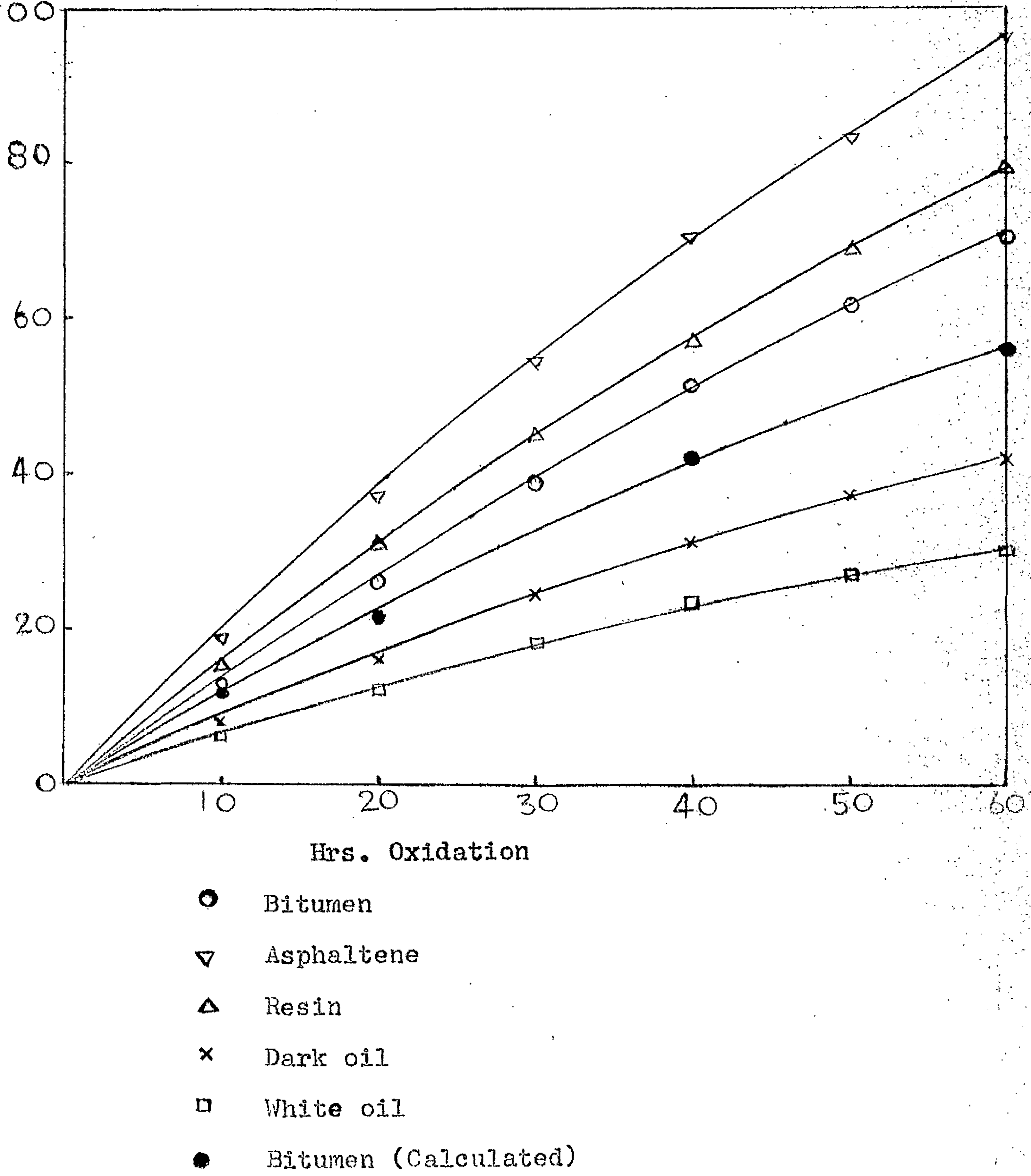


FIG. 12

THERMAL OXIDATION OF BITUMEN 2 & ITS FRACTIONS AT 60° C

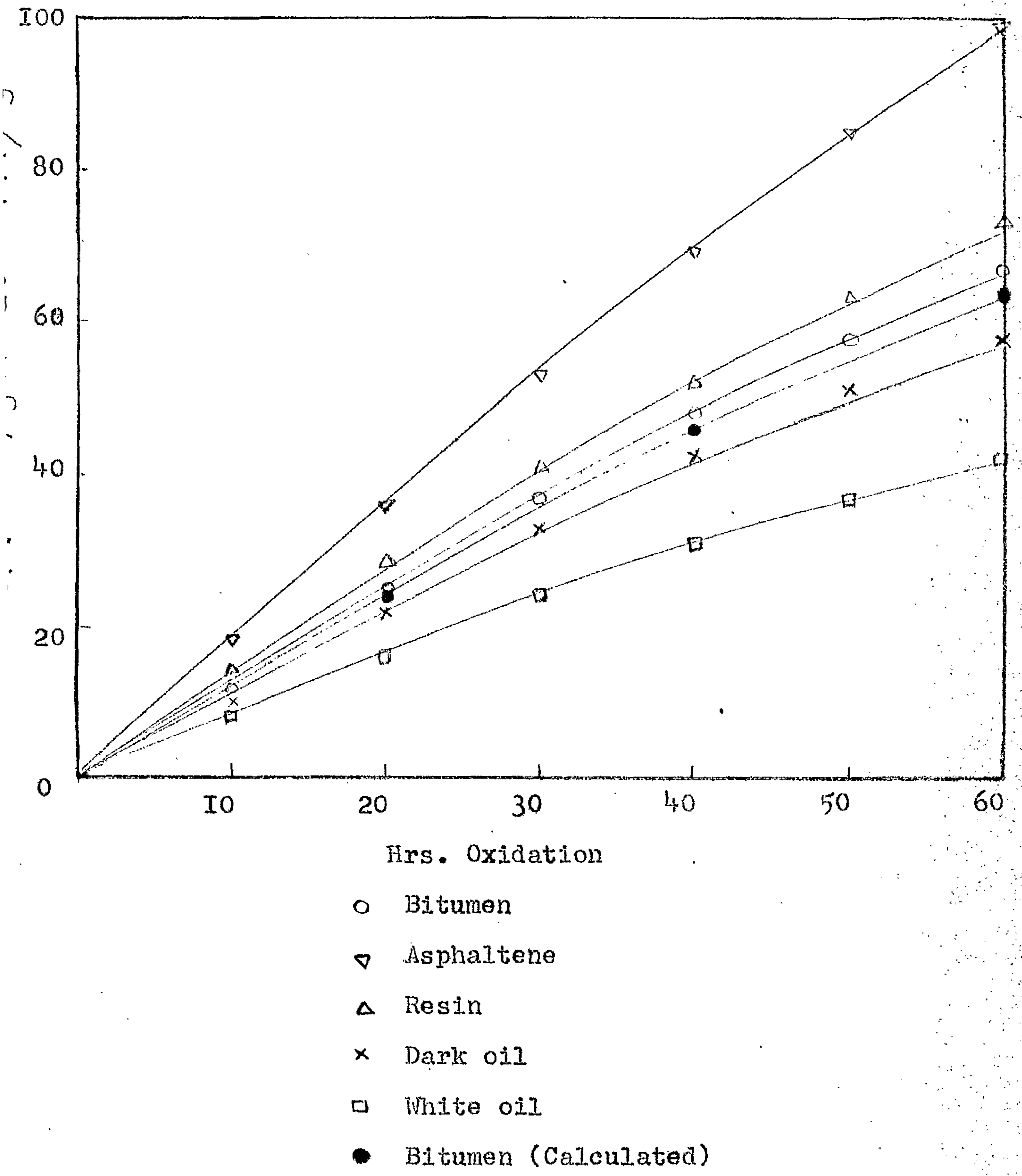


FIG. 13

THERMAL OXIDATION OF BITUMEN 3 & ITS FRACTIONS AT 60° C.

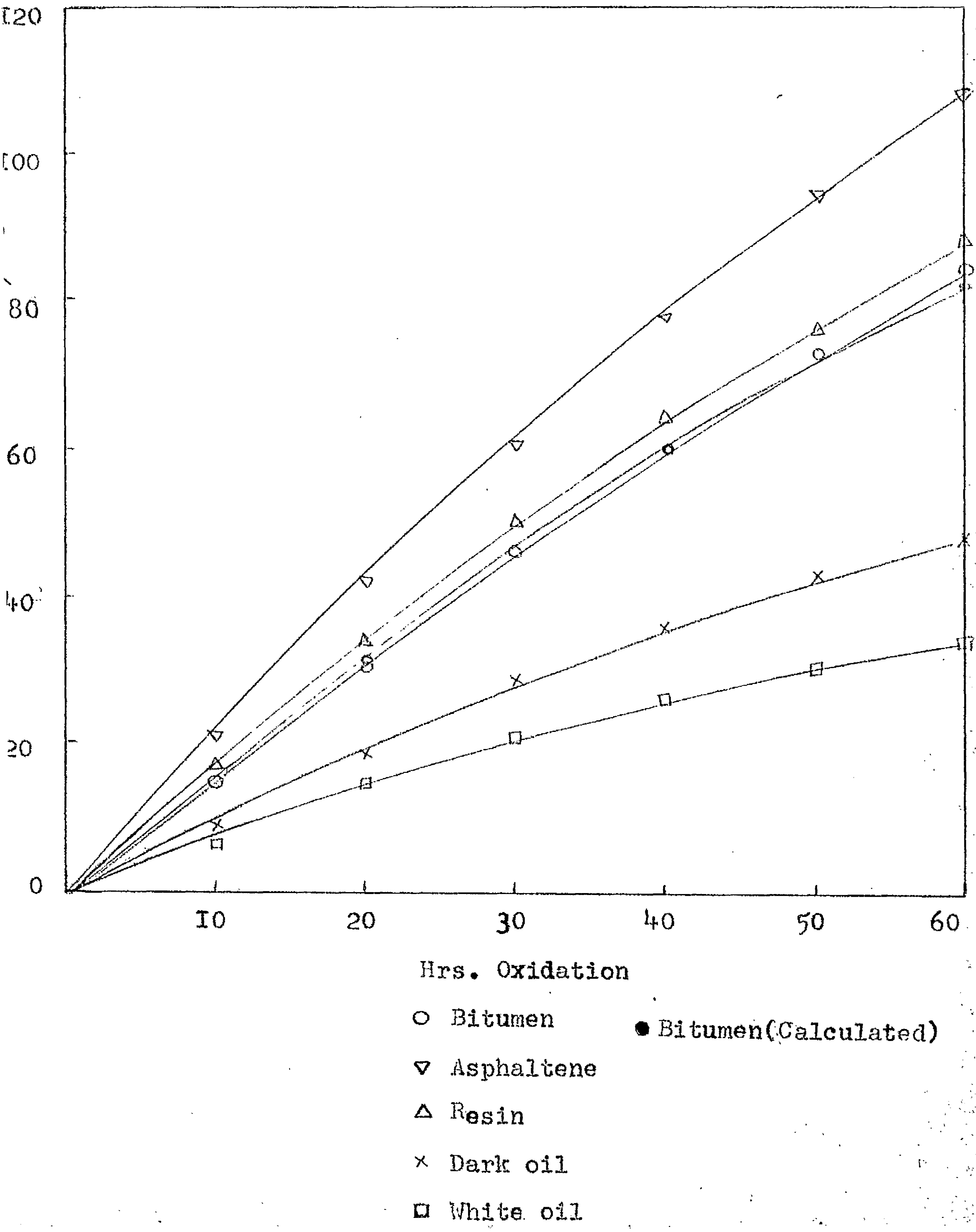
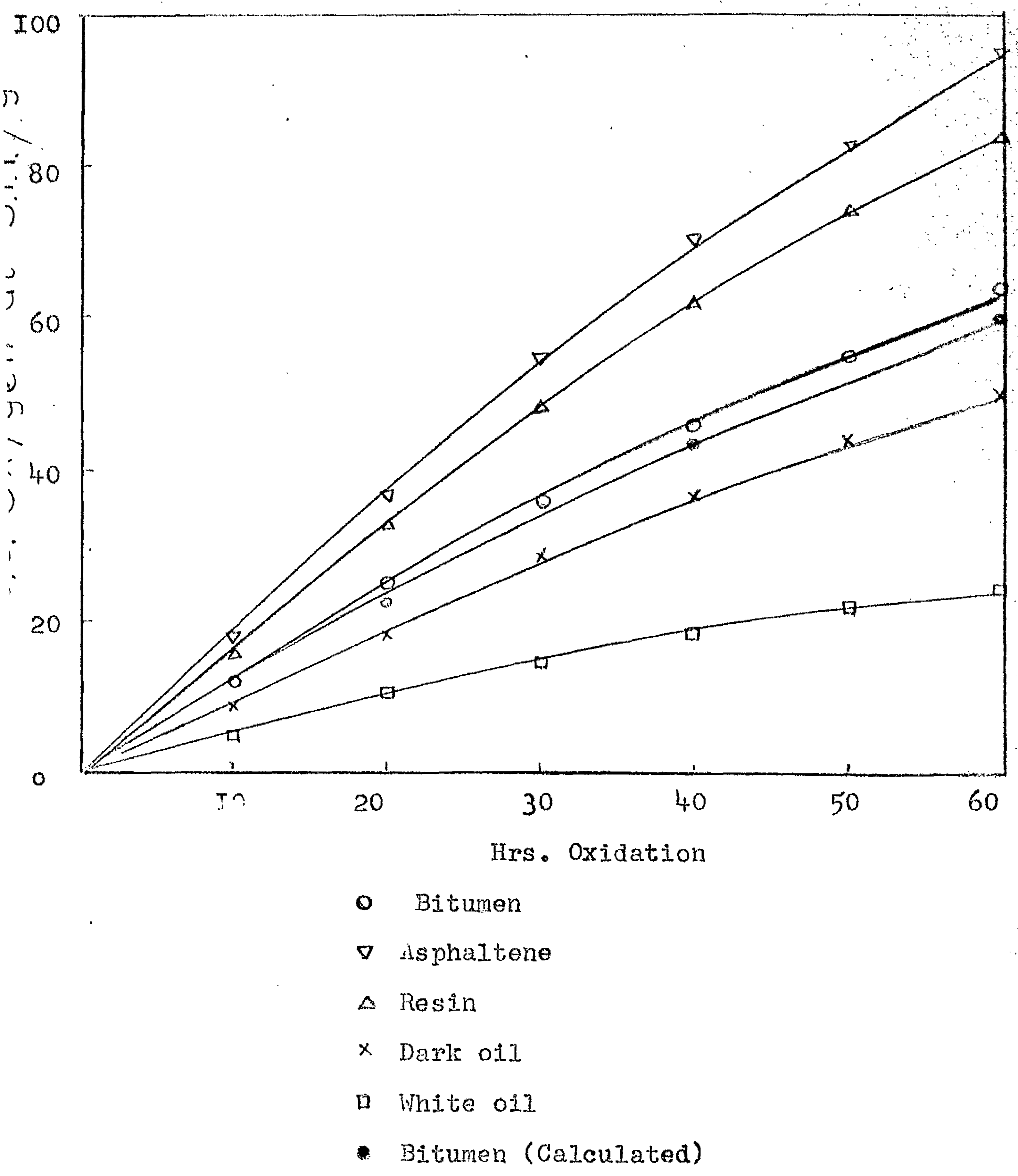
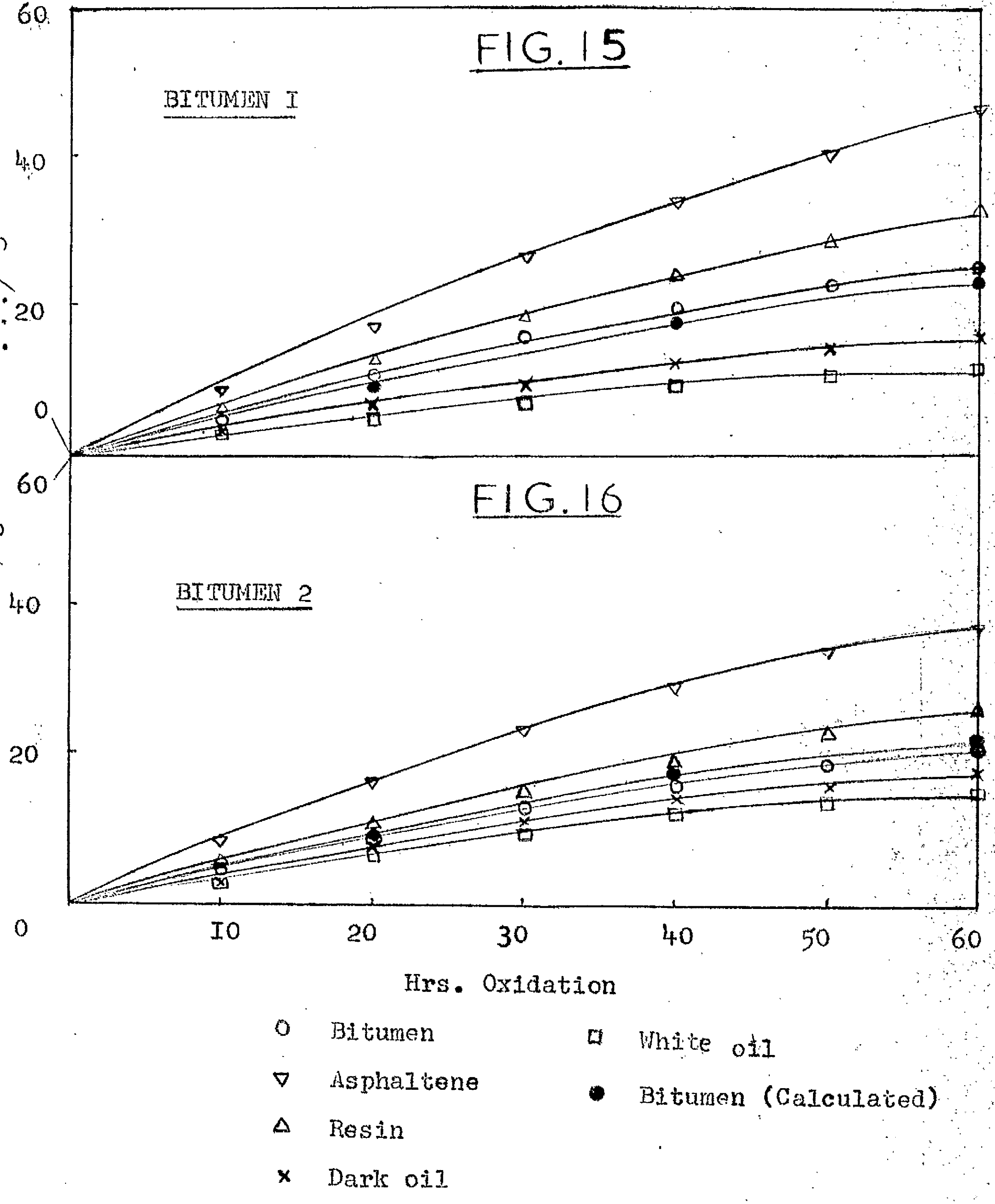


FIG 14

THERMAL OXIDATION OF BITUMEN4 & ITS FRACTIONS AT 60°C.



THERMAL OXIDATION OF BITUMENSI,2 & THEIR FRACTIONS AT 45° C.



THERMAL OXIDATION OF BITUMENS 3,4 & THEIR FRACTIONS AT 45° C.

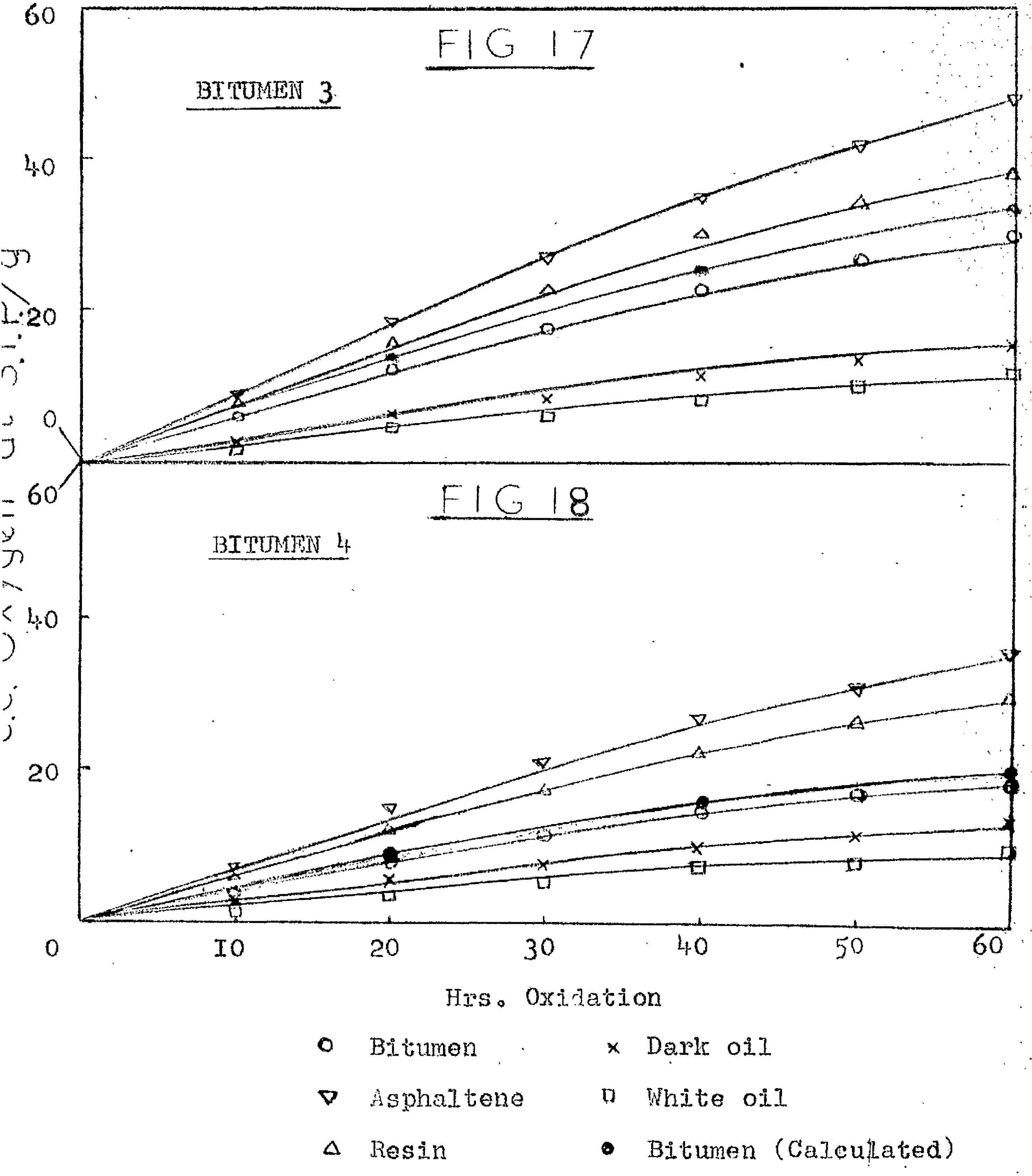


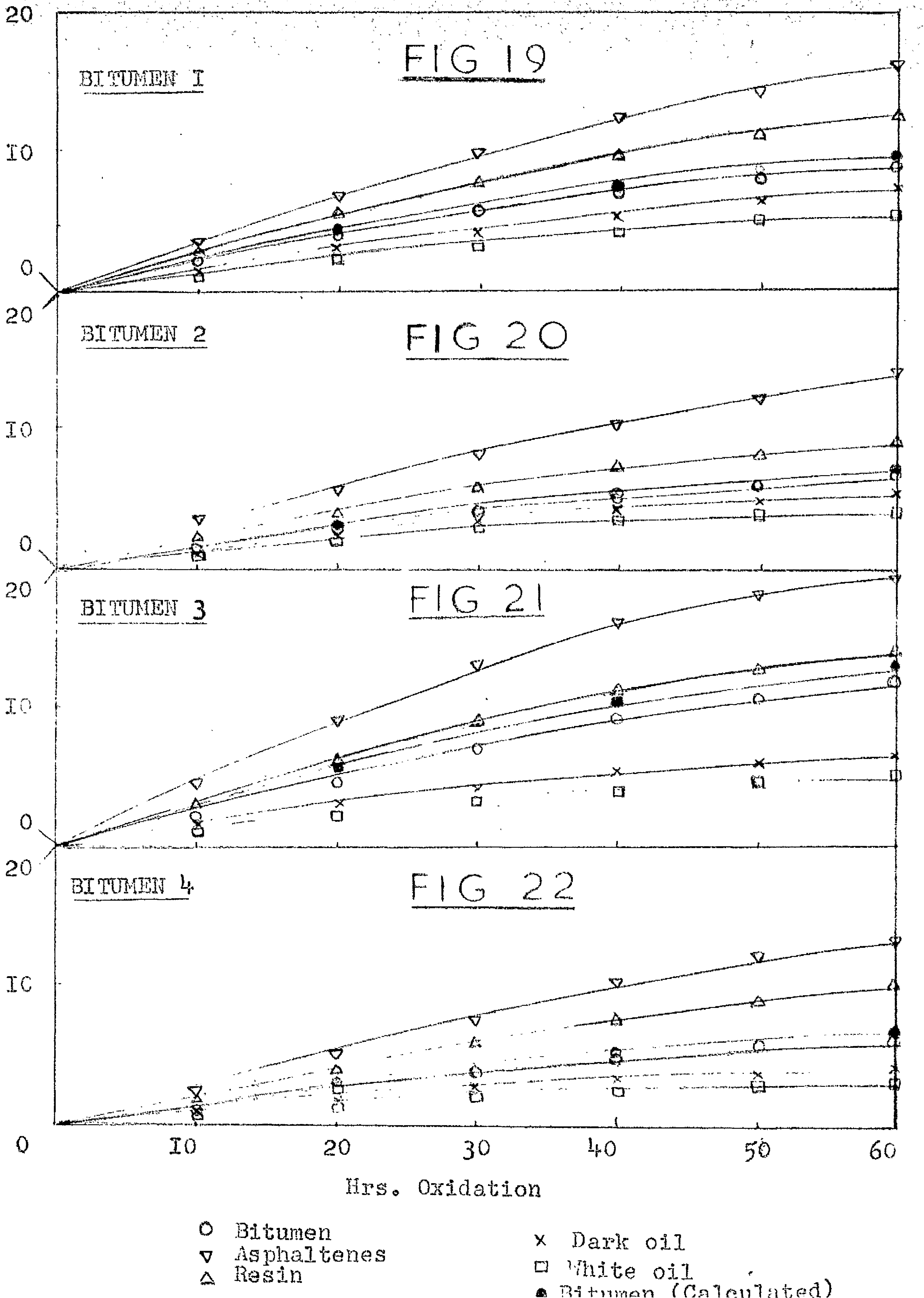
FIG 17

BITUMEN 3

FIG 18

BITUMEN 4

THERMAL OXIDATION OF BITUMENS I,2,3,4&THEIR FRACTIONS AT 30° C.



to the experimentally observed rates for the bitumens. This suggests that, on balance, individual reactivities of bitumen fractions are a fair representation of the way these fractions behave in a complete bitumen. No explanation can be advanced for the anomalous behaviour of Bitumen 1 but it may be connected to the fact that it contains appreciably more white oil than the others (Figure 3) and the low reactivities of this fraction may have some dominating effect in the synthetic blend.

3.8.1 - The effect of temperature on the rate of oxidation

As mentioned in Section 3, bitumen and fractions were oxidised at 60°C, 45°C and 30°C. Comparative rates of oxidation are tabulated in Table 8. This shows a relationship between oxygen uptake and temperature, the oxidation rate of 60°C being roughly about three times that at 45°C which is, in turn, about three times that at 30°C. Thus, every 15°C the thermal oxidation rate increases approximately by 3.

Bitumen 3 (Trinidad Lake Asphalt) shows a higher rate of oxidation than the refinery bitumens. It contains more than twice the asphaltene content of the other bitumens and it has also been shown that the asphaltene fraction has the highest reactivity of all the fractions. This appears to be a simple explanation of why Trinidad Lake Asphalt is so reactive and behaves so differently. To examine this point further, several synthetic bitumens were prepared and oxidised thermally at 60°C. This is described in Section 3.9.

OXIDATION RATES OF VARIOUS BITUMENS AND THEIR FRACTIONS AT 60°C, 45°C and 30°C

Description of sample	Rate of oxidation at 60°C (K_1)	Rate of oxidation at 45°C (K_2)	Rate of oxidation at 30°C (K_3)
Bitumen 1	1.24	0.42	0.13
White Oil	0.50	0.20	0.09
Dark Oil	0.68	0.27	0.12
Resin	1.33	0.55	0.22
Asphaltenes	1.60	0.77	0.27
Bitumen (calculated)	0.91	0.40	0.14
Bitumen 2	1.15	0.37	0.12
White Oil	0.70	0.25	0.07
Dark Oil	0.95	0.30	0.09
Resin	1.22	0.41	0.15
Asphaltenes	1.63	0.60	0.23
Bitumen (calculated)	1.07	0.37	0.12
Bitumen 3	1.42	0.50	0.17
White Oil	0.57	0.21	0.08
Dark Oil	0.80	0.27	0.11
Resin	1.47	0.63	0.20
Asphaltenes	1.81	0.80	0.17
Bitumen (calculated)	1.36	0.53	0.19
Bitumen 4	1.07	0.35	0.08
White Oil	0.40	0.17	0.05
Dark Oil	0.80	0.23	0.05
Resin	1.41	0.50	0.17
Asphaltenes	1.58	0.58	0.22
Bitumen (calculated)	1.00	0.35	0.09

Where K_1, K_2 and K_3 are cc of O_2 uptake/g sample/hr calculated at S.T.P.

3.8.2 - A study of the chemical changes on oxidation by infra-red spectroscopy

An attempt was made to study the changes caused by thermal oxidation of bitumens and their fractions using the infra-red spectroscopic technique. These are given in detail in appendix and discussed fully later.

3.8.3 - Determination of overall activation energies of bitumens

The oxygen absorption of four bitumens at 30°C, 45°C and 60°C were measured and the rate of oxygen absorption, designated as K, was calculated; K is expressed in cc of O_2/g of bitumen/hr. The values of log K and $\frac{1}{T}$ are shown in Table 9 and plotted in Figure 23.

The velocity constant (K) is given by the Arrhenius equation as:

$$K = Ae^{-E/RT}$$

Where
A is the frequency factor
E is the energy of activation
R is the gas constant
T is the absolute temperature.

The logarithmic form of above equation is:

$$\log K = \log A - \frac{E}{2.303\, RT}$$

and this equation shows a linear relationship between log K and $\frac{1}{T}$ the slope being $-^{E}/2.303\ R$ and the intercept on the log K axis is log A. The activation energy from this relationship can be calculated as follows:-

e.g. Bitumen 1:

$$\text{Slope} = \frac{0.7}{0.217 \times 10^{-3}}$$

$$\text{i.e. } \frac{-E}{2.303\,R} = \frac{0.7}{0.217 \times 10^{-3}}$$

$$\therefore\ E = \frac{2.303 \times 2 \times 0.7}{0.217 \times 10^{-3}}$$

$$= 14850 \text{ cals/mole}$$

$$= 14.85 \text{ K cals/mole}$$

the overall activation energies of other bitumens and fractions are calculated similarly and represented in Table 10.

Kolbanovskaya, et al(12) most recently studied the relationship between the aging and the structure type of bitumens of varying activation energies. According to them the coagulation structure type bitumen (except the bitumen from thermal cracking) with high activation energy (15.20 K cal/mole) on heating at 40-120°C showed no change in asphaltene contents, while the condensation structure type bitumen with low activation energy (2 - 4 K cal/mole) showed asphaltene formation at 40°C, which increased with temperature. The mixed structure bitumen with activation energy (8 - 12 K cal/mole) showed asphaltene formation at 120°C. Bitumens with coagulation structure were more stable at low temperatures, whilst those with condensation structure were more stable at high temperatures (160°C). They suggested that condensation type bitumens with mixed structure would be most suitable for road asphalts.

Thus, it could be seen that activation energy of bitumen could be used in assessing as a road binder. On this basis Bitumen 3 (T.L.A.) falls on the line of mixed structure type bitumen, the most suitable as a road binder.

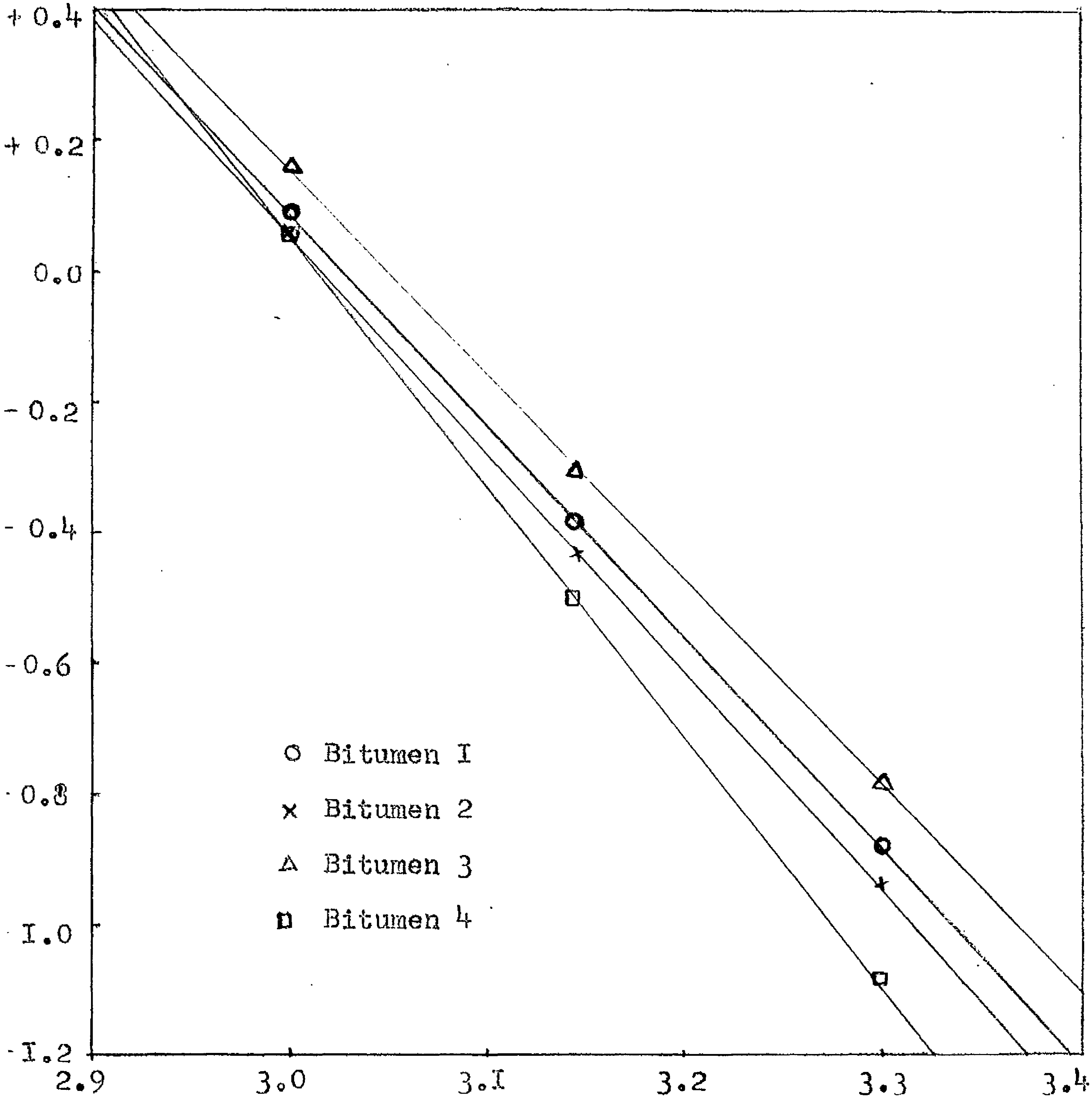
Other low grade bitumens could also be modified to desired type by either blending with suitable bitumens or their fractions.

TABLE 9

Bitumen number	cc O_2/g/hr K	log K	T °K	$\frac{1}{T}$ °K x 10^{-3}	Energy of activation k cal/mole
1	0.133	-0.8762	303	3.300	14.85
	0.417	-0.3796	318	3.144	
	1.240	0.0930	333	3.000	
2	0.166	-0.9356	303	3.300	14.99
	0.370	-0.4318	318	3.144	
	1.150	0.0607	333	3.000	
3	0.170	-0.7696	303	3.300	13.97
	0.500	-0.3010	318	3.144	
	1.420	0.1523	333	3.000	
4	0.083	-1.0810	303	3.300	17.60
	0.350	-0.4560	318	3.144	
	1.170	0.0682	333	3.000	

FIG. 23

TEMPERATURE DEPENDENCE OF CALCULATED REACTION CONSTANT FOR BITUMENS I,2,3 and 4.



$\frac{I}{T} \times I0^{-3} \,^{\circ}K$

TABLE 10

OVERALL ACTIVATION ENERGIES OF BITUMENS AND THEIR FRACTIONS

Description of sample	Energy of activation k cal/mole
Bitumen 1	14.85
White Oil	15.65
Dark Oil	13.15
Resin	12.79
Asphaltenes	12.28
Bitumen 2	14.99
White Oil	16.04
Dark Oil	15.35
Resin	13.64
Asphaltenes	12.28
Bitumen 3	13.97
White Oil	14.16
Dark Oil	14.16
Resin	12.28
Asphaltenes	11.51
Bitumen 4	17.60
White Oil	18.71
Dark Oil	16.74
Resin	13.64
Asphaltenes	13.15

3.9 - The thermal oxidation of synthetic bitumens

In order to examine further the relationship between composition and properties, a series of synthetic bitumens was prepared. Each of the four original bitumens was separated into asphaltenes and maltenes as described under Chapter 2, by fractional precipitation using 30-40°C petroleum spirit. The asphaltenes were dissolved in methylene chloride and added to the maltene fraction. This was stirred to give a homogenous solution and the solvent removed under vacuum. In this way several synthetic bitumens were prepared, each containing different amounts of asphaltenes shown in Table 11.

These bitumens were oxidised at 60°C as before and the oxygen uptake plotted against the time of oxidation. Figures 23 - 26 show the result obtained by the four different groups of synthetic bitumens. The composition of these bitumens and their respective rate of oxidation are given in Table 11.

3.9.1 - Discussion

From the Figures 24 - 27 and Table 11 it is clear that the rate of oxidation of the synthetic bitumens increases with increasing asphaltene content. The only asphaltene content common to all four bitumens is 15% (in view of the higher asphaltene content of T.L.A.) and at this level the oxidation rates are surprisingly very similar. One of the important factors determing the relationship between composition and properties of a bitumen is the dissolving power of the oil components which is related directly to the contents of oil aromatics in the respective bitumens. Bitumens in the synthetic series containing lower amounts of asphaltene were more homogenous than the high asphaltene content bitumens. On examination under a microscope for homogeneity, low asphaltene content bitumens showed good dispersion of the asphaltenes whereas materials with higher asphaltenes showed lower dispersion. This lower dispersion seems to have had little effect on the increasing oxygen uptake when measured against asphaltene content and when it is seen in Figures 24 - 27 that the synthetic bitumens to the original composition fall on the same curves as the original bitumens. Due to the complexity of bitumen oxidation the results cannot easily be expressed mathematically. The absorption of oxygen does not depend entirely on the weight of the sample but also on the area exposed to the oxygen: in this thermal oxidation work these factors have been kept constant by virtue of the use of solutions. It is evident from the above results that asphaltene content is an important factor in the overall reactivity of bitumens. Study of Table 11 indicates that the components of different bitumens lie in the same order of reactivity for each particular bitumen and are not so very different from similar fractions from the other bitumens. This suggests that bitumens may differ in dark oxidation reactivity more by the amounts of each fraction than by any major difference between reactivity of fractions.

TABLE 11

COMPOSITION & RATE OF OXIDATION OF ORIGINAL & SYNTHETIC BITUMENS AT 60°C

Designation of Bitumens	Asphaltenes %	Maltenes %	Oxidation rate at 60°C c.c. o2/g/hr
Bitumen 1 A (original)	20	80	1.21
Synthetic Bit:A 1	5	95	0.95
" " A 2	10	90	1.05
" " A 3	15	85	1.13
" " A 4	20	80	1.20
Bitumen 2 B (original)	20	80	1.18
Synthetic Bit:B 1	5	95	0.97
" " B 2	10	90	1.03
" " B 3	15	85	1.15
" " B 4	20	80	1.18
Bitumen 3 C (original)	57	43	1.41
Synthetic Bit:C 1	15	85	1.10
" " C 2	30	70	1.23
" " C 3	45	55	1.30
" " C 4	57	43	1.40
Bitumen 4 D (original)	20	80	1.11
Synthetic Bit:D 1	5	95	0.87
" " D 2	10	90	0.97
" " D 3	15	75	1.03
" " D 4	20	80	1.10

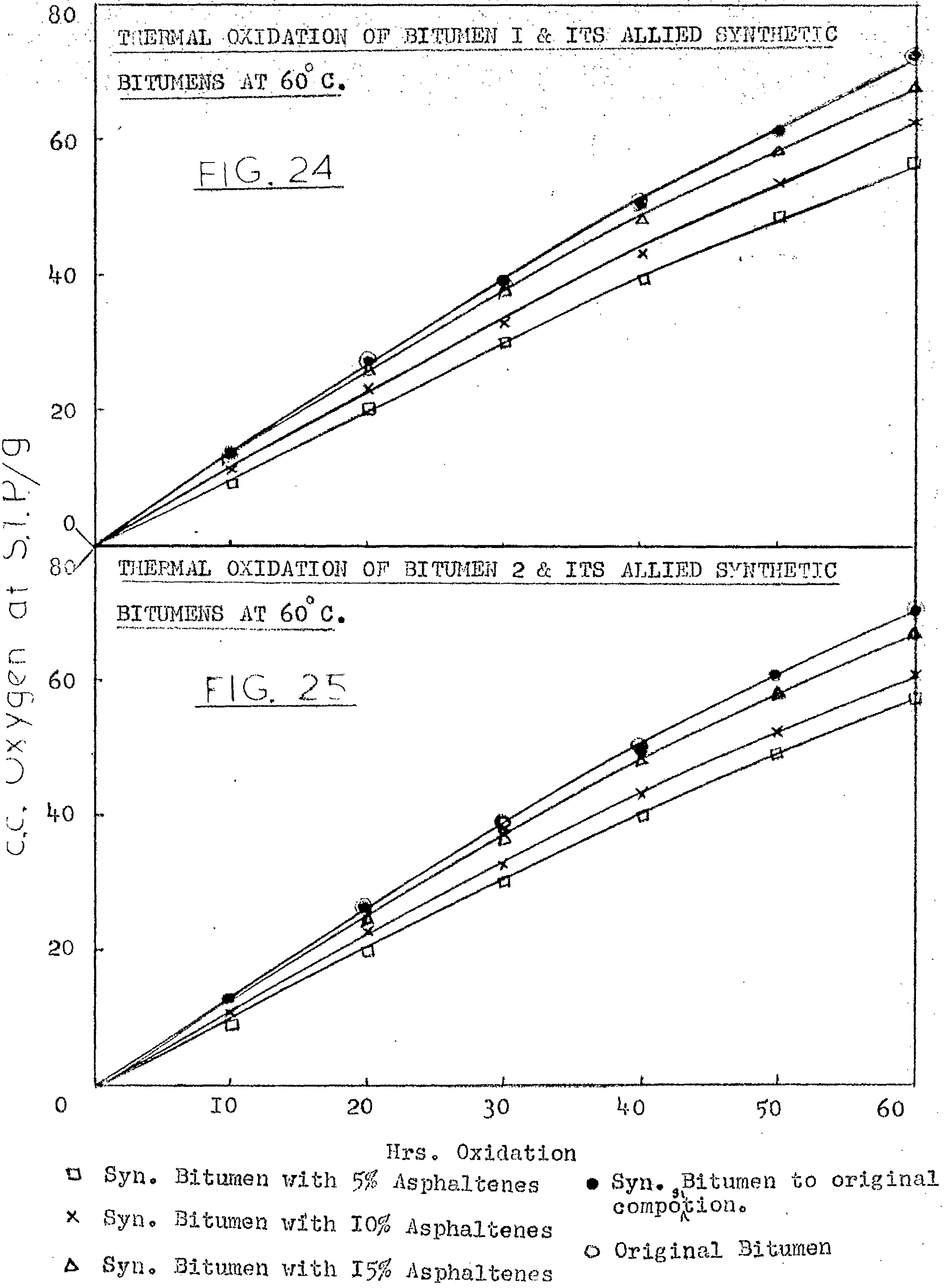


FIG. 24

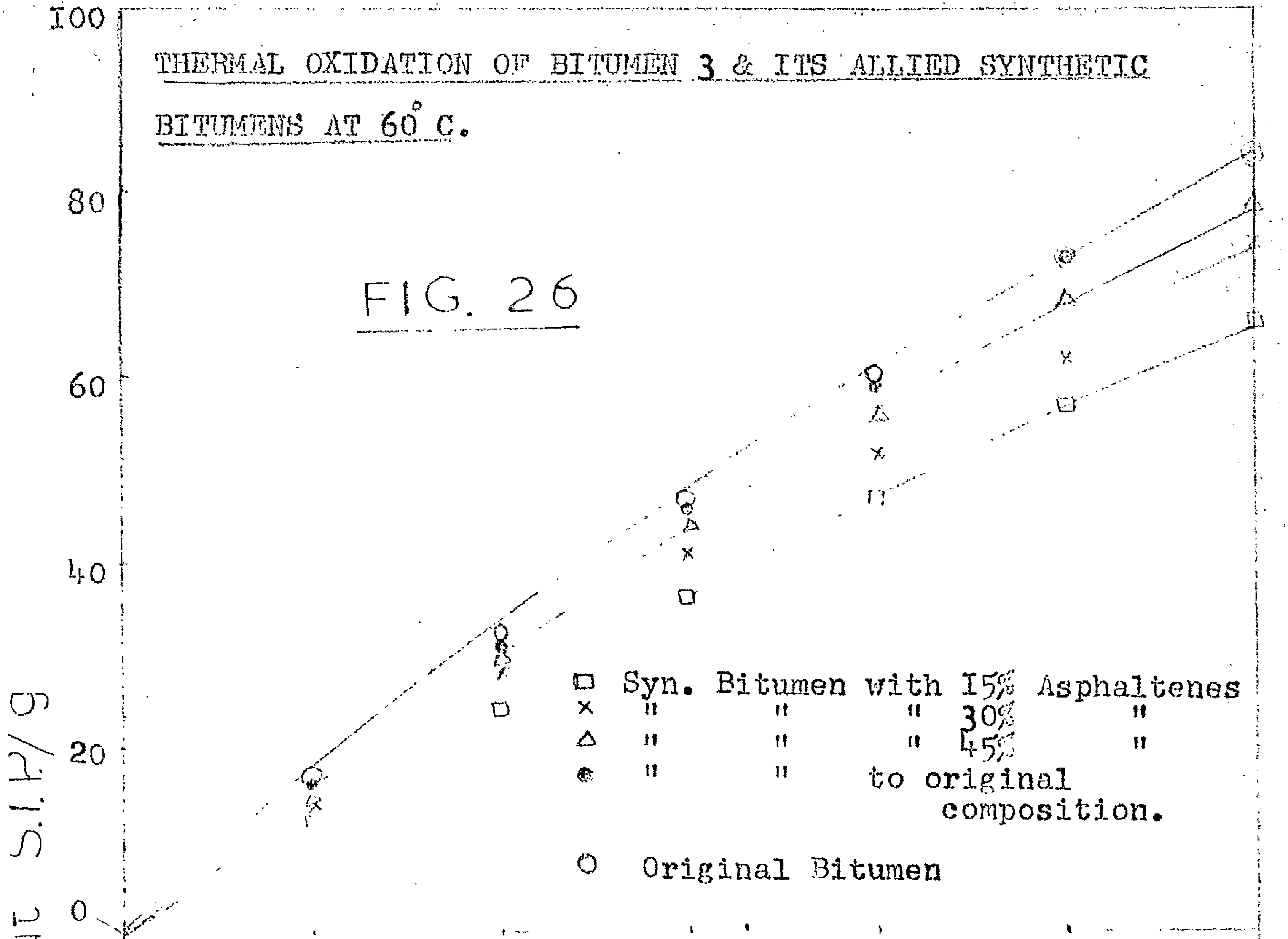
THERMAL OXIDATION OF BITUMEN I & ITS ALLIED SYNTHETIC BITUMENS AT 60°C.

FIG. 25

THERMAL OXIDATION OF BITUMEN 2 & ITS ALLIED SYNTHETIC BITUMENS AT 60°C.

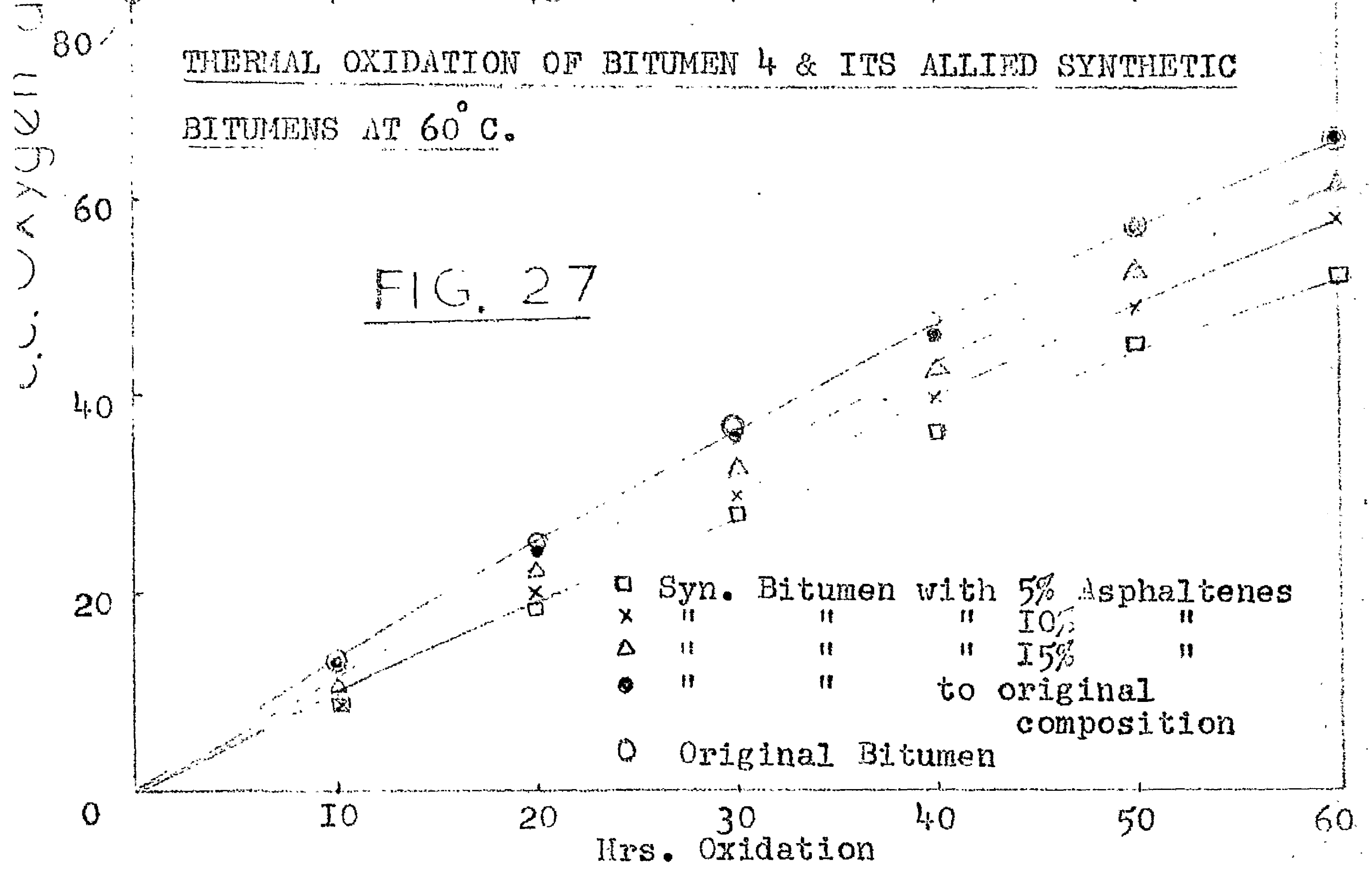
THERMAL OXIDATION OF BITUMEN 3 & ITS ALLIED SYNTHETIC BITUMENS AT 60° C.

FIG. 26



THERMAL OXIDATION OF BITUMEN 4 & ITS ALLIED SYNTHETIC BITUMENS AT 60° C.

FIG. 27



CHAPTER 4

THE PHOTO-OXIDATION OF BITUMENS AND THEIR FRACTIONS

4.1 - Accelerated weathering apparatus

4.2 - Development of photo-oxidation apparatus

4.3 - Experimental procedure

4.4 - Results and discussion

4.5 - The formation of water-soluble products of oxidation on irradiation of bitumens and bitumen fractions

4.6 - A study of the water-soluble degradation products of photo-oxidised petroleum bitumens and Trinidad Lake Asphalt

4.7 - Sensitised photo-oxidations

4.8 - The effect of irradiation on skin formation

4. THE PHOTO-OXIDATION OF BITUMENS AND THEIR FRACTIONS

It is well known that petroleum bitumens when used in dense road materials, tend to produce surfacings of relatively low skid resistance. Materials containing Trinidad Lake Asphalt on the other hand, produce a rougher texture, this is often attributed to the more rapid hardening of the binder film concentrated at the surface, with subsequent exposure of fine aggregate by traffic abrasion. The development of pitch-bitumen as a satisfactory binder for rolled asphalt confirms to some extent that a binder more susceptible to oxidation will give improved skid resistance.

Bitumens on exposure to sunlight or artificial ultra-violet light undergo physical and chemical change. Bitumens coatings do not undergo appreciable deterioration during long periods in the dark but rapid surface changes occur on exposure to light. Vojtech(100) studied as early as 1906, the action of light on bitumens in presence of hydrogen, nitrogen, carbon dioxide, oxygen and air. In the presence of oxygen considerable absorption of the gas was noted and the amount of absorption depended on the intensity of light. The oxidised bitumen surface became insoluble in oil of turpentine. In the presence of nitrogen, hydrogen and carbon dioxide no absorption was noted. Hubbard and Reeve(101) showed the influence of exposure on bitumens confirming that hardening was not only due to volatilisation but also due to oxidation, which proceeded slowly at low temperatures and increased at high temperatures.

Rosinger(102) studied the action of light on thin films of bitumens and found that on exposure the bitumen surface became insoluble in benzene, chloroform and other solvents. He also showed the effect of photosensitisers on bituminous surfaces in the presence of light and concluded that the sensitivity to light and heat was increased. Reeve and Lewis(103) studied the effect of exposure on bitumens and concluded that polymerisation occurred in the presence of atmospheric oxygen due to the accelerating effect of heat and light on intermolecular reactions. Errera(104) showed that the colloidal state of bitumen is mainly responsible for its sensitivity to light. Sunlight seems to have a coagulating effect which decreases the solubility of bitumens in solvents. Benson(18) exposed thin films of bitumen to infra-red and ultra-violet light in the atmospheres of oxygen, air and carbon dioxide respectively. He examined microscopically the changes termed as film coagulation and concluded that the presence of air and oxygen accelerated coagulation whereas carbon dioxide retarded coagulation.

The weathering of bituminous coating of 0.5 mm films on steel plates was studied by Pfeiffer(106) with the conclusion that ultra-violet and atmospheric oxygen bring about oxidation and polymerisation which lead to the formation of a hard, shrinking skin on the exposed surface; quick temperature changes then cause sudden internal tensions which produce cracks. Thurston(107) studied the effect of accelerated weathering on the synthetic bitumens prepared by combining the resin, asphaltenes and oil fractions in various proportions. He concluded that resistance to weathering increased with resin contents. Higher proportions of asphaltenes or oil led to reduced resistance. Corbett and Swarbrick(58) studied the relation of asphalt composition to weathering and concluded that the aromatic oils tend to increase weathering resistance and paraffins + naphthenes have the opposite effect.

Thurston and Knowles(26) studied the photo-oxidation of bitumens and their fractions by exposing samples in oxygen filled sealed pyrex containers under a sun lamp (Mazda S-1) at about 77°C. All constituents absorbed oxygen, the resin and naphthenic oil fractions being a little more readily oxidised. Part of the used oxygen was eliminated as water and carbon dioxide and all the residues showed a weight increase. Weetman(109) studied the effect of variables such as temperature, light intensity, wavelength of light, etc., on the bitumens using an 'Atlas weatherometer'. He found that temperature was of vital importance and elimination of ultra-violet by filters decreased the weathering.

Leroux(111) summarising his fifteen years work in France, showed that the aging process was due to evaporation and oxidation. He also showed that bitumens were very sensitive to ultra-violet and visible radiation but less sensitive to radiation of longer wavelength. Tars on the other hand were most affected by infra-red radiation and less sensitive to shorter wavelengths.

Kleinschmidt and Snoke in their weathering study of bitumens concluded that the white oil and dark oil progressively decreases its refractive indices on longer exposures. Greenfeld(34) showed similar changes in the refractive index, C:H ratio and the degree of unsaturation of dark oil and white oil fractions separated from bitumens at various stages of aging.

The absorption of oxygen by thin films of bituminous road binders in the presence of radiation from a high pressure mercury arc was studied by Dickinson et al(33). They found that irradiation of the thin film of bitumen with light in the wavelength range 3000-5000 °A produced a marked acceleration of the reaction forming a hard skin on the surface of the binder. The effective depth of penetration of the light reaction was probably only about 10 µ.

Sparlin(40) studied the effect of ultra-violet light on thin films of bitumen in the absence of atmospheric oxygen and found that viscosity of the bitumen film increased suggesting that ultra-violet energy is capable of hardening bitumen even without oxidation. Gallaway(45) also showed that bitumen films exposed to artificial light in the absence of oxygen had a higher viscosity than unexposed samples.

More recently, Campbell, Wright and Bowmen(29) inevestigated the effects of temperature on the rate of oxidation and the time required to produce film cracking under controlled weathering conditions using a weatherometer. The oxidation rates were determined by measuring the changes produced in the infra-red spectra at 5.88 µ (carbonyl band). They concluded that the time required to cause film failure due to cracking varied inversely with temperature and the oxidation rate varied directly with temperature. Greenfeld and Wright(134) also studied the change in absorption of the carbonyl band due to carbon-arc exposure of bitumens in an accelerated weathering machine.

Prolonged natural weathering of three bitumens was studied by Stewart(113) who showed that on subsequent chromatographic separation, the C/H ratio of the various fractions decreased whilst oxygen content increased. Heithaus(30) studied the relationship between weather resistance and the viscosity of the maltene phase of bitumen. He found bitumens with maltenes of high viscosity were most weather resistant and suggested that hardening of bitumen is largely diffusion controlled. A high viscosity intermicellar liquid provides greater hindrance to diffusion, slowing down the hardening process.

Martin(32) in his studies on durability of roofing bitumens showed that bitumens on exposure to air and to solar radiation oxidise much more rapidly than in the dark (about 200 times). The reaction is confined to the surface, which may crack and expose new surface. He also showed the relationship of viscosity change with oxidation rates, showing that softer bitumens harden more rapidly during initial exposure but that hardening rates soon become similar for hard and soft grades. He also showed that water immersion does not influence the hardening rate of bitumen films but variation in humidity during oxidation may influence the rate of reaction. This agrees with Campbell(29) and other workers findings.

Tajima and Fushima(43) showed the relationship on a qualitative basis between the results of four years outdoor exposure tests of bitumen films and the results of accelerated weathering tests. Skog(105) also showed co-relationship of the actual performance of bitumens on roads and results obtained by a weatherometer.

Labout and van Oort(108) developed and used a microviscometer to measure the hardening of bitumens caused by exposure to weathering conditions. They showed that the mechanical properties changed due to atmospheric exposure were restricted to a surface layer of a few microns thick. They also showed that in the presence of daylight bitumens hardening occurs at room temperature and in absence of light at 40°C.

Change in characteristics (penetration and ductility at 77°F) of bitumens in pavements under natural weathering conditions for a period of five to ten years was shown by Shattuck(110).

4.1 - Accelerated weathering apparatus

The weatherometers available at present are very costly and the reproduction of natural condition is doubtful. The development of an exposure cycle giving correlation with actual exposures for any particular climatic region is very difficult and involved. It was, therefore, proposed that a simple apparatus would be used with no real attempt made to simulate natural weather cycles.

4.2 - Development of photo-oxidation apparatus

This apparatus consisted of the following items:

(1) Cylindrical aluminium holder.

(2) Medium pressure mercury arc tube.

(3) Light intensity stabiliser.

(4) Air extractor to control the temperature of the system.

(5) Reaction flasks and beakers.

Aluminium holders

This consisted of an aluminium cylinder 2' in length and approximately 2' in diameter with two rows of ½" diameter holes round the base of the cylinder. An aluminium reflector plate (1' diameter) was placed horizontally just inside the cylinder top and was held in position by four threaded rods. This provided light reflection on samples and also acted as a holder.

Medium pressure mercury arc tube

The source of radiation was a U-shaped medium pressure mercury arc tube (U.V. S500 Hanovia Lamp), suspended from the reflector. This tube operates at an initial input of 3.4 amps/135 volts; 380 watts. This generated the characteristic medium pressure mercury arc, extending from 1849 °A in the far ultra-violet up to 17193 °A in the infra-red. The visible radiation is mainly concentrated into the lines 4358 °A (Violet), 5416 °A (Green) and 5770/90 °A (Yellow). The wavelengths of photo-chemical importance lie, however, mainly in the short visible and ultra-violet regions, i.e. from about 2000 °A to 8000 °A wavelength.

Light intensity stabiliser

The intensity stabiliser maintains the output of the tube at a reasonably constant intensity for an operating life of about 1000 hours. By adjustment at specified intervals the output of the tube is stepped up by increments just sufficient to offset the inherent aging loss.

Air extractor

The cylinder was placed beneath a fume extracting hood with a high throughput fan. By the use of baffle plates set against the double row of holes in the cylinder base the air flow over the plates could be controlled and a reasonably constant sample temperature maintained. For this purpose thermometers were placed inside the cylinder.

Reaction flasks and beakers

The flasks used in this work were similar to those used for thermal oxidation and described in 3.4.4. Beakers used were 100 mls capacity with 2" bottom diameter.

The complete apparatus is shown in Figure 28.

4.3 - Experimental procedure

Photo-oxidation of thin films of bitumens and bitumen fractions was designed so that (1) the rate of oxygen uptake of the films could be measured and (2) the amount of water soluble degradation products could be determined and the skin produced on irradiation examined.

FIG. 28.

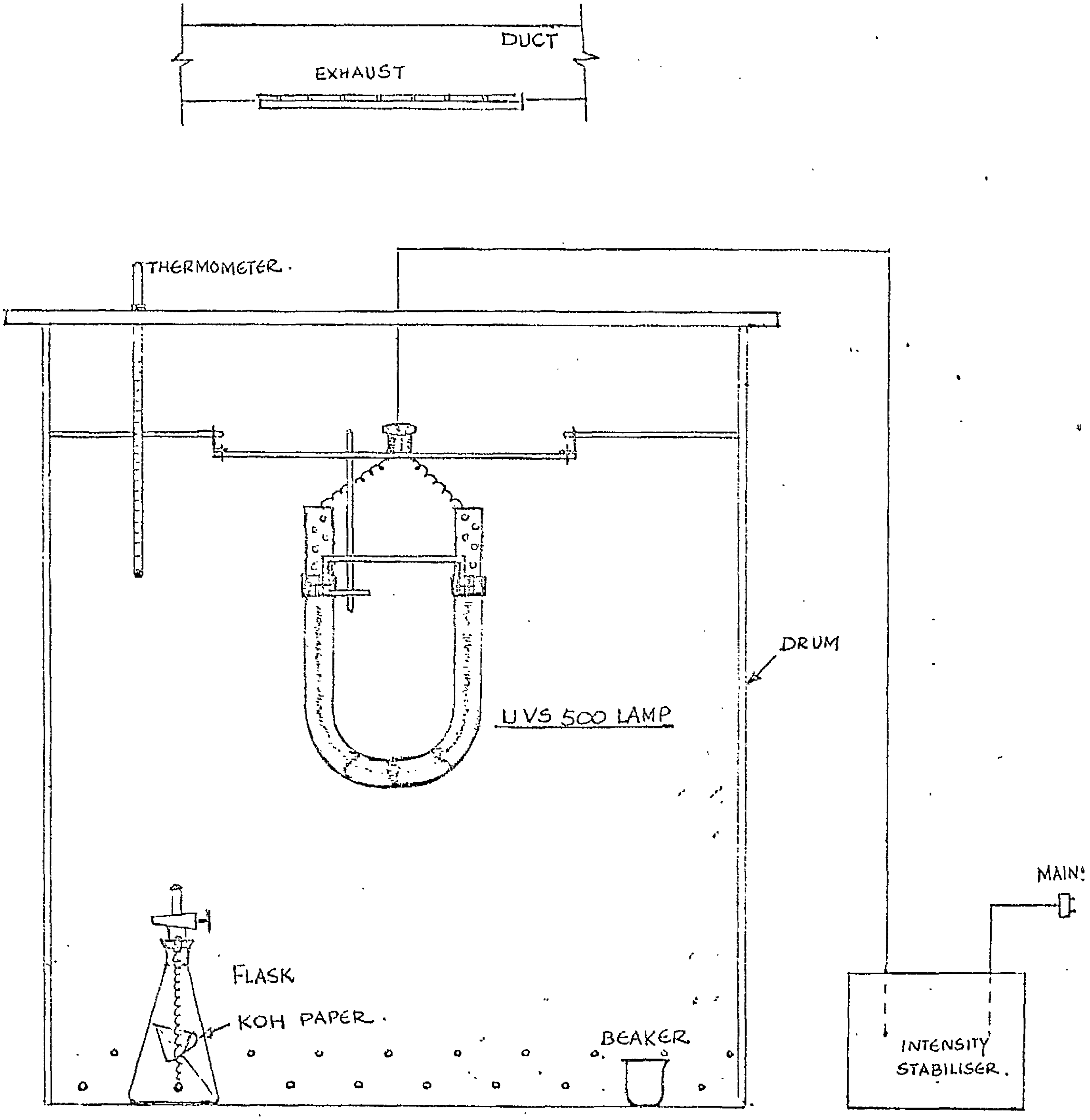


PHOTO OXIDATION APPARATUS

4.3.1 - Preparation of thin films

Films preparation was first attempted by depositing bitumens and bitumen fractions from a methylene chloride solution but it was found difficult to evaporate the solvent completely from viscous liquids. However, the method was satisfactory for preparation of asphaltene films. It was also found difficult to use a brush for making uniform films. It was also found difficult to use a spray for making uniform films. Films were then produced by putting 2 g of bitumen and the liquid fractions in the flasks and placing them on a levelled glass plate under an infra-red lamp for half an hour. The contents of the flask softened and spread on the bottom forming a uniform film.

4.3.2 - Filling the flasks

Reaction flasks were filled with oxygen as described under 3.7.1. The temperature of the flasks was maintained at 25°C by placing them in a thermostatically controlled water bath for 30 minutes and the stopcocks were vented to air to bring the pressure in the flasks at atmospheric.

4.3.3. - Setting the experiment

During the oxidation run the flasks were placed inside the apparatus equidistant from the u.v. lamp near the wall of the drum as shown in Figure 28. Skin formation started inside the flask at about 20 hours. The oxidation cycle for measuring O_2 uptake was initially 20 hours as this was convenient.

4.3.4 - Measurement of oxygen absorption

Oxygen uptake by the thin films was measured by a Warburg manometer as described under 3.7.2. Oxygen uptake by these films after 40 hours was approximately double that absorbed at 20 hours, so for convenience, readings were taken every 40 hours during subsequent work.

4.4 - Results and discussion

4.4.1 - Repeatability of the absorption measurements

In order to check for repeatability three films of Bitumen 1 were prepared and photo-oxidised as described under 4.3.3. The first readings at 20 hours gave the absorption figures ranging from 0.00625 $cc/cm^2/hr$ to 0.00630 $cc/cm^2/hr$. The second reading at 40 hours gave results from 0.00625 $cc/cm^2/hr$ to 0.00640 $cc/cm^2/hr$. These results indicated a satisfactory repeatability.

4.4.2 - Rates of photo-oxidation of original bitumens, and their fractions

Bitumens described under Table 1, and their fractions were photo-oxidised in the form of thin films. The oxygen absorbed every 40 hours was measured and rates of oxidation in terms of cc O_2 uptake/cm^2/hr were calculated. Oxidation was carried out for a total period of 200 hours using throughout, a 40 hours' oxidation cycle. The oxidation rates were plotted against the time of oxidation and produced the same general rate curve. All the curves were of the auto-retardant type and in general resemble those obtained in thermal oxidation. Figure 29 gives oxidation curves for three bitumens. Bitumen 3 (Trinidad Lake Asphalt) showed the highest reactivity and Bitumen 2 (Venezuelan) the lowest. The oxidation rate which is high in the beginning

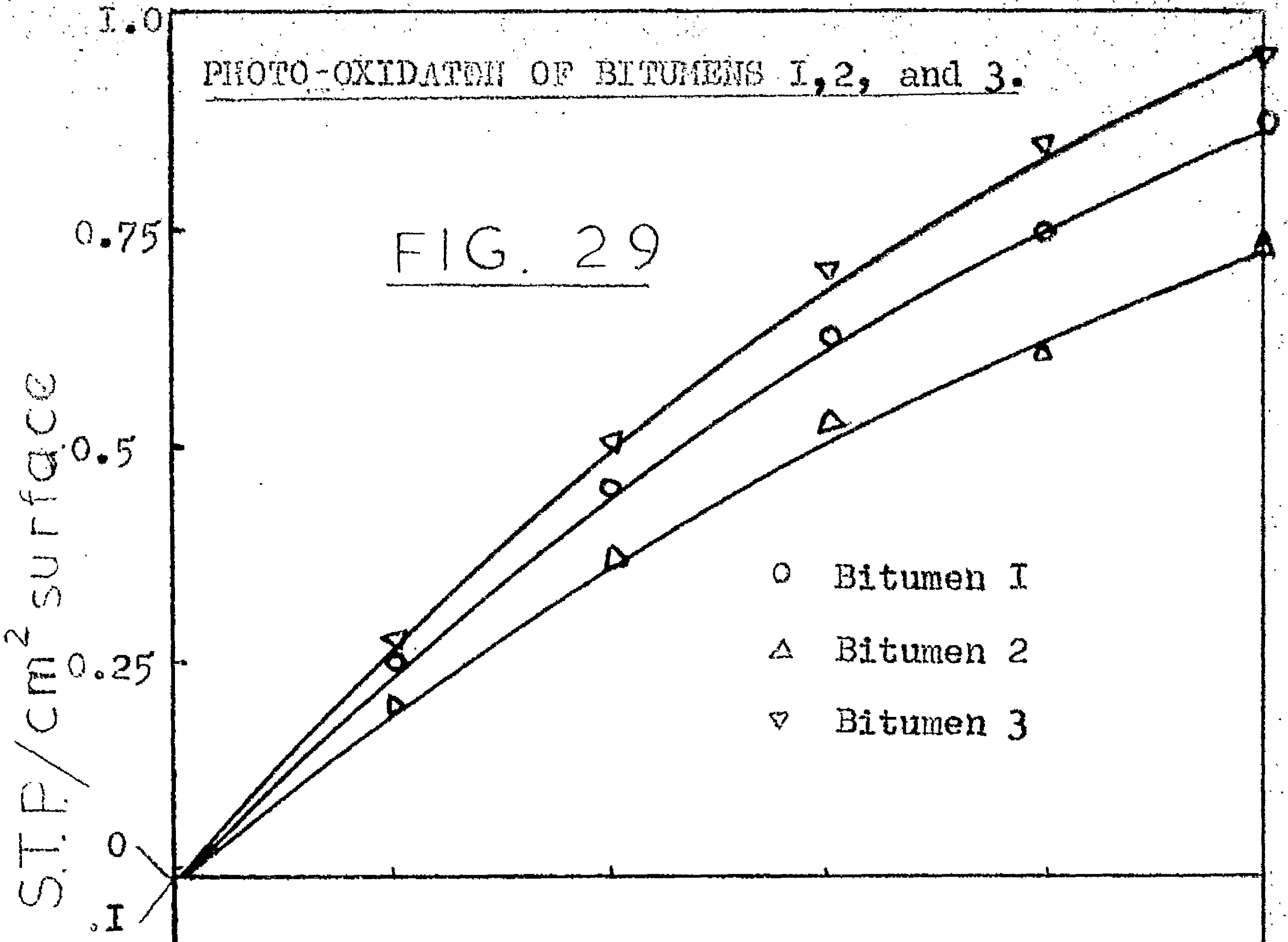


PHOTO-OXIDATION OF BITUMENS I,2, and 3.

FIG. 29

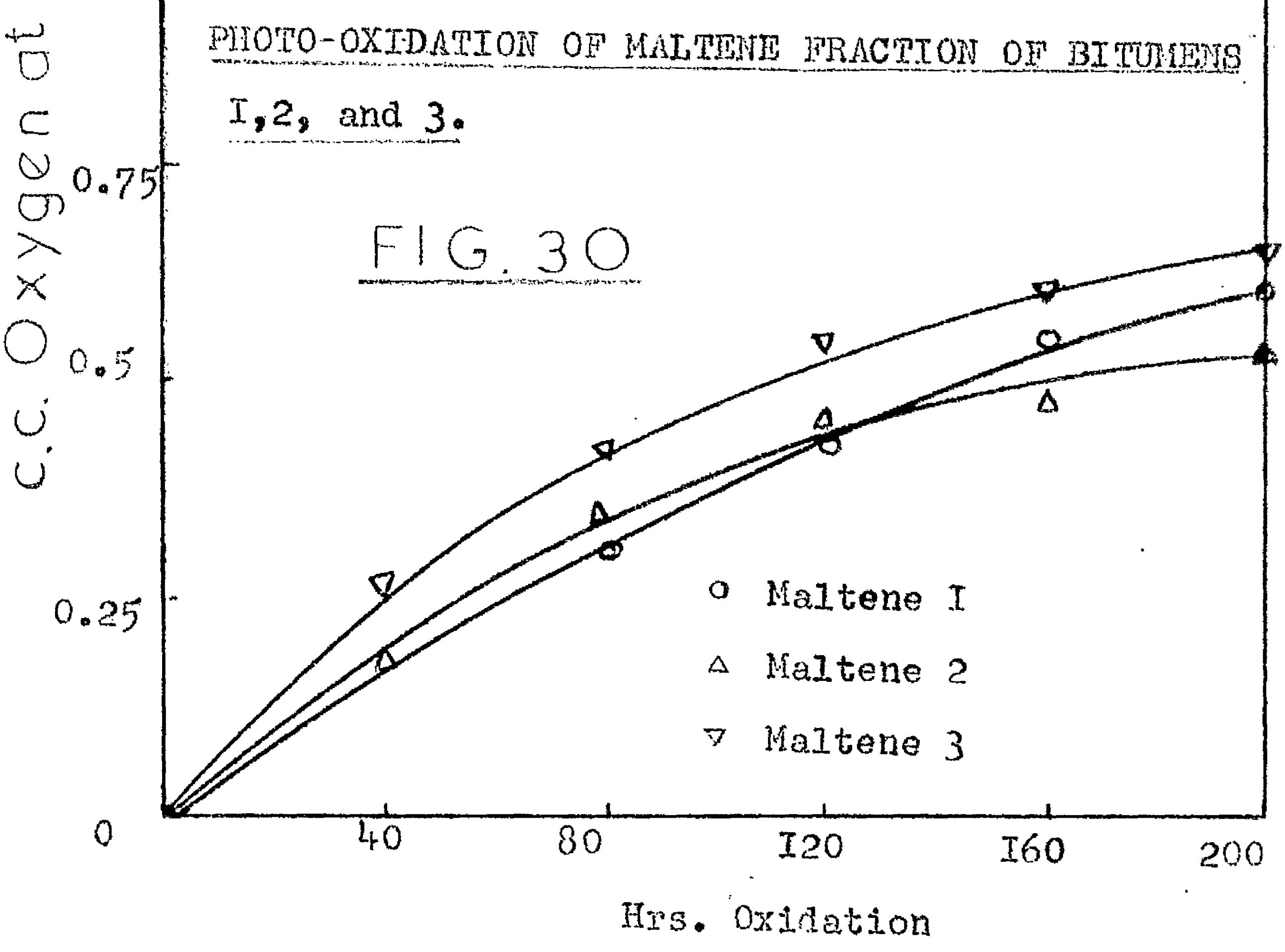


PHOTO-OXIDATION OF MALTENE FRACTION OF BITUMENS I,2, and 3.

FIG. 30

gradually falls with time and this behaviour is shown by all the bitumens.

Figure 30 represents the oxidation curves for maltene fractions of the three bitumens. Maltene 3 shows the highest reactivity. Maltenes 1 and 2 give the same general shape of curve, although lower in oxygen absorption. After about 120 hours Maltene 2 showed a greatly diminished rate, i.e. a strongly auto-retardent effect and the final overall absorption figures put the oil fractions in the order 3>1>2.

From these two figures it can be seen that bitumens have a higher rate of oxidation than their maltene fractions. It may be assumed from this that asphaltenes have a greater influence on the rate of oxidation of bitumens. To study this further, fractions of all the bitumens were photo-oxidised as described before and the results in the form of graphs are represented in Figures 31 - 33. As before all the curves are of the auto-retardant type.

In each case the white oil fraction was the most reactive with dark oil showing the lowest reactivity. Resins were second in reactivity and the asphaltenes third. It can be seen that the reactivity of the white oil fraction is approximately double that of the asphaltenes for all bitumens. By calculating, from the percentage and reactivity of each fraction, an oxidation figure for the bitumens and comparing these with the original bitumen oxidation figure it was noted that the calculated curve fell below the observed curve. This suggest that in the bitumen oxidation a certain synergetic effect might exist, due to the influence of fractions on each other.

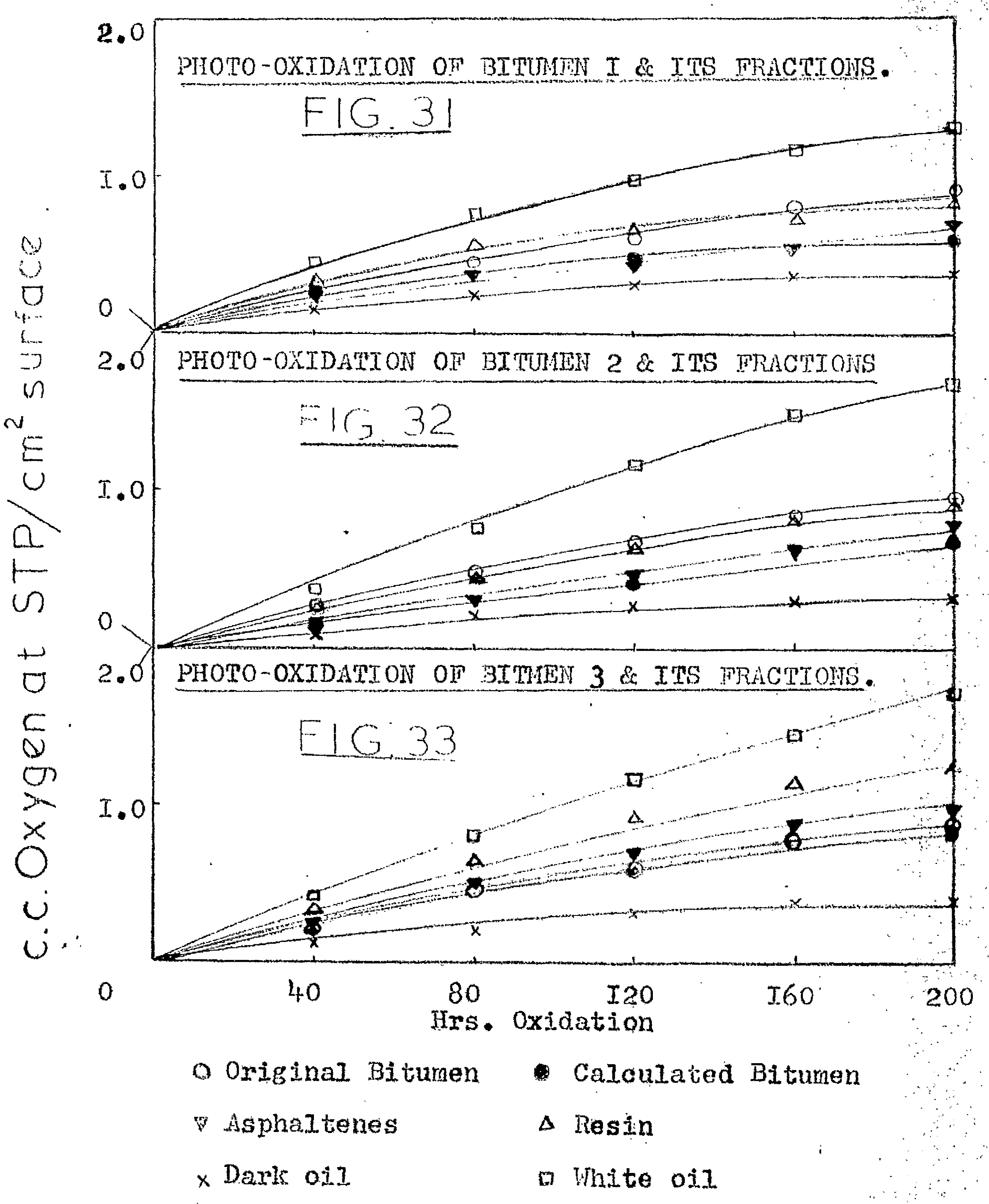


PHOTO-OXIDATION OF BITUMEN I & ITS FRACTIONS.

FIG. 31

PHOTO-OXIDATION OF BITUMEN 2 & ITS FRACTIONS

FIG. 32

PHOTO-OXIDATION OF BITMEN 3 & ITS FRACTIONS.

FIG. 33

4.4.3 - Rates of photo-oxidation of synthetic bitumens

Three sets of synthetic bitumens were prepared as described for thermal oxidation in Section 3.9, by taking the three original bitumens and fractionating them into asphaltenes and maltene fractions. Asphaltenes were then blended into maltenes in varying proportions as shown in Table 11. These samples were then photo-oxidised in the form of thin films and the oxygen uptake measured. The results are shown plotted in Figures 34 - 36. Figure 34 represents photo-oxidation curves for Bitumen 1 and its allied synthetic bitumens. For all the bitumens similar auto-retardant curves were obtained but a considerable difference in reactivity was noted. Bitumen 1 with 5% asphaltenes gave almost the same rate of oxidation as that obtained for the maltene fraction. Rather surprisingly bitumen with 10% asphaltenes approached the same reactivity as the original bitumen while bitumen with 15% asphaltenes was more reactive. Synthetic bitumens with 20% asphaltenes, i.e. the reconstituted original bitumen gave the same rate of oxidation as the original bitumen. It is apparent that, in general, susceptibility to oxidation increase with asphaltene content, reacting a maximum at about 15% asphaltenes and this maximum is above the reactivity of the original bitumen. On increasing the asphaltenes to the natural figure reactivity falls and approaches that of the original bitumen. Bitumen 2 with its synthetic variations, demonstrated similar phenomena. Increase of asphaltenes gave increasing rates of photo-oxidation, as measured by oxygen uptake and a maximum figure was obtained again at about 15% asphaltenes. The synthetic original bitumen with the same percentage of asphaltenes and maltenes as the original material showed in this case, a slightly

FIG.34

PHOTO-OXIDATON OF BITUMEN I & ITS ALLIED SYNTHETIC BITUMENS.

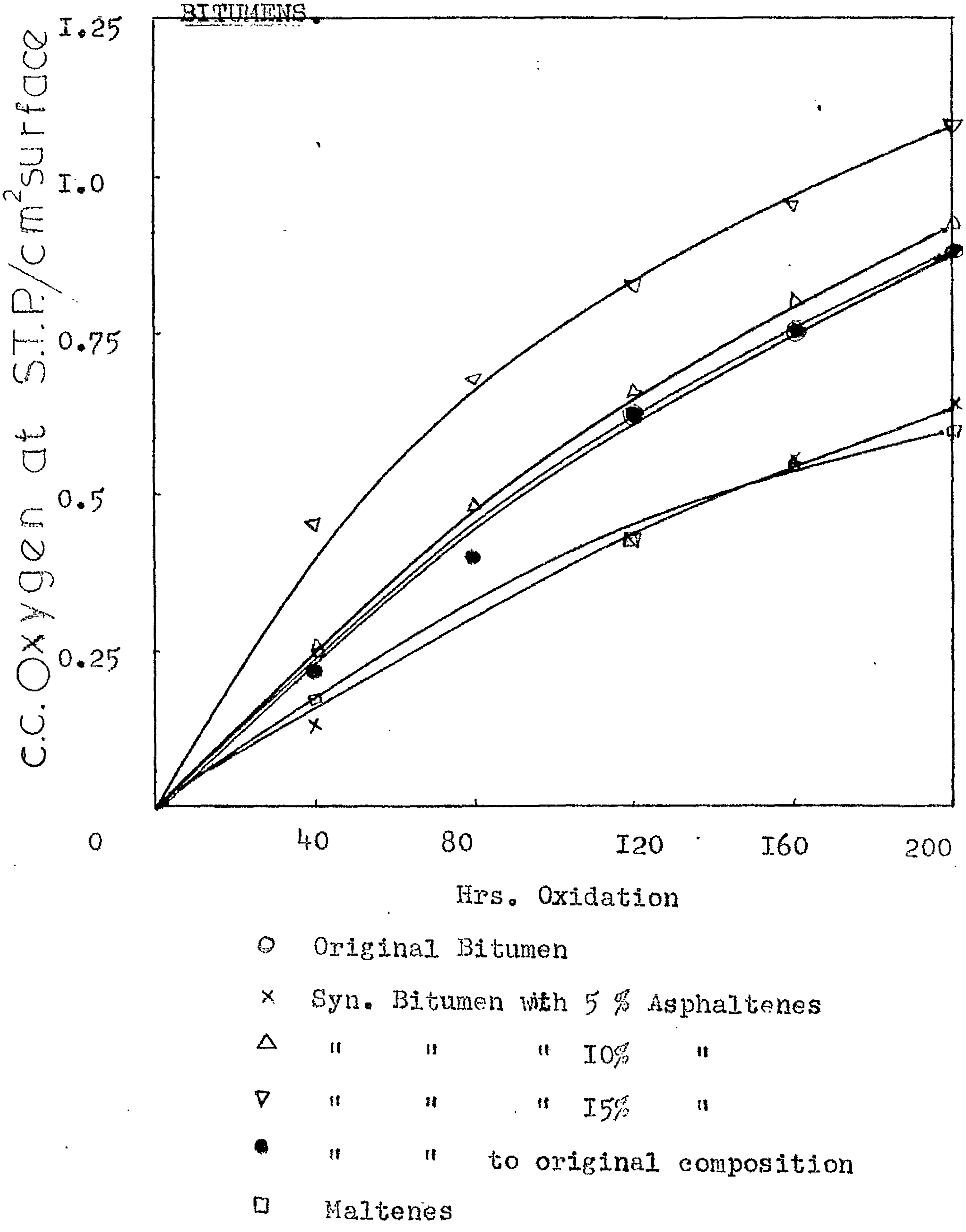


FIG. 35

PHOTO-OXIDATION OF BITUMEN 2 & ITS ALLIED SYNTHETIC BITUMENS.

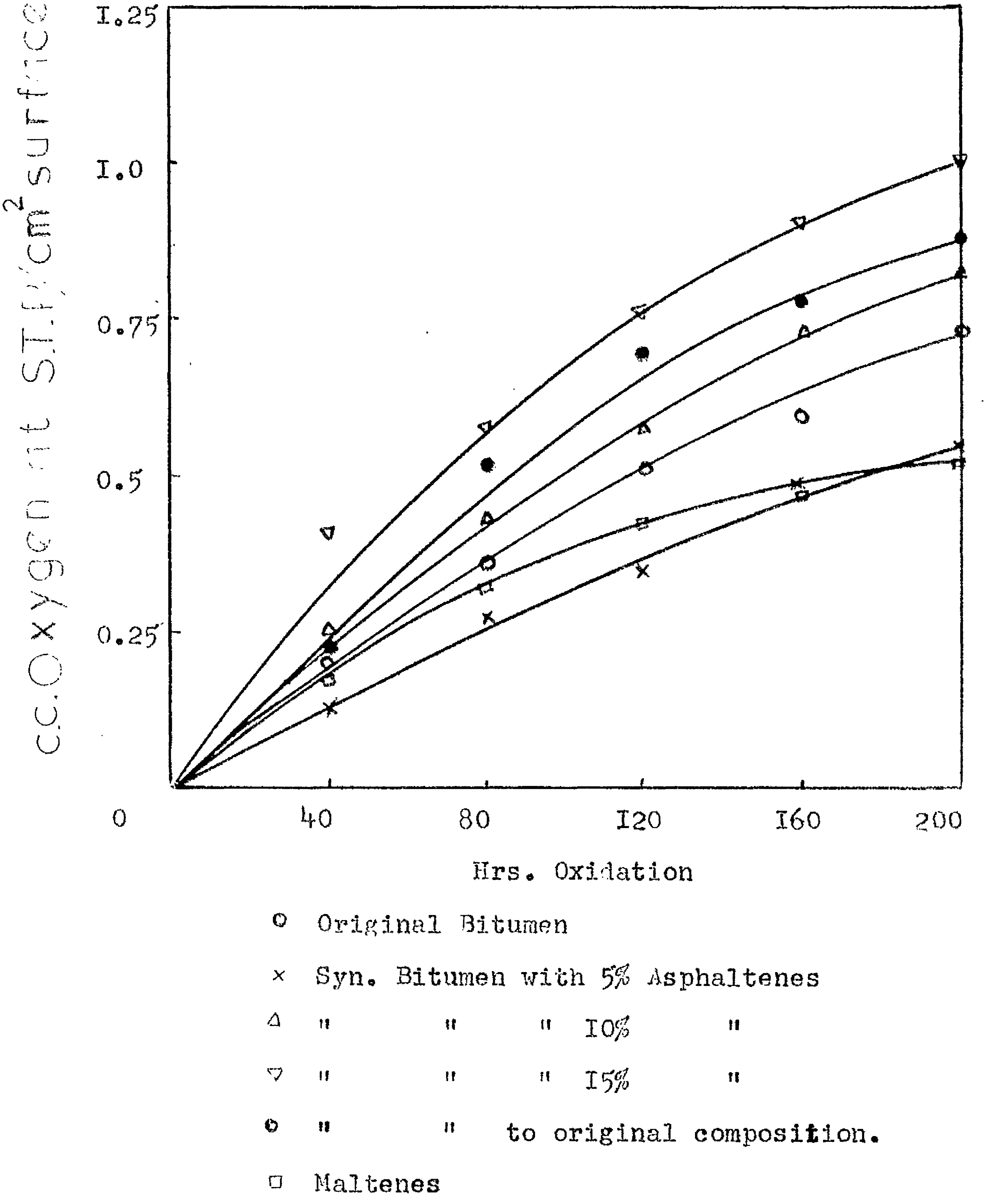
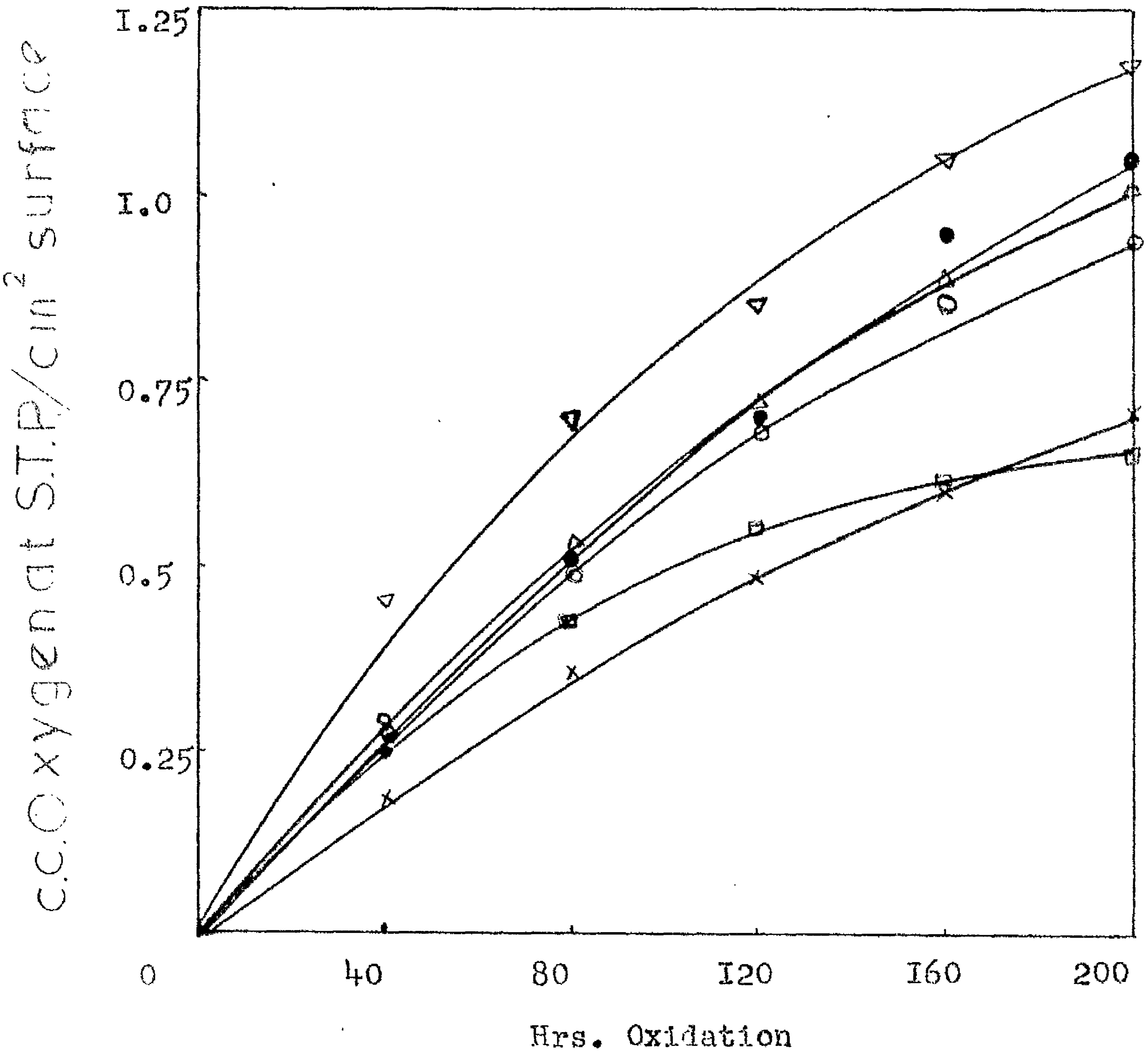


FIG 36

PHOTO-OXIDATION OF BITUMEN 3 & ITS ALLIED SYNTHETIC BITUMENS.



○ Original Bitumen

× Syn. Bitumen with I5% Asphaltenes

△ " " " 30% "

▽ " " " 45% "

● " " to original composition

□ Maltenes

higher susceptibility to oxidation than the starting material. Figure 35 shows the curves obtained.

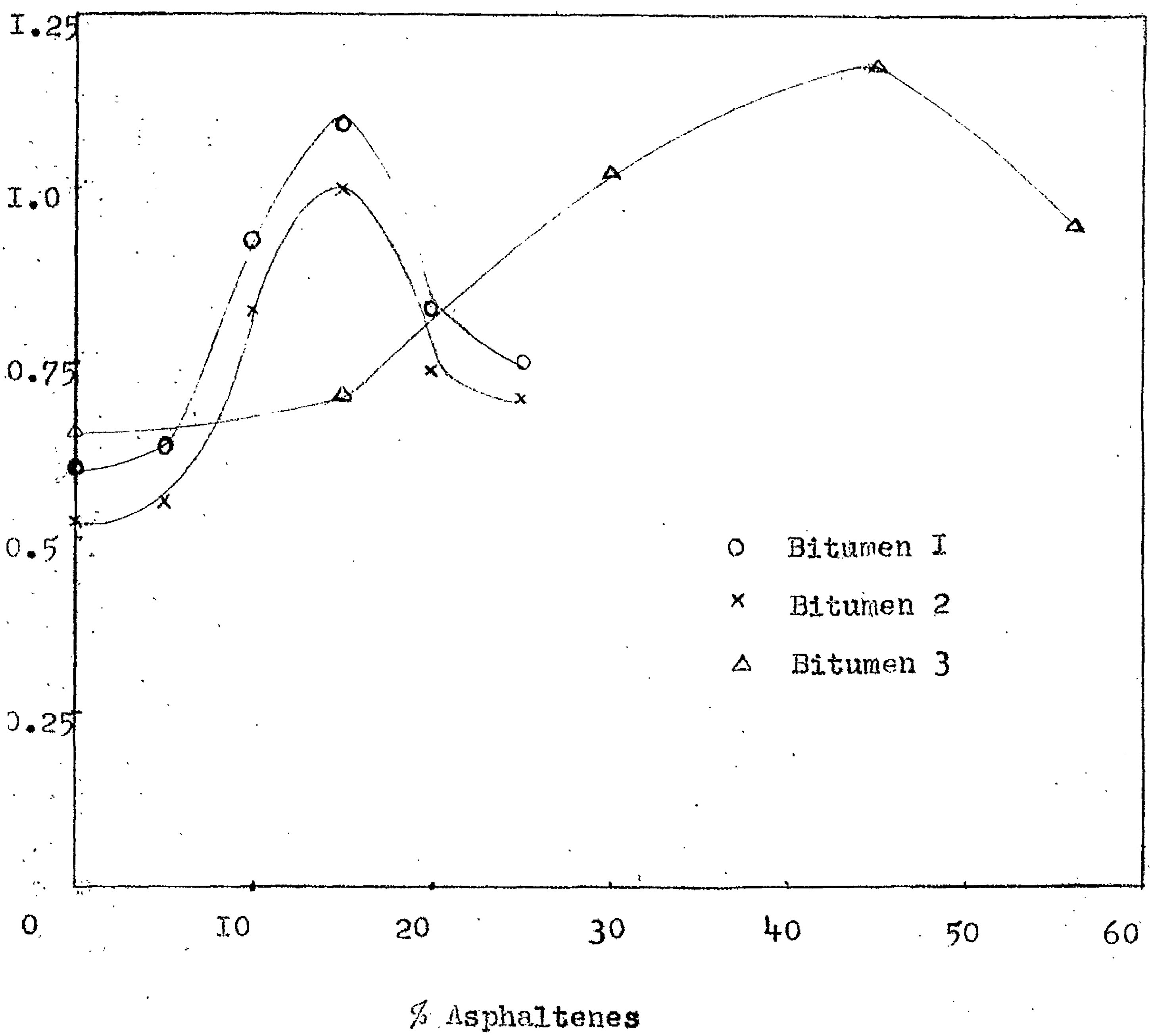
Trinidad Lake Asphalt (Bitumen 3) showed similar behaviour in that a maximum rate was obtained with an asphaltene content below the normal. The maximum in this case was obtained with 45% asphaltenes, the normal asphaltene content being about 55%. The photo-oxidation curves obtained for 200 hours reaction are shown in Figure 36.

The effect of asphaltene content on oxidation rate is seen more clearly in Figure 37 where oxygen absorbed at 200 hours is plotted against % asphaltenes for the three series of bitumens studied. The three maltene fractions (0% asphaltenes) differ only slightly in susceptibility to photo-oxidation but the effect of adding asphaltenes shows a marked difference. In the case of the two petroleum bitumens (1 and 2) parallel curves are obtained and the effect of the asphaltene fractions is almost identical. Asphaltenes from Trinidad Lake Asphalt have less effect on the oxidation rate although, because of the large amount in the natural material, the overall oxidation rate for Bitumen 3 is greater.

Two things were of interest and would have been studied had circumstances allowed. These were (1) the effect of asphaltenes on viscosity of the synthetic bitumens, although this would not be expected to show much deviation from linearity. This study was not possible due to the lack of a suitable viscometer and (2) the effect of adding asphaltenes from petroleum bitumens to the T.L.A. maltenes to see whether an accelerated effect was obtained. Whilst time did not allow this to be done it is obviously necessary for

THE EFFECT OF ASPHALTENES ON RATE OF PHOTO-OXIDATION.

FIG 37



further study of this phenomenon.

4.4.4 - The study of chemical changes on photo-oxidation by infra-red spectroscopy

The scope of technique is given in detail in Appendix and discussed fully later.

4.5 - The formation of water-soluble products of oxidation on irradiation of bitumens and bitumen fractions

A study was made of the formation of water soluble degradation products of bitumens and fractions on exposure to u.v. radiation in the presence of atmospheric oxygen. Thin films were prepared at the bottom of beakers as described in Section 4.3.1. The beakers with sample were first dried in an oven at 40°C for 30 minutes and after cooling in a desiccator were weighed. They were then photo-oxidised in the usual apparatus using the following cycle:

(1) Photo-oxidation for 40 hours.

(2) Desiccator for 15 minutes. Weigh.

(3) Addition of 25 ml distilled water to the beaker, leave for 30 minutes, shake and wash twice with 10 ml of water and collect the water solubles.

(4) Drying in an oven at 40°C for 30 minutes, desiccator for 15 ml and weigh. This difference in weight from (2) shows the amount of water-solubles produced.

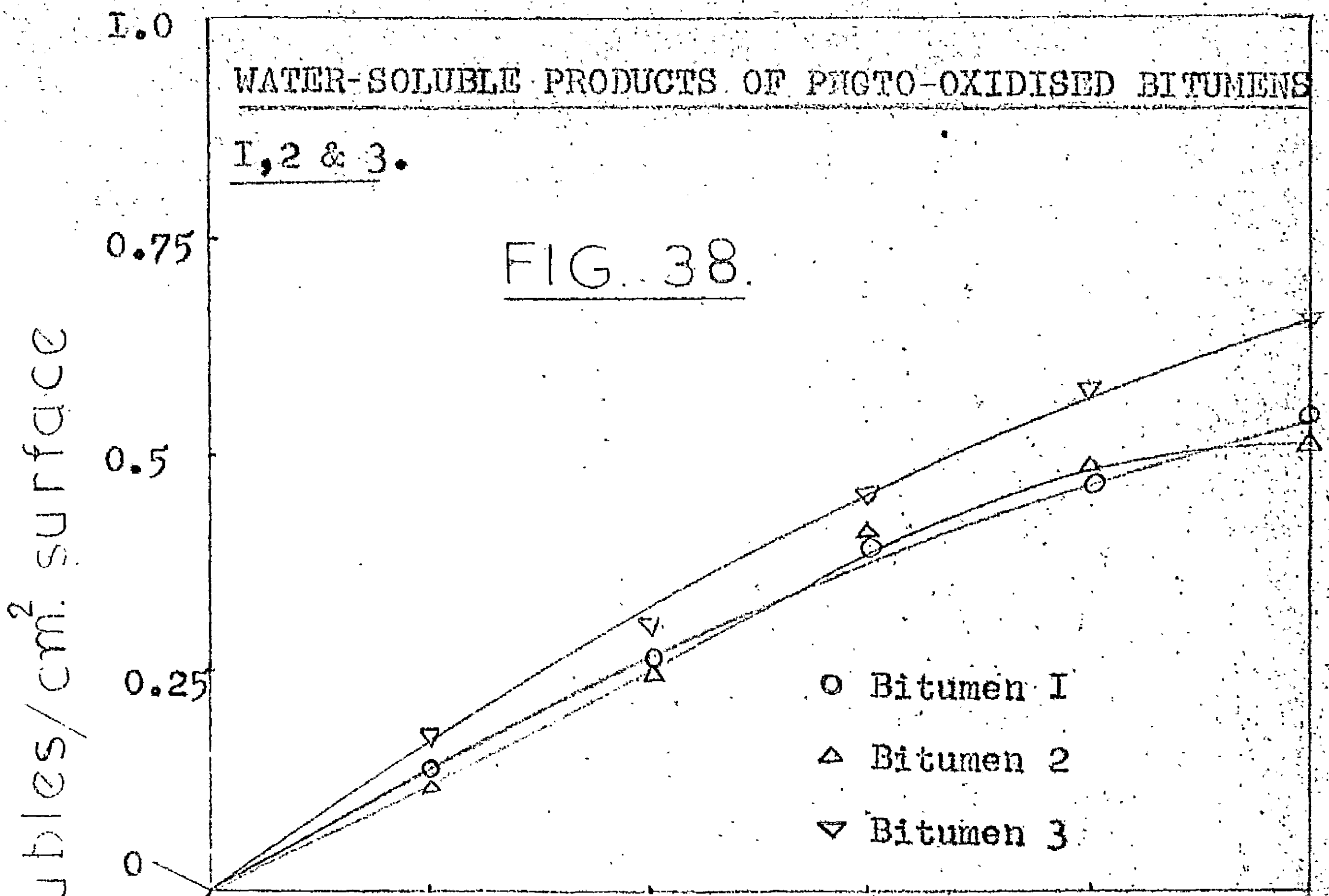
Several samples were photo-oxidised in this manner, the rate of production of water-solubles determined and the types of skin produced examined. This study was made with (a) three original bitumens, (b) bitumen fractions and (c) synthetic bitumens. Water-solubles produced per cm^2 was calculated and plotted against hours of oxidation. (Figures 38 - 45).

4.5.1 - Results and discussion

Rates of production of water-soluble degradation products of photo-oxidised bitumens are represented in Figure 38. The shape of the curves obtained were similar throughout but the amounts obtained showed a variation. The rate of water-soluble production shows a falling off after 80 hours exposure. Bitumen 3 gave the highest rate of production with Bitumen 1 second and Bitumen 2 last. This order of reactivity is in agreement with the rates of oxygen uptake shown in Figure 29.

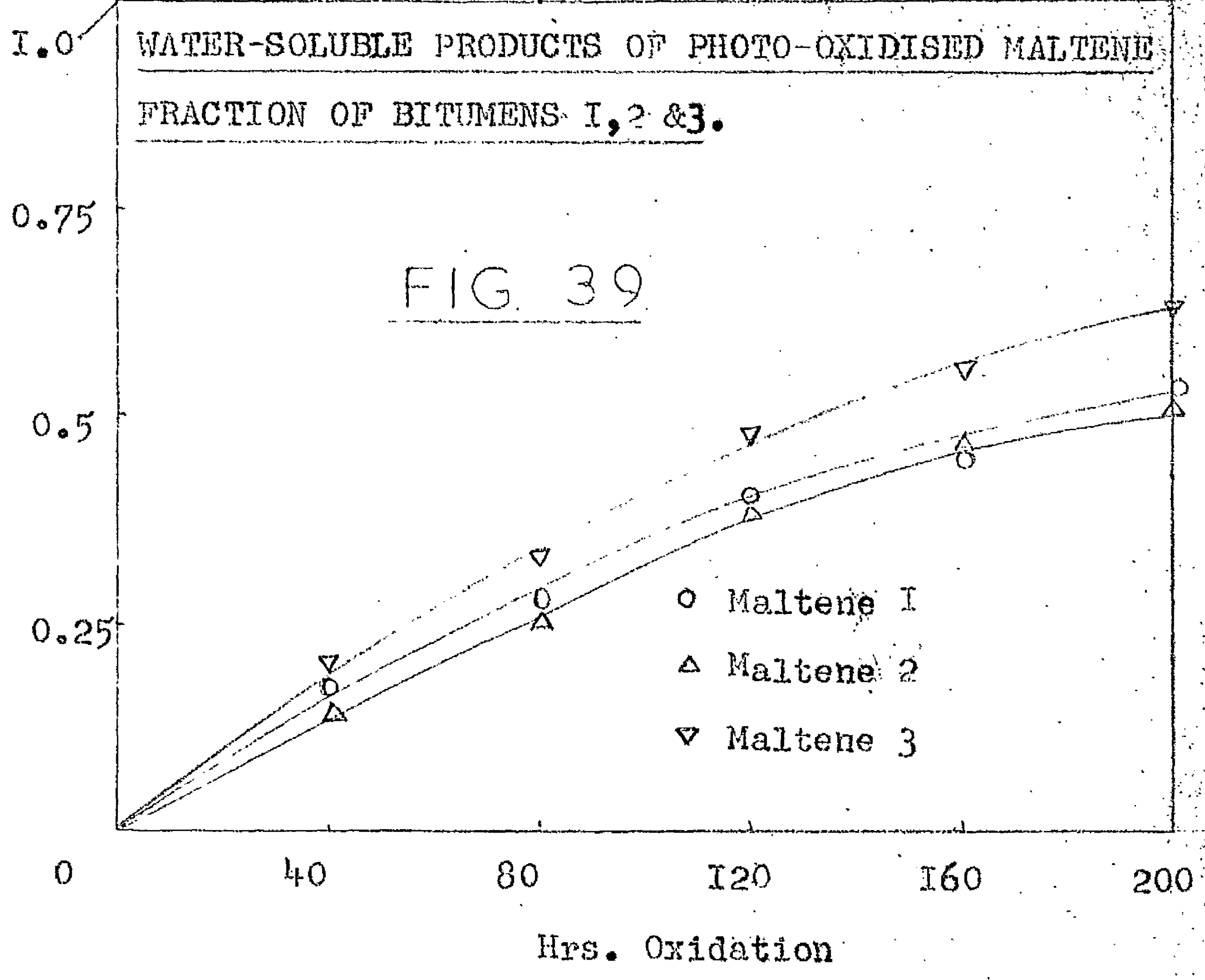
Figure 39 represents water-soluble products formation by thin films of maltene fractions of the bitumens and again follows the same reactivity pattern. The maltene fraction of Bitumen 3 shows the largest amount of solubles with the fraction from Bitumens 1 and 2 next in order. This suggested that these fractions might be responsible for the total production of water-solubles in their original bitumens.

To investigate this further, various bitumen fractions were photo-oxidised and the water solubles determined. Figures 40-43 represent the water-solubles produced over 200 hours by the bituminous fractions. The white oil fraction being less viscous and easily emulsifying with water was difficult to handle. The highest rate of water-soluble production was found with the asphaltene fractions, with resin and dark oils in descending order. Similar behaviour was observed in fractions from all the bitumens but it is noticeable that the fractions do not



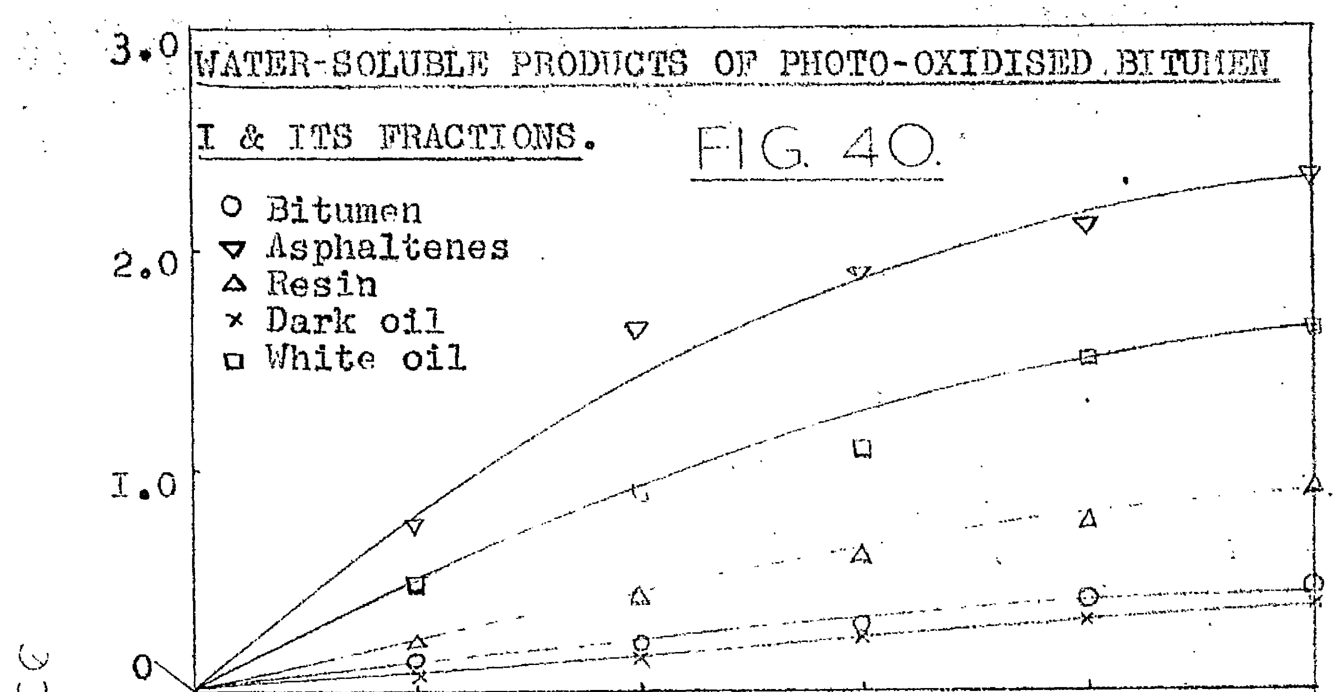
WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMENS I,2 & 3.

FIG. 38.



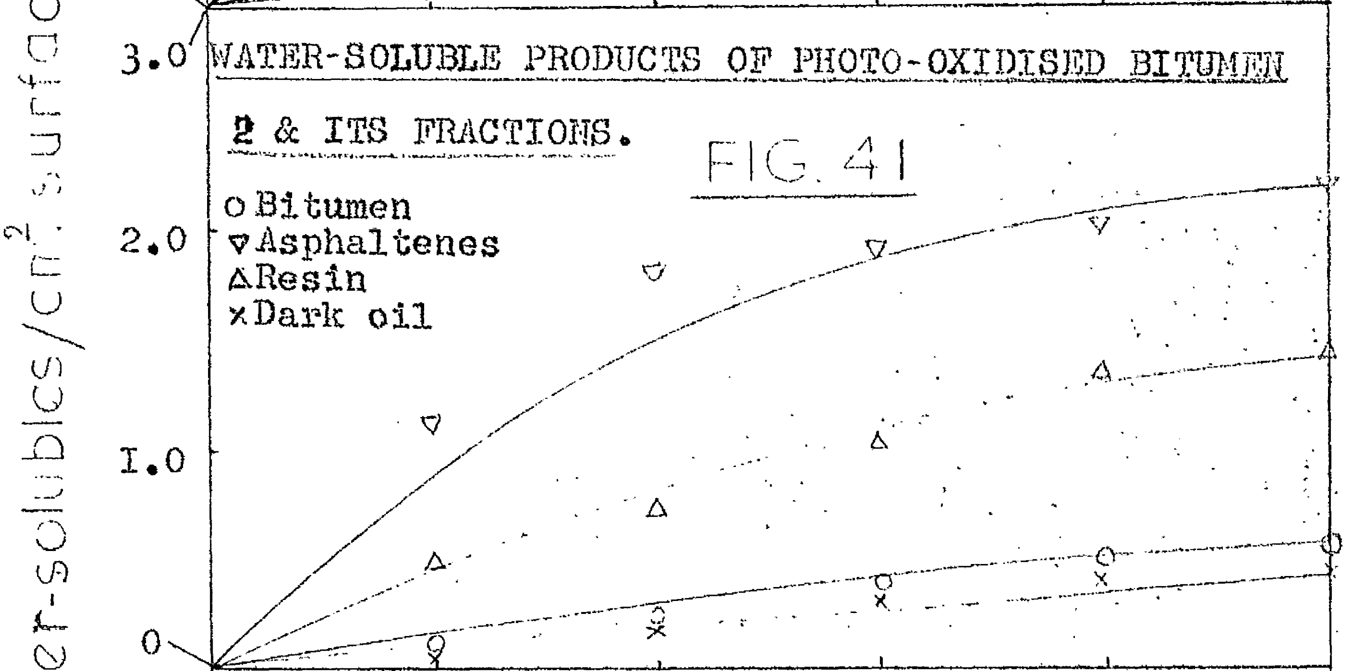
WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED MALTENE FRACTION OF BITUMENS I,2 &3.

FIG 39



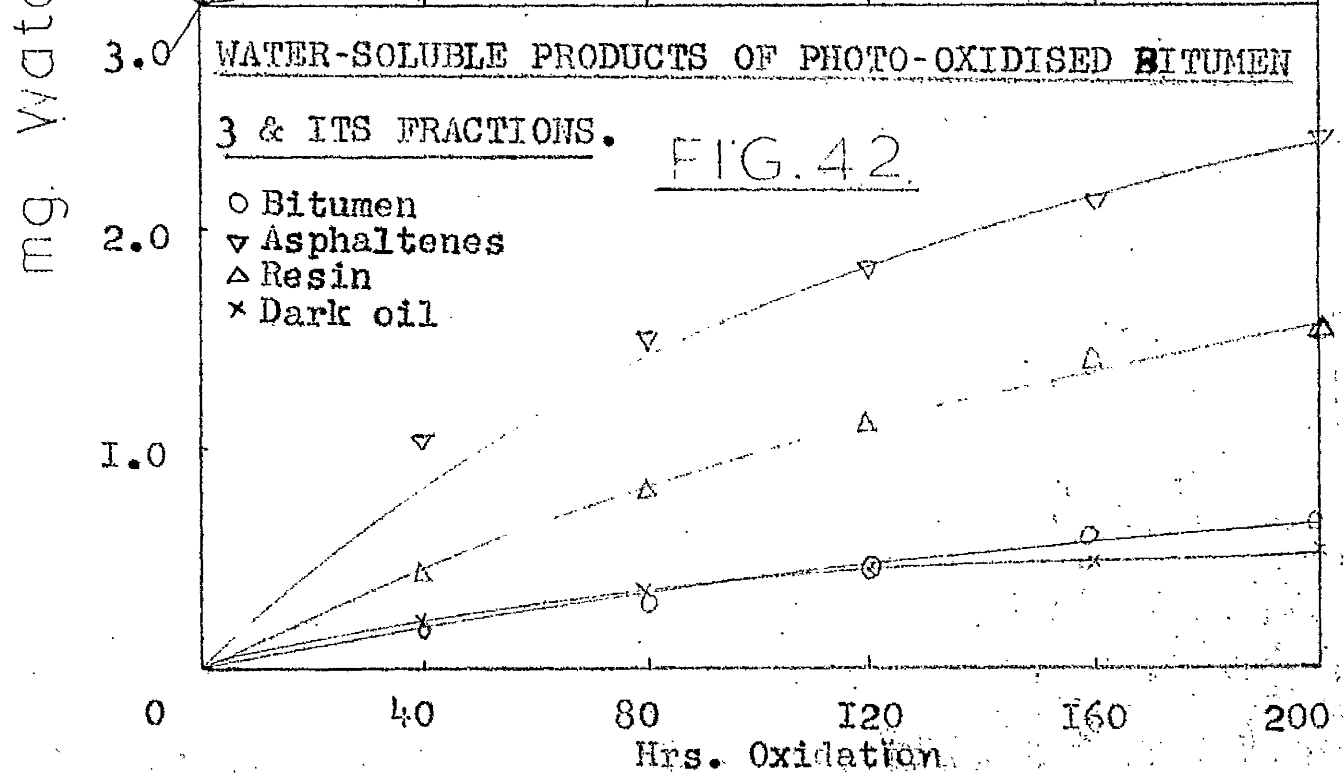
WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN I & ITS FRACTIONS.

FIG. 40.



WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN 2 & ITS FRACTIONS.

FIG. 41



WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN 3 & ITS FRACTIONS.

FIG. 42

FIG. 43

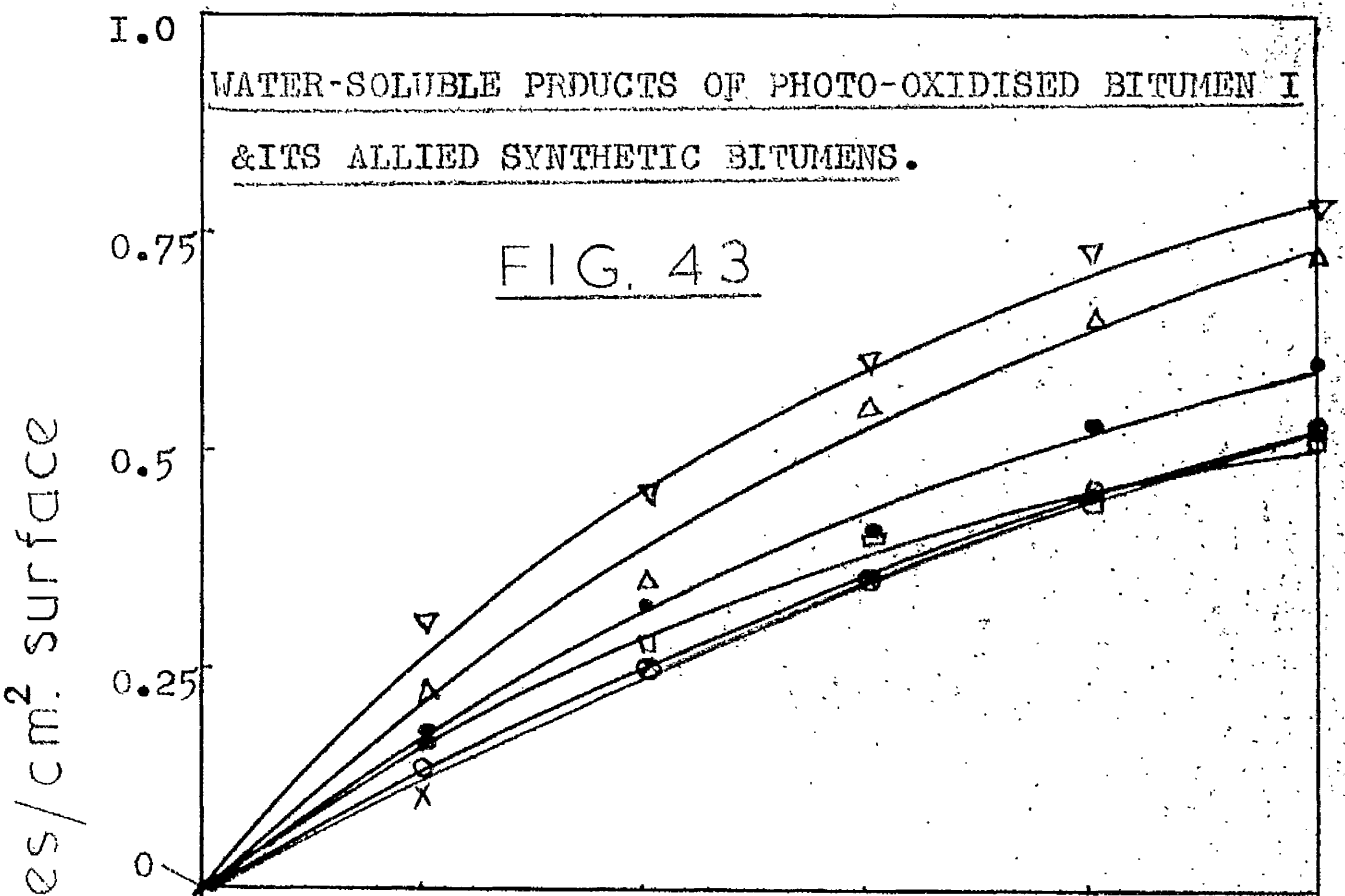
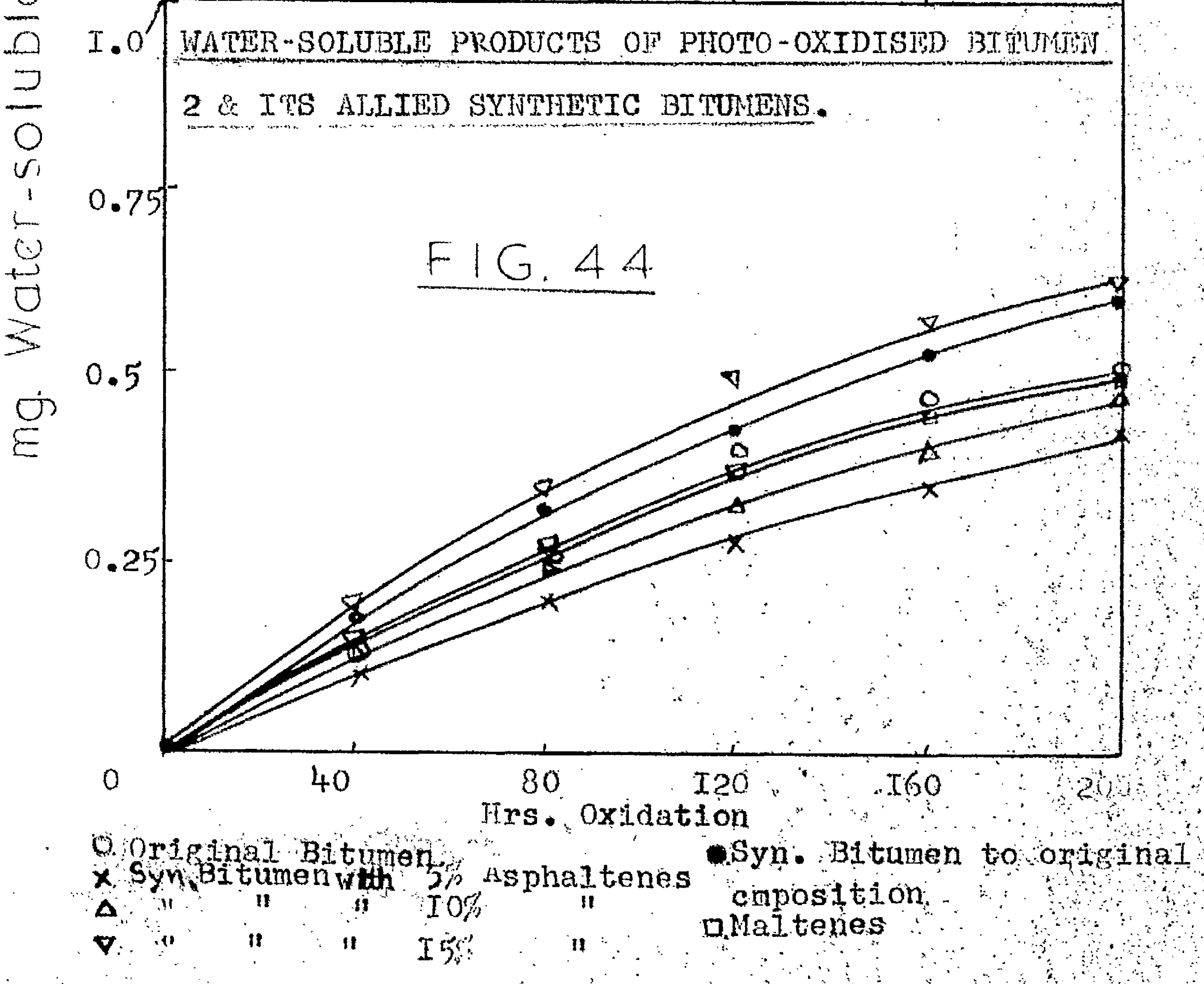

WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN I &ITS ALLIED SYNTHETIC BITUMENS.
I.0
0.75
0.5
0.25
0
mg. Water-solubles/cm.^{2} surface

FIG. 44


WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN 2 & ITS ALLIED SYNTHETIC BITUMENS.
I.0
0.75
0.5
0.25
0
40
80
I20
I60
20
Hrs. Oxidation
○ Original Bitumen
× Syn. Bitumen with 5% Asphaltenes
△ " " " I0% "
▽ " " " I5% "
● Syn. Bitumen to original cmposition
□ Maltenes

WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMEN 3 & ITS ALLIED SYNTHETIC BITMENS.

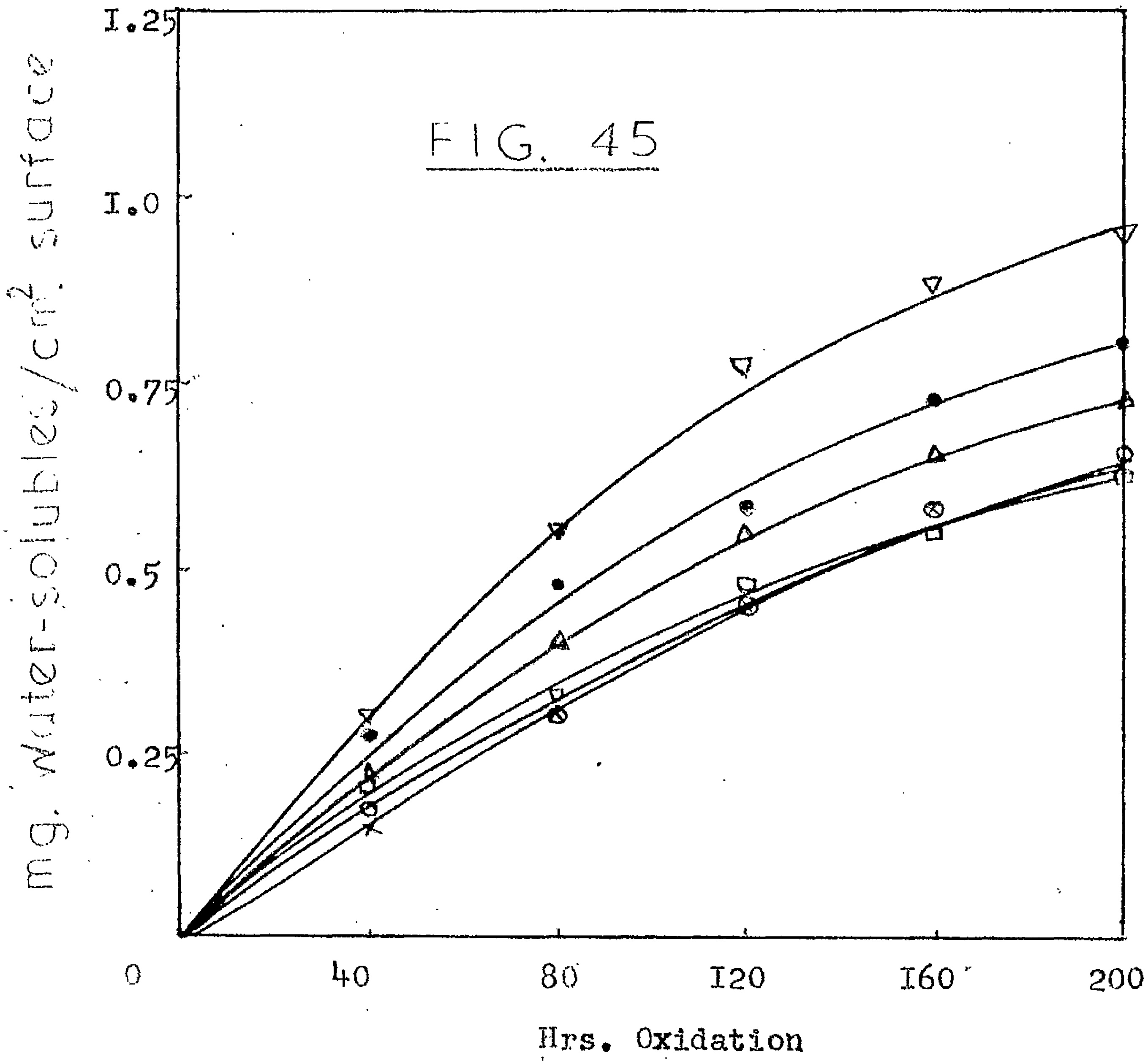


FIG. 45

○ Original Bitumen

× Synthetic Bitumen with I5% Asphaltenes

△ " " " 30% "

▽ " " " 45% "

⊙ " " to original composition

□ Maltenes

show up an exact parallel between water-solubles produced and oxygen uptake.

The synthetic bitumens, previously studied, were again photo-oxidised and the water-solubles produced determined. Figure 43 represents the water-soluble products of Bitumen 1 and allied synthetic bitumens. The original bitumen, synthetic bitumen with 5% asphaltenes and maltene fraction gave the same rate of water-soluble formation while increasing amounts of solubles were obtained from the materials with 10% and 15% asphaltenes. As in the work on oxygen uptake a falling off in rate was observed when 20% asphaltenes were added. Bitumens 2 and 3 (Figures 44 - 45) did not differ appreciably in their respective rates of solubles production by fractions and also showed similarity to the oxygen uptake curves.

It can be seen then that with an increase in asphaltene content up to 15% in petroleum bitumen and 45% in T.L.A., the water-soluble products increase proportionally. Larger asphaltene contents produce a decrease in the water-soluble products fraction. This is conveniently shown in Figure 46 where weight of water-soluble formed is plotted against asphaltene content for three bitumens. The fall in water-soluble formation with more than 15% asphaltenes in petroleum bitumens could be due to the following reasons:

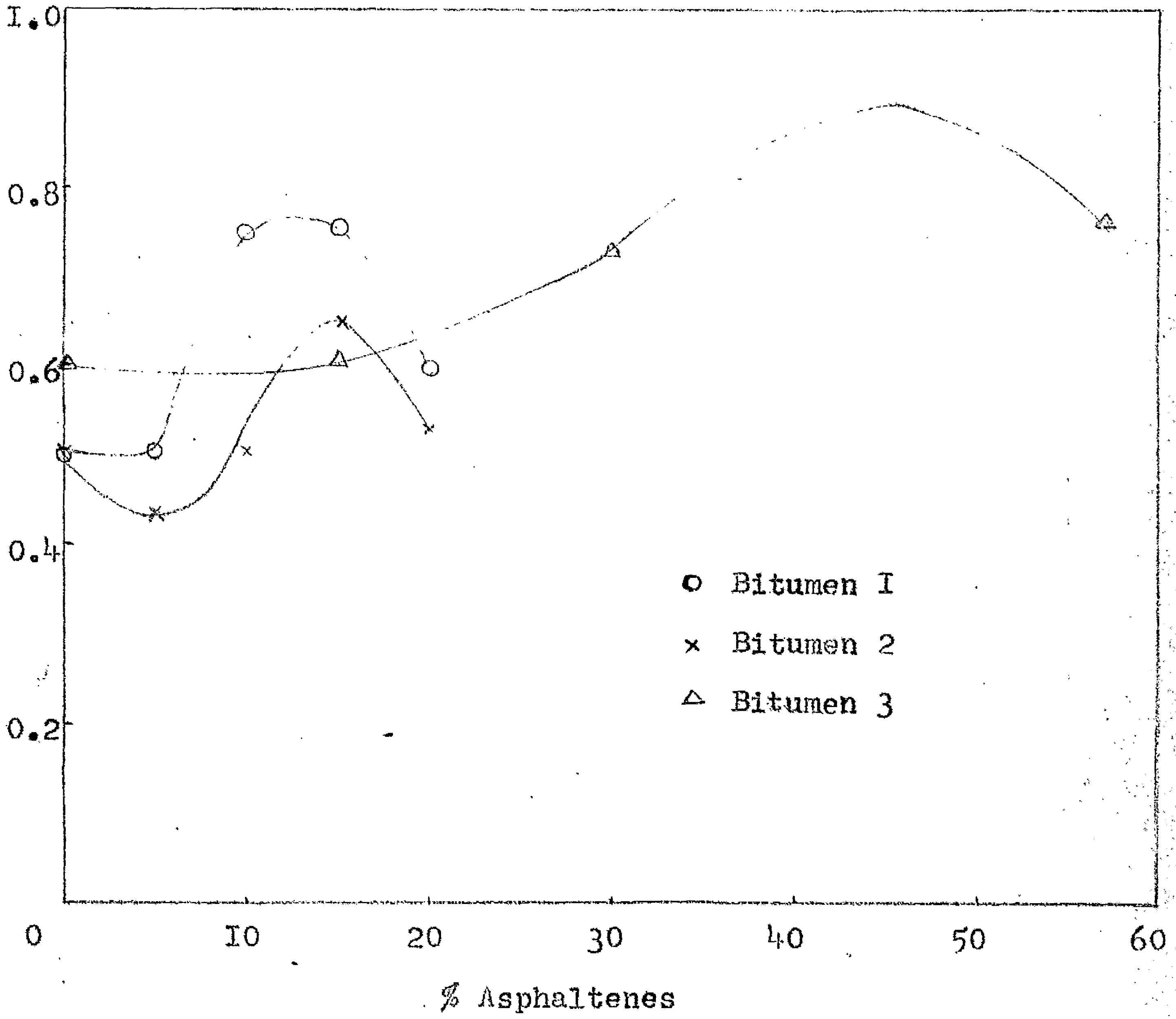
(1) Increase in viscosity with addition of asphaltenes.

(2) Change in bitumen internal structure.

(3) Asphaltenes in excess acting as an antioxidant or changing any synergetic effect.

THE EFFECT OF ASPHALTENES ON RATE OF WATER SOLUBLES

FIG. 46



Similarity of the results for both water-soluble production and oxygen uptake suggests a direct relationship between the two. Figure 47 shows the relationship between the two plotted for all three bitumens and their synthetic forms taking figures for both oxygen uptake and water-soluble at 200 hours oxidation. It is seen that, whilst the slope differs slightly and the relationships do not quite agree in amount, there does exist a direct relationship between water-solubles and oxidation susceptibility.

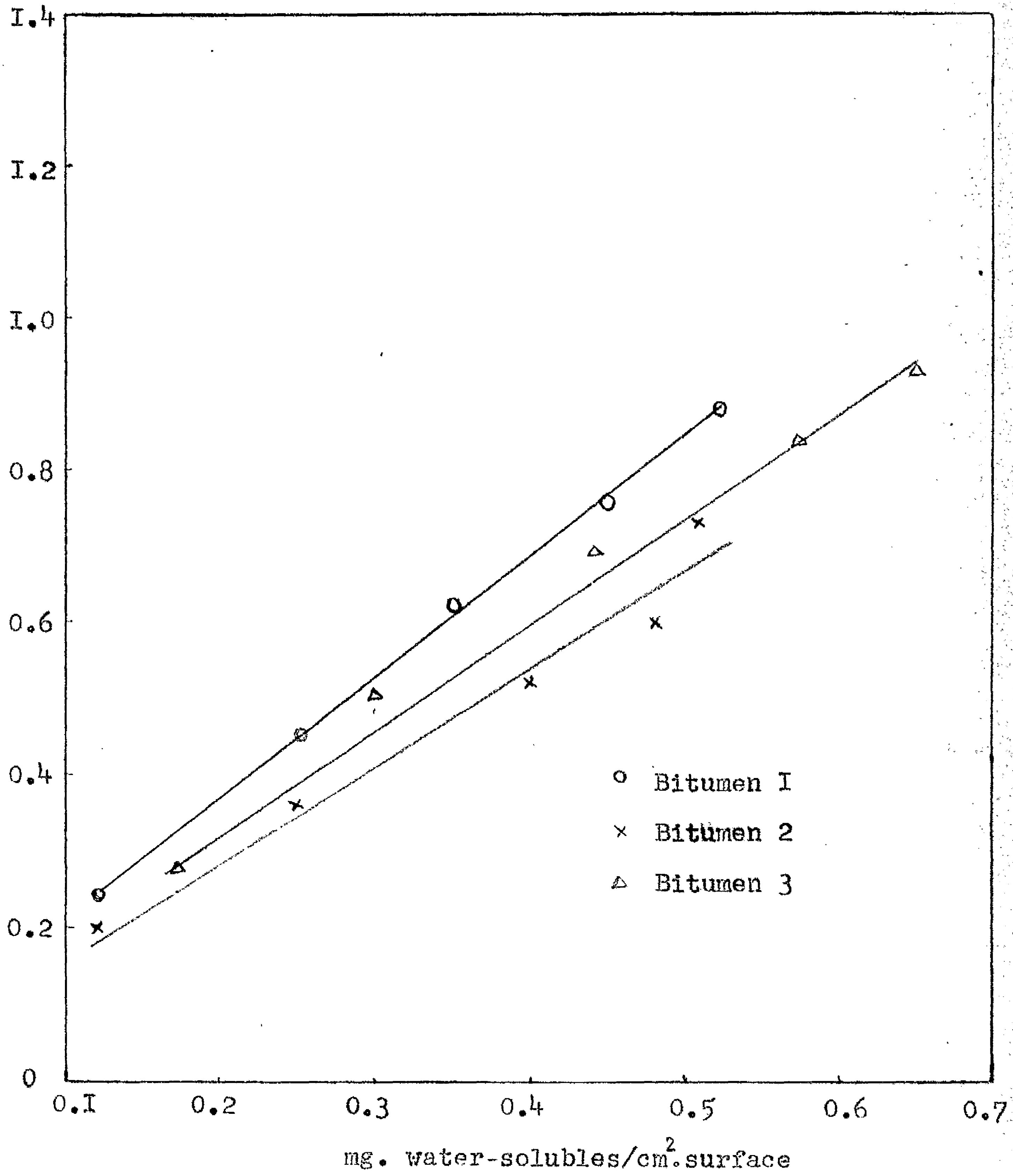
4.6 - A study of the water-soluble degradation products of photo-oxidised petroleum bitumens and Trinidad Lake Asphalt

Little work has been done in the study of the nature of water-soluble products. Kleinschmidt et al(115) and Schriescheim et al(44) were among the first to investigate these products but worked with blown bitumens, i.e. gel type. In the present work the amount of water-solubles collected was too small to carry out qualitative and quantitative tests, it was, therefore, decided to employ infra-red spectroscopy to study the nature of water-soluble products which were pale brown in colour and exhibited acidic characteristics.

Solutions containing water-soluble products of photo-oxidised petroleum bitumens and Trinidad Lake Asphalt were filtered (through Whatman No.1 filter paper). Each filtrate was then concentrated to 100 ml under vacuum distillation. One 25 ml portion of concentrated solution of each sample was taken into an evaporating dish and another 25 ml portion of the same sample passed through cation exchange resin (Amberlite Resin CG-120 B.D.H) to remove primary and secondary amines. Each was then mixed

RELATION BETWEEN OXYGEN UPTAKE & WATER-SOLUBLES.

FIG. 47



with 80 mg of KCl powder and was evaporated to dryness on a waterbath. Finally, they were placed in the vacuum oven to remove last traces of water. Discs of these were prepared and infra-red spectra scanned on the Infra-Cord.

4.6.1 - I.R. spectra of water-soluble matter before and after passing through cation-exchange-resin

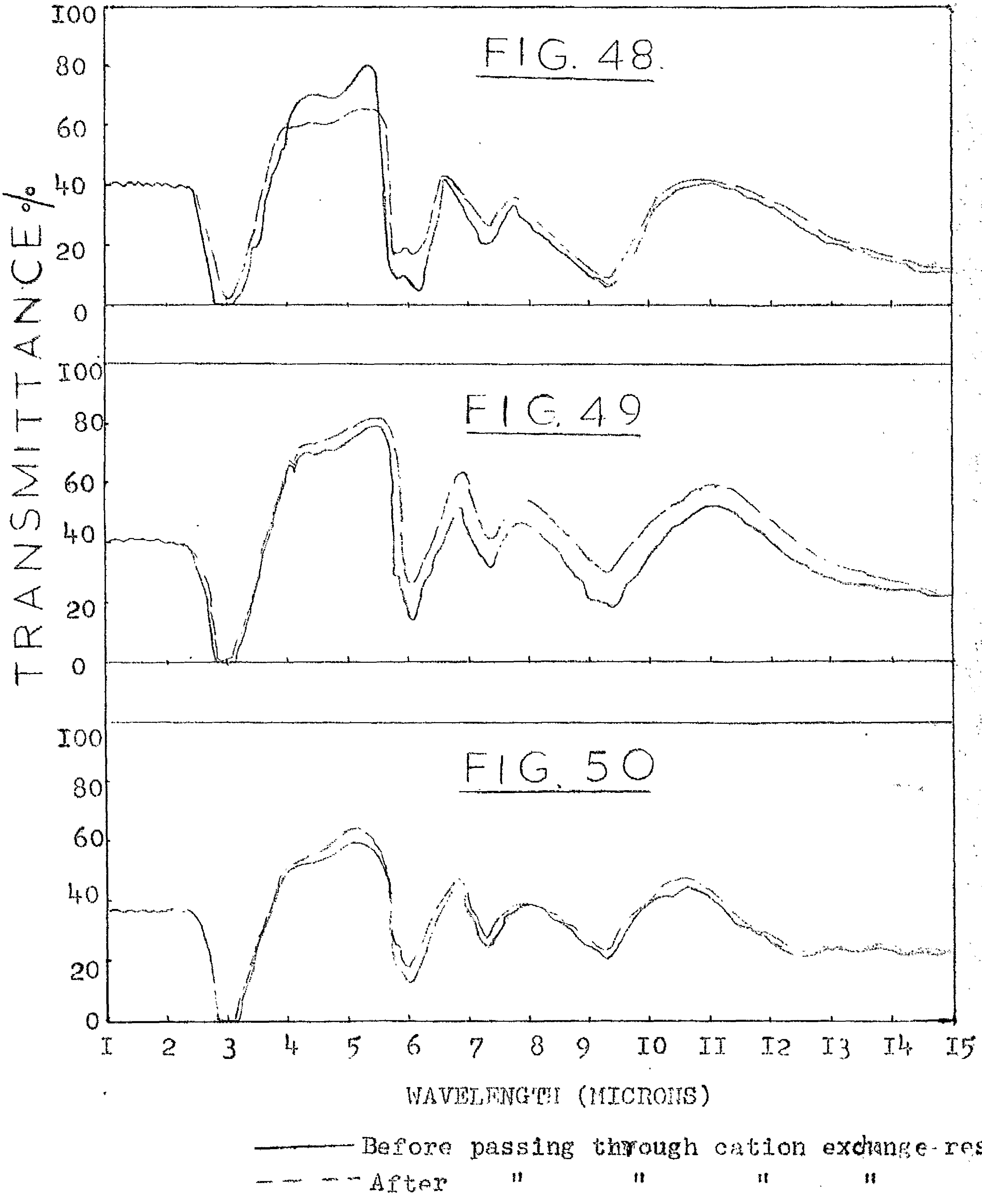
The I.R. spectra of water-soluble products of photo-oxidised petroleum bitumens and Trinidad Lake Asphalt before and after passing through cation-exchange-resin showed similar absorption bands, Figures 48 - 50. I.R. spectra of water-solubles passed through cation-exchange-resin were presumed to show the removal of primary and secondary amines by the indication of reduction in the intensity of the absorption band at 3.0 u. This showed very little change suggesting the presence, if any, of primary and secondary amines in very small quantities. Other changes in the absorption region in Bitumens 1 and 2 were noted at 5.8, 6.25, 7.2 and 8.10 micron regions. This was not of much significance. These changes were not observed in Bitumen 3.

The absorption band at 3.0 μ is due to the presence of OH··· O; - OH (hydroperoxide)(138,141) and/or -NH stretching (amines)(114,140).

The absorption band at 5.9 μ is due to C-O stretching(138,143) suggesting the presence of carbonyl group but it is very difficult to identify whether the carbonyl group present is an aldehyde, ketone and/or acid.

The absorption band in the region of 7.7 to 10 μ is probably due to stretching vibrations, which is evident for

I.R.SPECTRA OF WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED BITUMENS I,2,&3 BEFORE & AFTER PASSING THROUGH CATION--EXCHANGE RESIN.

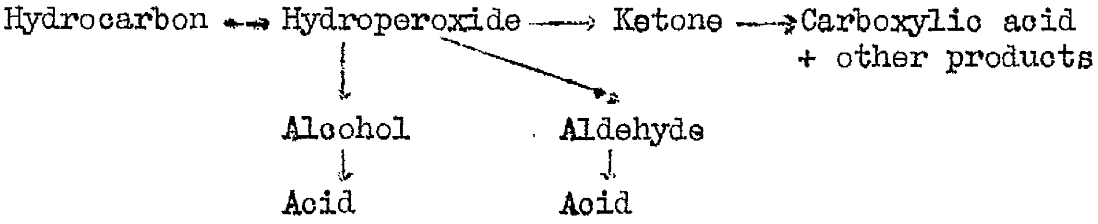


carboxyl(115) group. It might also be due to C-O(114,140) Str. (phenols, alcohols)(129); Car-O-Car str.,(128,129) Car-OCar(114,138) str; and/or Cal-O-Cal(114,141) str., where ar, al and str., represents aromatics, aliphatics and stretching respectively.

The absorption band at 7.25 is due to CH_3(112,114) symmetrical deformation.

4.6.2 - Discussion

Similarity in infra-red spectra of water-solubles from photo-oxidised petroleum bitumens and Trinidad Lake Asphalt, suggest that they have undergone a similar oxidation mechanism and they also possess a similar structure. The presence of different oxygen functional groups observed in the above infra-red spectra suggest that the complex hydrocarbon (bitumen) on photo-oxidation might have undergone the following changes:



The ultimate products include acid, water and sometimes aldehydes. The intermediate products may be hydroperoxide, ketones, alcohol, aldehydes, etc.

4.7 - Sensitised photo-oxidations

As early as 1914, Resinger(102) studied the effect of photo-sensitisers such as anethole, eugenol, safrole and iso-safrole on bitumen oxidation. He observed that the presence of these chemicals in little amounts in bitumens increased the light and heat sensitivity. Photo-sensitisers are also used to initiate polymerisation. In sensitised photo-oxidation reactions the light absorbing substance does not undergo any permanent chemical change(117). The sensitiser either transfers its energy of activation to a reactant molecule or enters into a cycle of reaction steps which form the reaction products and regenerate the sensitiser in its original form. In some instances the situation is complicated by the simultaneous photo-chemical reaction of the sensitiser. In photo-sensitised reaction the excited sensitiser molecule either reacts with oxygen or the reductant to form intermediates (pair of radicals) or associates with one of the reactants to form a labile reactive complex.

Anthracene, in its triplet state, readily forms a reactive, short-lived moloxide. The kinetics of the autoxidation of anthracene and that of anthracene sensitised reactions seem to be identical(118). In the direct oxidation anthracene serves both as sensitiser and as reductant. The following type of mechanism has been proposed by Lundberg(89).

$$hv + A \longrightarrow A^*$$

$$A^* \longrightarrow A + hv'$$

$$A^* \longrightarrow A$$

$$A^* \longrightarrow A'$$

$$O_2 + A^* \longrightarrow A'\,O_2$$

$$A' \longrightarrow A$$

$$O_2 + A' \longrightarrow A'\,O_2$$

$$A'\,O_2 \longrightarrow A + O_2$$

$$HR + A'O_2 \longrightarrow (A \text{ and products})$$

The reaction between moloxide and certain reductants could produce a pair of radicals and thus induce a chain reaction.

Most of the photosensitisers are substances which can give radicals by thermal or photo-dissociation at moderate temperatures. Certain dyes such as fluorescein, thiazine, azodyes, etc., have been used as photo-sensitisers to initiate polymerisation. Metal alkyls are also employed as sources of radicals in photolysis. Marvel et al(119) mentioned tetraethyl-lead as a photo-initiator in polymerisation. Chlorophylls and perphyrins are used as sensitisers in the photo-oxidations of amines; olefins, aldehydes, thioureas, etc.

Radicals are formed by thermal or photo-dissociation of stable peroxide molecules. Radicals formed by photo-dissociation may not be in their ground states and their reactivity may, therefore, be somewhat different from those of radicals generated thermally at the same temperature. Radicals can be produced by transfer reactions of different types.

(1) Electron transfer process either thermal or photo-chemical.

(2) Radical displacement which include hydrogen or halogen abstraction.

The former process gives a pair of radicals whereas the latter gives single radicals.

Di-tert-butyl peroxide is a very good source of radicals for radical polymerisation. Russel(120) has shown the **existence of** complexes between aromatic hydrocarbons and the tert-butoxy radicals and that in its complex form the radical may exhibit reduced but more selective reactivity. The reactions are:

$$(CH_3)_3C.O.OC(CH_3)_3 \xrightarrow{h\nu} 2\,(CH_3)_3C\dot{O}$$

$$(CH_3)_3C\dot{O} \longrightarrow (CH_3)_2CO + \dot{C}H_3$$

$$(CH_3)_3C\dot{O} + \text{cyclo } C_6H_{12} \longrightarrow (CH_3)_3C.OH + \text{cyclo } C_6H_{11}^{\bullet}$$

$$(CH_3)_3C.\dot{O} + CH_2{:}CH.C_6H_5 \longrightarrow (CH_3)_3CO.CH_2^{\bullet}\ CH(C_6H_5^{\bullet})$$

Frey(121) showed that when shorter wavelengths are used for the photolysis, the dissociation may take a different course and at 3000 °A about 10% of peroxide dissociates as follows;

$$(CH_3)_3C.O.OC(CH_3)_3 \longrightarrow 2(CH_3)_3\dot{C} + O_2$$

The tert-butoxy radical readily abstracts H atoms from stable molecules and this process completes successfully with addition of olefinic bonds.

4.7.1 - Investigation of photo-oxidation characteristics of bitumens containing photo-sensitising chemicals

Godrich(122) noted the increase in sensitivity to light of the naturally occurring bitumens with incorporation of sulphur. Krenkler(123,124,125) studied the effect of anthracene oil on the hardening properties of tar. He showed that a very high percentage of anthracene oil in the tar reduced the hardening properties leading to failure in hot weather. Hubrecht(126) studied the changes caused in the penetration of tar on addition of 5% of anthracene crystals. Tyutyunnikov et al(127) studied the oxidation of bitumen films containing 5-10% of manganese and cobalt naphthenates and found that the metallic naphthenates accelerated hardening of the bituminous films.

In the present work it was intended to study the effect of photo-sensitising chemicals on the photo-oxidation properties of the bitumen. A number of materials were prepared by adding different photo-sensitising chemicals (Table 12) in different proportions to 100 pen Venezuelan bitumen. A known amount of photo-sensitising material was added to a weighed amount of bitumen and mixed thoroughly by stirring after heating the mixture to 80°C for 5 minutes. These bitumens were subjected to photo-oxidation in thin films as described before with measurement of oxygen uptake and amounts of water-soluble degradation products. The complete list of materials and the rates of photo-oxidation and water-solubles formation are shown in Table 13.

TABLE 12

PHOTO-SENSITISING CHEMICALS

Nos.	Chemical	Formula	M.P. °C.	B.P. °C.
1	Anthracene	$(C_6H_4CH)_2$	216	354
2	Anthracene oil	containing 15% anthracene	-	-
3	Anethole	$CH_3.CH:CH.\ C_6H_4.OCH_3(1:4)$	22.5	235
4	Eugenol	$CH_2:CH.CH_2.\ C_6H_3(OCH_3).OH$ (1:3:4)	-	248
5	Safrole	$CH_2:CH.CH_2.C_6H_3(O_2CH_2)$ (1:3:4)	-	233
6	Di-tert-butyl peroxide	$(CH_3)_3C.O-.OC(CH_3)_3$	-	111

TABLE 13

RATE OF PHOTO-OXIDATION AND WATER-SOLUBLE OF MODEL BITUMENS

Sample No.	Photo-sensitising compound	% Photo-sensitiser in bitumen	cc O_2 uptake/cm^2/hr at S.T.P./10^{-3}	mg Water-solubles/cm^2/hr/10^{-3}
1	-	-	2.78	1.85
2	Anthracene oil	2	2.97	1.95
3	"	5	3.22	2.07
4	"	7	3.45	2.22
5	"	10	3.62	2.37
6	"	20	4.01	2.67
7	"	30	4.62	3.07
8	Anthracene	1	2.95	2.12
9	"	2	3.20	2.32
10	"	5	3.55	2.50
11	Anethole	1	2.92	2.27
12	"	2	3.20	2.40
13	"	5	3.47	2.65
14	Eugenol	1	2.92	2.05
15	"	2	3.17	2.15
16	"	5	3.45	2.42
17	Safrole	1	2.95	1.97
18	"	2	3.02	2.12
19	"	5	3.27	2.35
20	Di-tert-butyl peroxide	0.1	2.85	1.95
21	"	0.2	2.95	2.22
22	"	0.5	3.32	2.32

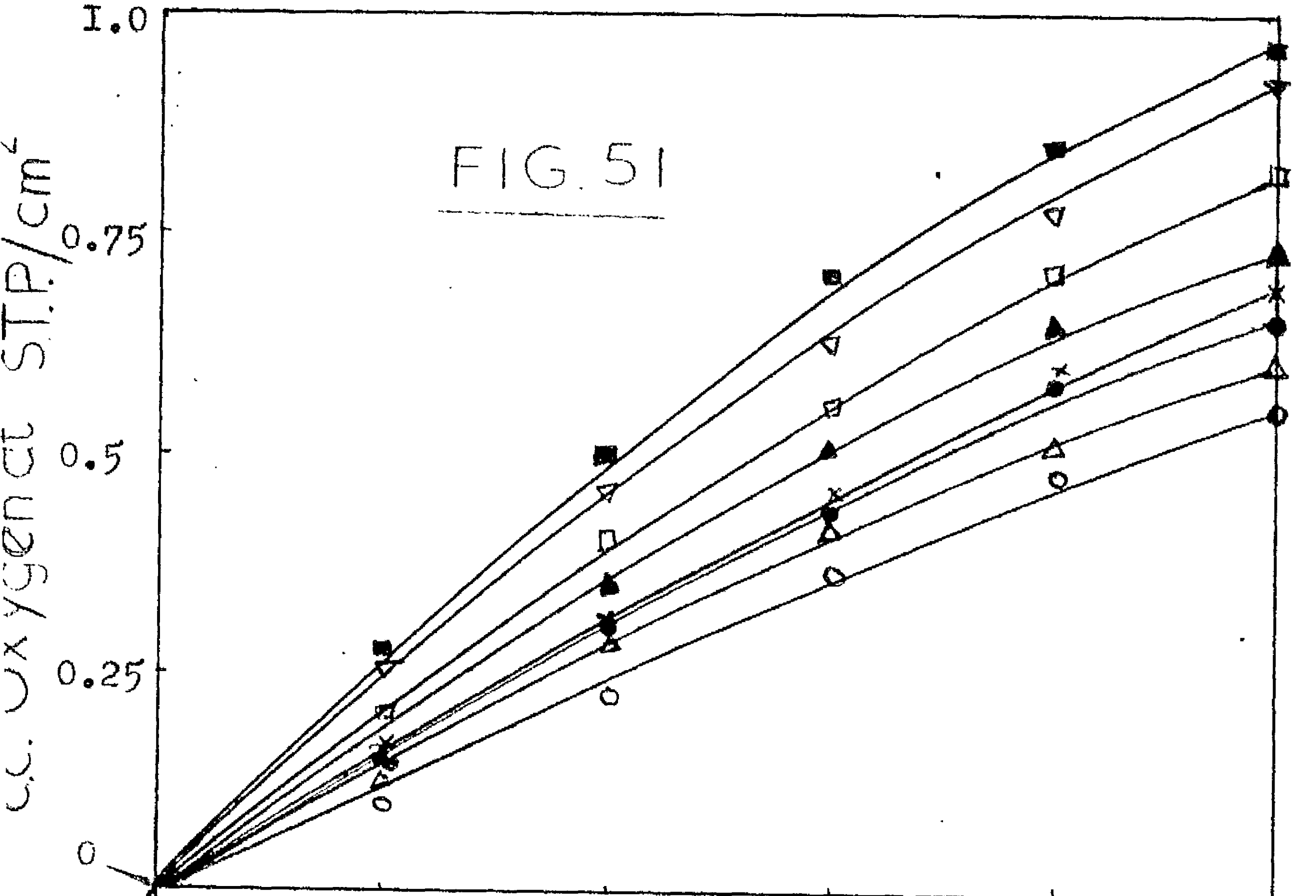
4.7.2 - Results and discussion

The photo-sensitising materials used were anthracene oil, anthracene, anethole, eugenol, safrole and di-tert-butyl peroxide. The amount of oxygen absorbed was calculated in terms of cc of oxygen/cm^2/hr. The amount of water-solubles produced was measured and calculated in terms of mg of water-solubles/cm^2/hr. From Table 13 it can be seen that oxygen absorption increases with increase in % of photosensitising chemicals. Anthracene oil at an added concentration as low as 2% increases the reactivity and is similar to the effect of 1% anthracene and 1% safrole. Anthracene crystals and anthracene oil in varying amounts produced large increases in reactivity. Di-tert-butyl peroxide gives a large acceleration with as little as 0.1% although this material is unstable at high temperatures and is not really a possibility as a bitumen additive.

Anethole, eugenol and safrole have an effect on reactivity but would not be economical for general use. If the increase in reactivity is reflected in a corresponding increase in viscosity (and skid-resistance due to traffice abrasion) then for special conditions they might be possible. The rates of photo-oxidation of model bitumens containing varying amounts of anthracene oil are also plotted in terms of cc of O_2 uptake at S.T.P./cm^2 of surface area against hours of oxidation as shown in Figure 51. The water-solubles for the said model bitumens are also plotted in terms of mg of water-solubles/cm^2 of surface area to the base of hours of oxidation, Figure 52. These show that in both cases the

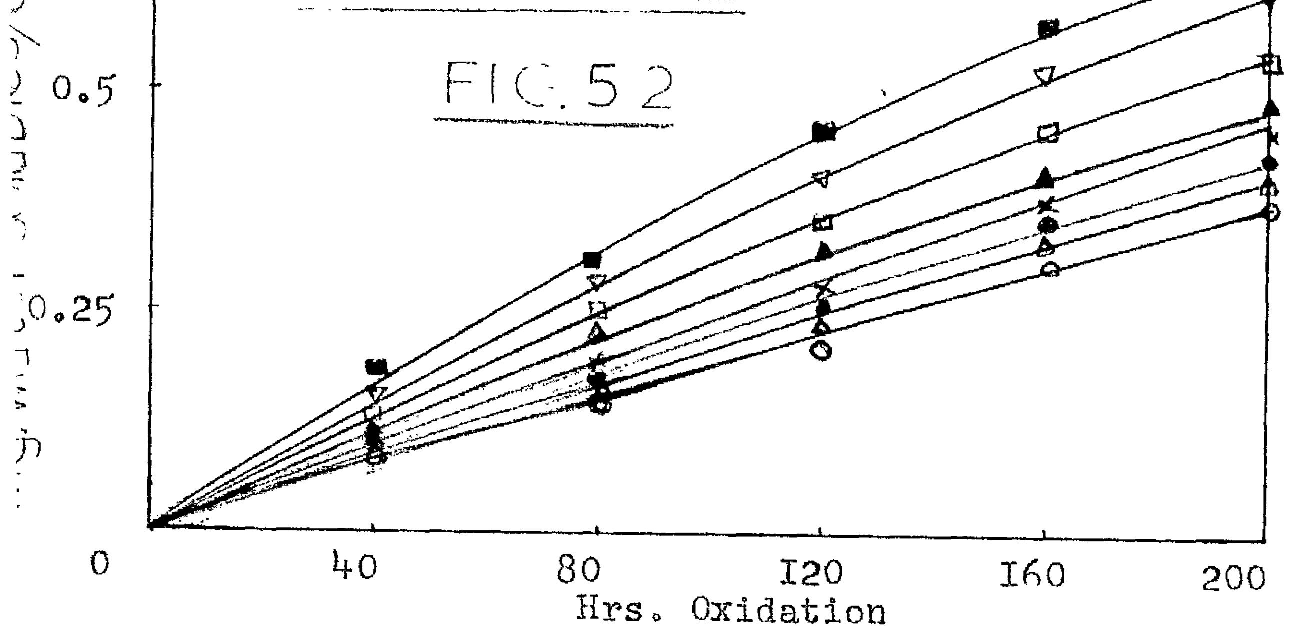
PHOTO-OXIDATION OF MODEL BITUMENS WITH VARYING AMOUNTS OF ANTHRACENE OIL

FIG. 51



WATER-SOLUBLES OF MODEL BITUMENS WITH VARYING AMOUNTS OF ANTHRACENE OIL

FIG. 52



○ Original Bitumen
△ Bitumen+2% Anthracene oil
◎ " + 5% " "
× " + 7% " "
▲ Bitumen + 10% Anthracene oil
□ " + 20% "
▽ " + 30% "
■ Trinidad Lake Asphalt

curves follow the same pattern. The relationship between oxygen absorbed and water-solubles produced is shown in Figure 53 for all the photo-sensitising additives and indicates a nearly linear relationship in almost every case.

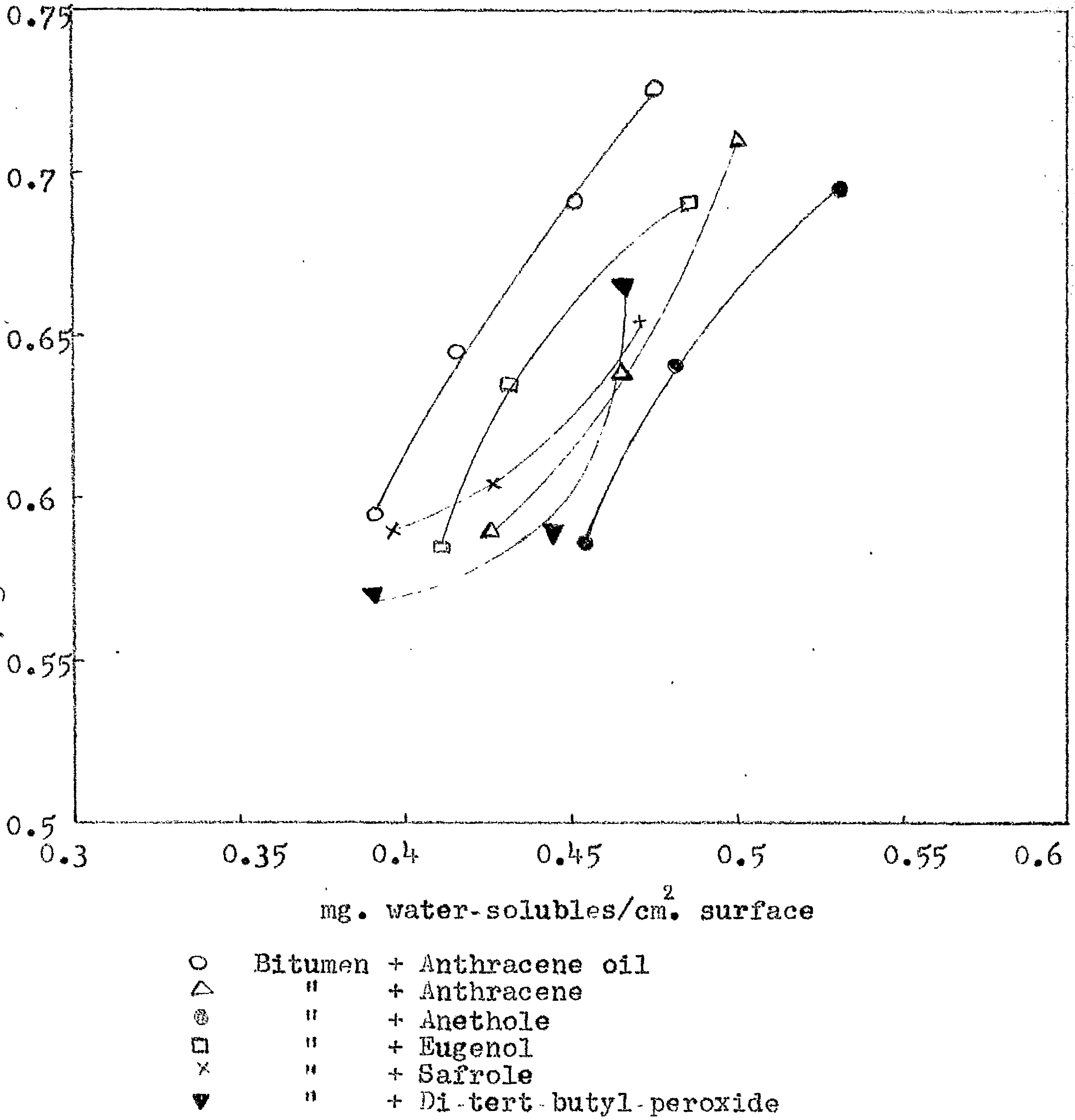
In order to study the amount of water-solubles produced and the amount of O_2 uptake ~~every~~ after 200 hours, with varying amounts of photo-sensitising chemicals, their results are represented in Figures 54 and 55. It could be seen from the figures that the quantity of di-tert-butyl peroxide required to photo-sensitise bitumen is very low, whereas the quantity of anthracene oil required is very high to produce the same effect. The decreasing order of photo-sensitiser reactivity is in order of di-tert-butyl peroxide, anthracene, anethole, eugenol and safrole for O_2 uptake. This slightly varies for water-solubles where anethole gives slightly more water-solubles than anthracene though anthracene is more reactive regarding absorption. This might be due to slight solubility of anethole in water.

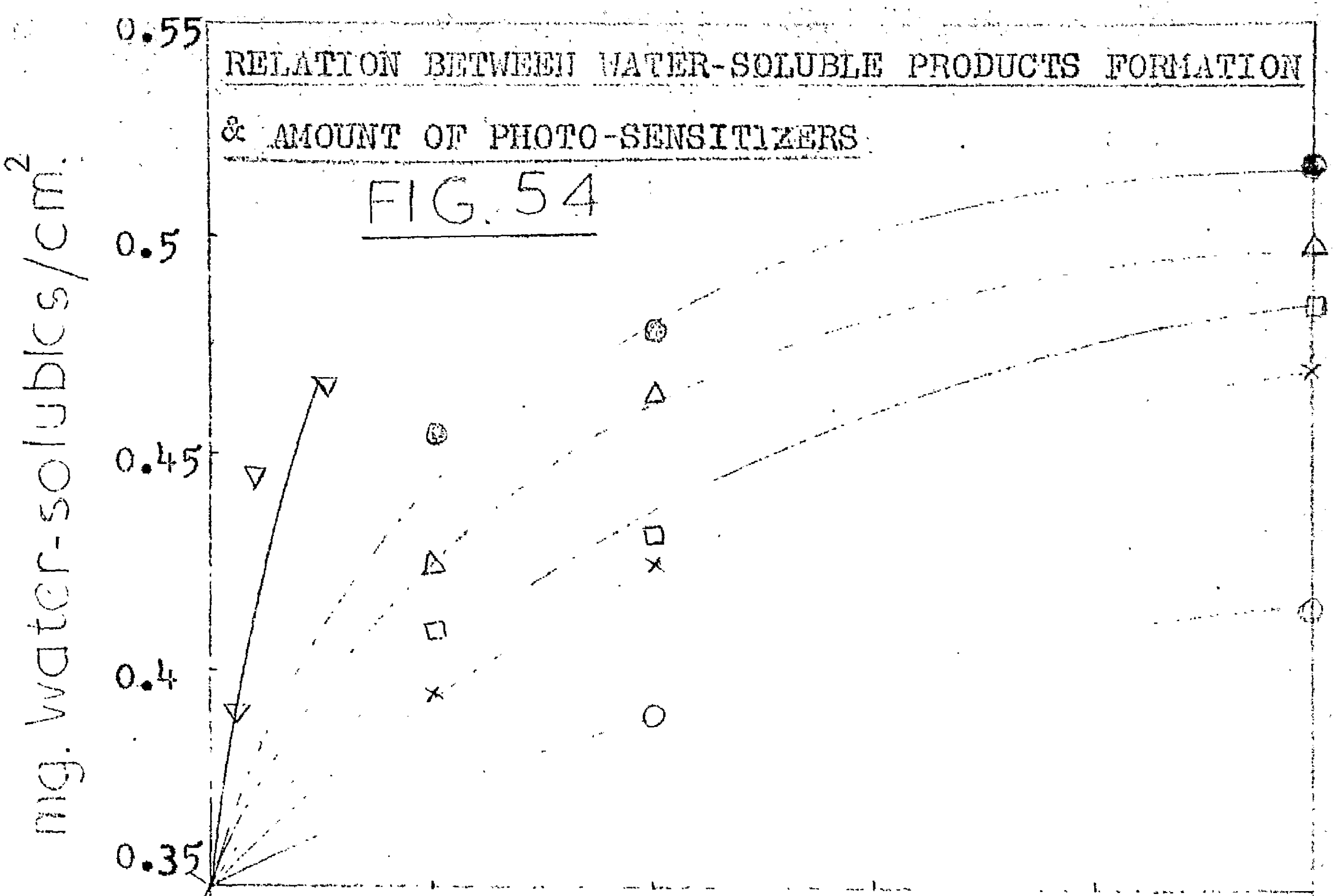
4.8 - The effect of irradiation on skin formation

Bitumen, synthetic bitumen, modified bitumens with photo-sensitising chemicals and bitumen fractions in the form of thin films on exposure to U.V. radiation formed a skin on the surface. The first indication of this skin was noted by the appearance of a slightly dull layer on the film surface at 20 hours exposure to U.V. radiation. This produced measurable amounts of water-solubles. It was found that the quantity of water-soluble products produced at 40 hours was approximately double to that produced at 20 hours. This shows that longer exposure did not have any adverse effect in the rate of

RELATION BETWEEN OXYGEN UPTAKE & WATER-SOLUBLE PRODUCTS OF PHOTO-OXIDISED MODEL BITUMENS.

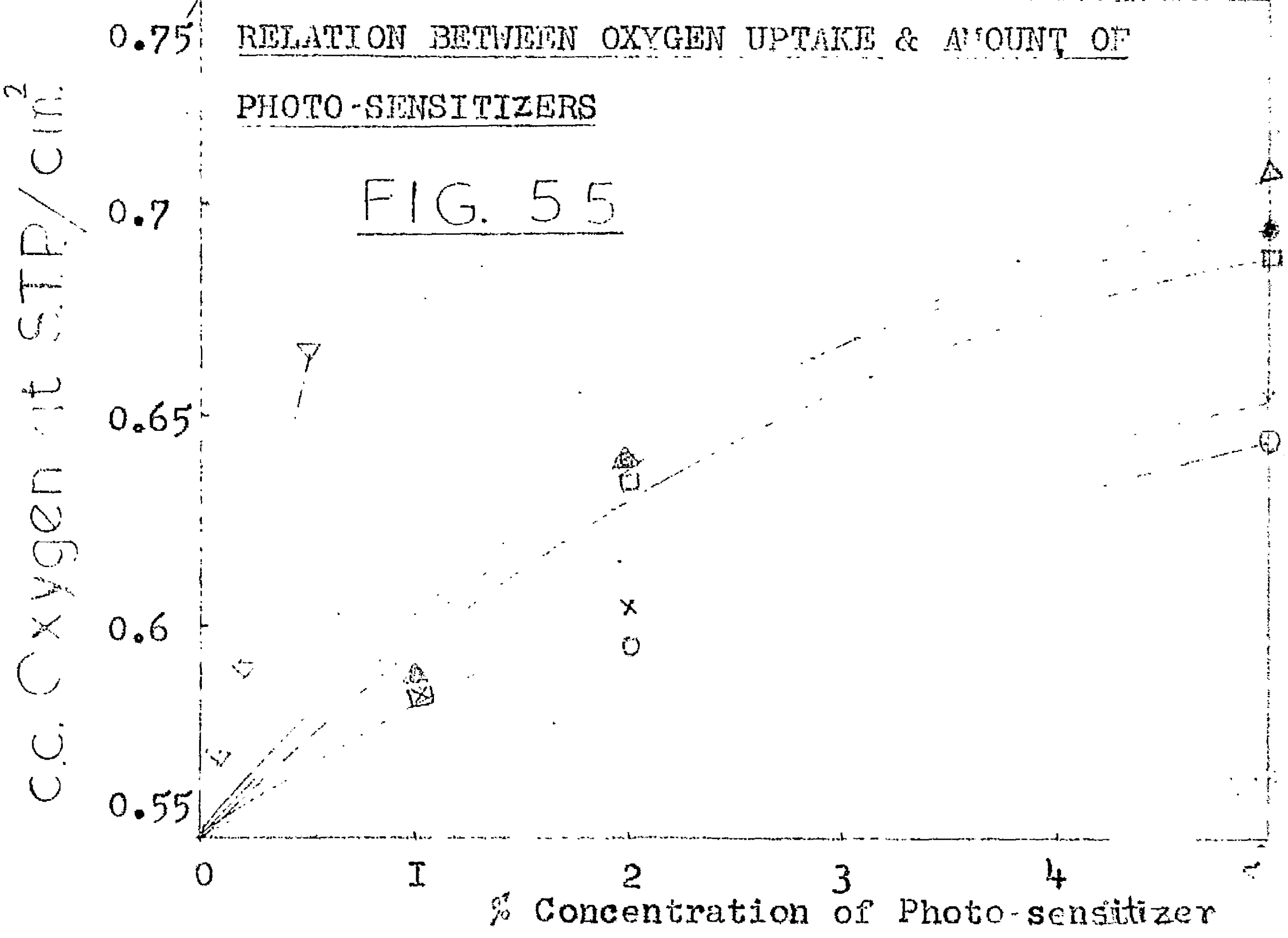
FIG. 53





RELATION BETWEEN WATER-SOLUBLE PRODUCTS FORMATION & AMOUNT OF PHOTO-SENSITIZERS

FIG. 54



RELATION BETWEEN OXYGEN UPTAKE & AMOUNT OF PHOTO-SENSITIZERS

FIG. 55

○	Anthracene oil	□	Eugenol
△	Anthracene	×	Safrole
◉	Anethole	▽	Di-tert-butyl peroxide

oxidation due to increased concentration of water-soluble products at the surface. Using 40 hours' oxidation cycles water-soluble products were removed as described under 4.5.

Skin formation was not prominent on the surface of white oil, dark oil and asphaltenes. White oil on longer exposure to u.v. radiation changed first to yellow and finally to dark brown. Dark oil was not much affected. Resin changed its skin colour forming a golden blue film. Asphaltene showed little change in skin appearance.

When the exposed samples were removed from u.v. radiation and allowed to cool down, the skin contracted and on further exposure the skin expanded. Thus it underwent all the time physical stresses and strain which eventually resulted in crack formation. A network of hair checks was observed on the surfaces of bitumens and resins. When these surfaces were exposed for a period of 200 hours, cracks were noticed which healed by new skin forming on the newly exposed surface and joining up with the original surface skin. The visual effect of the different types of skins on the surfaces are detailed in Tables 14, 15 and 16.

4.8.1 - Results of discussion

Skin formation may be of some importance from the viewpoint of road surfaces and skid-resistance in that traffic abrasion may expose aggregate more easily. Bitumens forming smooth surfaces of low skid resistance are of less importance for dense road surfacings than those forming a rougher texture.

Dull and rougher skin was formed on the Trinidad Lake Asphalt surface. This was also observed by some workers a decade(11,13) ago. In the present work it was noted that similar effects were produced on the surfaces of the modified bitumens. Photo-sensitising chemicals such as anthracene crystals, anthracene oil, eugenol and safrole when mixed with bitumen, produced similar surface textures to that produced by Trinidad Lake Asphalt. Anthracene oil is easily available from coal tar distillation and being cheap, could be used effectively with petroleum road binders to produce skid resistant properties.

TABLE 14
CHARACTERISTICS OF SKIN FORMED ON THE SURFACE OF BITUMENS AND FRACTIONS EXPOSED TO U.V. RADIATION FOR 200 HOURS

(A)	Bitumens	Characteristics of surface skin
	(1) Refinery Bitumen 1	Bright, slightly wavy skin with a network of checks. Broad checks healed.
	(2) Refinery Bitumen 2 (Venezuelan)	"
	(3) Trinidad Lake Asphalt (Filler free)	Very dull and rough skin with a network of hair checks. Very few broad healed cracks
(B)	Bitumen Fractions	Characteristics of surface skin
	(1) White oil	Very thin brown skin with a network of hair checks.
	(2) Dark oil	Slightly dull skin without checks
	(3) Resin	Golden blue skin with a network of checks
	(4) Asphaltenes	Slightly dull skin with few hair checks.

TABLE 15

CHARACTERISTICS OF SKIN FORMED ON THE SURFACES OF SYNTHETIC BITUMENS EXPOSED TO U.V. RADIATION FOR 200 HOURS

Synthetic bitumens	Characteristics of surface skin
I. Refinery Bitumens 1	
(1) Maltenes + 5% Asphaltenes	Bright, wavy skin with a network of hair checks.
(2) " + 10% "	Bright, slightly tight skin with a network of hair checks and few healed cracks.
(3) " + 15% "	Bright, tight skin with a network of hair checks and healed cracks.
II. Refinery Bitumen 2 (Venezuelan)	
(i) Maltenes + 5% Asphaltenes	Skin similar to 1 (i)
(ii) " + 10% "	" " " 1 (ii)
(iii) " + 15% "	" " " 1 (iii)
III. Trinidad Lake Asphalt	
(i) Maltenes + 15% Asphaltenes	Dull and slightly loose skin with a network of fine checks.
(ii) " + 30% "	Dull and slightly tight skin with a network of fine checks and few broad healed cracks.
(iii) " + 45% "	Very dull and rough surface skin with a network of hair checks and broad healed cracks all over.

TABLE 16

CHARACTERISTICS OF SKIN FORMED ON THE SURFACE OF MODIFIED BITUMENS WITH PHOTO-SENSITISING CHEMICALS EXPOSED TO U.V. RADIATION FOR 200 HOURS

Bitumens	Characteristics of surface skin
1 100 pen.Venezuelan bitumen	Bright, wavy skin with network of hair checks and no broad cracks
2 (i) " " 1% Anthracene crystals	Dull, wavy skin with network of hair checks and no broad-deep cracks
(ii) " " 2% "	" " " " "
(iii) " " 5% "	Very dull and rough skin with network of checks and few healed broad cracks
3 (i) " " 1% Anethole	Bright, wavy skin with network of fine checks and no deep cracks
(ii) " " 2% "	" " " " "
(iii) " " 5% "	Slightly dull wavy skin with network of checks and few broad healed cracks
4 (i) " " 1% Eugenol	Dull, wavy skin with few blisters
(ii) " " 2% "	" " " "
(iii) " " 5% "	Very dull, wavy skin with blisters, hair cracks and broad healed cracks
5 (i) " " 1% Safrole	Dull, wavy skin with network of hair checks
(ii) " " 2% "	" " " " "
(iii) " " 5% "	" " " " " and very few broad healed cracks
6 (i) " " 0.1% di-tert-butyl peroxide	Bright, wavy skin with hair lines
(ii) " " 0.2% "	" " " " " "
(iii) " " 0.5% "	" " " " " " network of hair lines with few broad healed cracks
7 (i) " " 2% anthracene oil	Slightly dull; wavy skin with few hair checks
(ii) " " 5% "	Dull " " " " "
(iii) " " 7% "	"wavy skin with network of hair checks
(iv) " " 10% "	" " " " " " " "
(v) " " 20% "	Very dull,wavy skin with network of hair checks and broad healed cracks
(vi) " " 30% "	" " " " " "

CHAPTER 5

APPENDIX - INFRA-RED SPECTRA OF ORIGINAL, THERMAL AND PHOTO-OXIDISED BITUMENS AND FRACTIONS

5. APPENDIX - INFRA-RED SPECTRA OF ORIGINAL, THERMAL AND PHOTO-OXIDISED BITUMENS AND FRACTIONS

Infra-red spectroscopy is a very useful analytical tool in studying the chemical structure of complex hydrocarbons like bitumens. The object of the present work is to study the functional groups of bitumens and their fractions and also to study the changes occurring in them when subjected to thermal and photo-oxidation.

Knotnerus(128) employed I.R. spectroscopy to study the oxygen containing functional groups formed during the air blowing of bitumens. He concluded that as hydrogen bridges were not observed between the high molecular acids and solvent, this ruled out the possibility of predominant acids. This was taken as proof that esters were the predominant oxygen-containing types. This was argued by Campbell and Wright(116) who maintained that the presence of 'acid-solvent hydrogen bridges' would be extremely difficult to detect in a solution containing the bitumen by I.r. spectroscopy and regarded the earlier work as weak evidence for selecting esters rather than acids as predominant oxygen-containing molecules.

Stewart(113) studied changes produced in the constitution of bitumen on outdoor exposure using infra-red analysis. Fischer and Schram(129) studied the constitution of asphaltic bitumen spectroscopically in connection with mild hydrogenation. THey also used polarographic methods for 'model bitumens' and concluded that asphaltenes consisted of aromatic ring systems strongly substituted by paraffinic chains with multiple oxygen links. Naphthene rings were present to a minor extent and the aromatic rings were condensed systems. Beitchman(130) studied the changes caused in blown bitumens when subjected to carbon arc radiant exposure in 25 μ thick films by using infra-red analytical techniques. He observed that the absorption band increased at 2.91, 5.88 and 9.71 micronregion suggesting increase of OH, C=O and C–O groups respectively. Yen and Erdman(71) used infra-red spectroscopy to study asphaltene structures.

Campbell et al(29) examined the oxidation of bitumens after both accelerated and natural weathering. Using infra-red analysis to measure changes after fixed periods of exposure and also as a function of exposure time. Schweyer(131) applied infra-red analysis to the study of the properties of bituminous materials. Romberg et al(132) used similar techniques to study the bitumen components from gel, sol-gel and sol bitumens. Campbell et al(116) added model organic compounds to bitumens and compared the infra-red spectra of these new synthetic model compounds with that of photo-oxidised bitumens. By this technique they concluded that the principal oxygen containing products formed in the bitumen during natural exposure or photo-oxidation were aldehydes, ketones and acids. Wright and Campbell(133) also studied the oxidation rates of blown bitumens exposed to a carbon arc by measuring the change in the infra-red absorption in the 5.88 micron region. They concluded that there was an induction period followed by a steady oxidation rate until near the failure point when the oxidation rate accelerated until film failure took place as indicated by bitumen film cracking. Greenfeld and Wright(134) in their photo-degradation studies also measured the carbonyl absorption at 5.88 micron, this being relatively free from interference by absorption of other groups.

5.1 - Experimental procedure

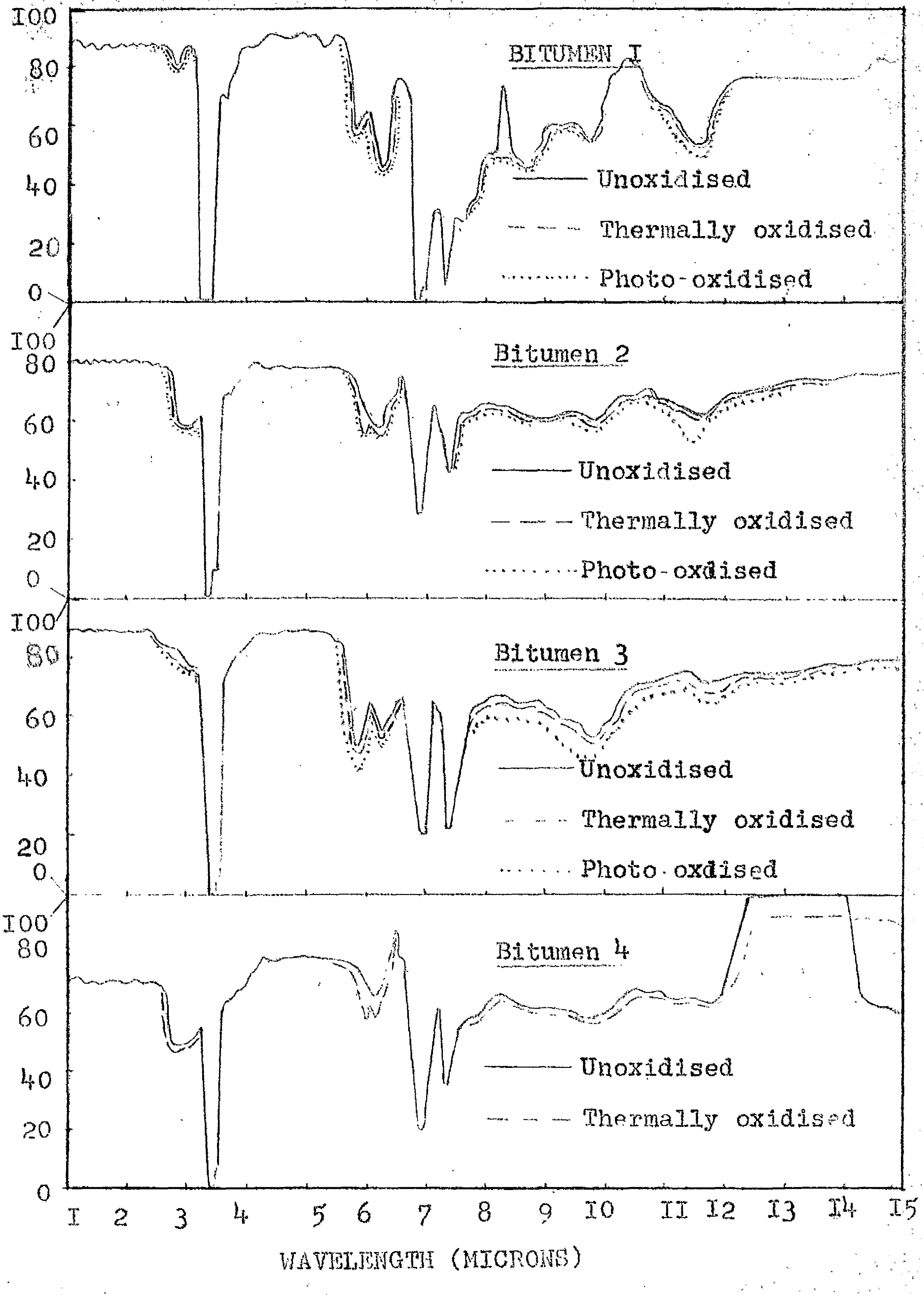
I.R. spectra of bitumens and fractions before oxidation were scanned as described under Section 2.1. Thermally oxidised samples were similarly scanned after removal of xylene solvent under vacuum. I.R. of photo-oxidised samples were scanned by dissolving the surface of the oxidised samples using carbon tetrachloride and then employing the methods described under Section 2.1

5.2 - Infra-red spectra of original bitumens

Infra-red spectra of the four bitumens used are shown in Figure 56. In general, all look similar with some variation in absorption band heights. It is possible to determine the types of group present in the molecule from the position of the absorption bands. Table 17, represents the types of groups present at different band locations. The presence of poor absorption band in the region of 2.95 micron in 1 and 3 suggested the presence of OH and/or NH groups in a very small amount. These absorption bands were well defined in 2 and 4 suggesting the presence of OH and/or NH groups in a fair amount. The characteristic of 3 was that it showed a prominent carbonyl (C=O) absorption band

INFRARED SPECTRA OF BITUMENS I,2,3 AND 4.

FIG. 56



at 5.88 µ region which was due to aldehydes, ketones and/or acids(113), 1 showed little carbonyl absorption in this region, whilst 2 and 4 did not show any distinct absorption band in this region probably due to overlapping of aromatic band.

All four spectra showed signs of the aromatic nature of the bitumens. The absorption in the region of 6.25, 11.5, 12.24 and 13.35 micron were characteristic of aromatics(113,136). 1 showed absorption of very high intensity at 6.25 and 11.5 micron regions, suggesting that 1 was highly aromatic compared to others. The aromatic character observed in the remaining three were in increasing order of 2, 4 and 3. Absorption bands on the region of 12.24 and 13.35 micron were not very well defined in any of these four spectra.

Absorption in the 3.0 to 3.5; 6.5 to 7.5 and 12.5 to 14.3 micron regions were characteristic of CH stretching, HCH bending and CH_2 wagging vibrations respectively(137). Absorption in the 3.0 to 3.5 micron region was due to C-H stretching in methyl (CH_3) and methylene (CH_2) groups present in the paraffin hydrocarbons, naphthene hydrocarbons and paraffinic side chains on aromatic hydrocarbons. Absorption at 6.5 to 7.0 micron was due to methyl and methylene groups present in paraffins and naphthenes. Absorption in 7.1 to 7.5 micron region was only due to methyl groups present in paraffins, naphthenes and aromatics. Absorption from 12.5 to 14.3 micron was primarily due to methylene groups in paraffins and paraffinic side chains. Paraffinic methylene groups could be determined by the average absorption in this region along withthe absorption at 3.38 to 3.42 micron which is due to methyl and methylene groups(137).

Bitumens 1 and 4 showed absorption of high intensity in the 6.8 micron region due to the presence of methylene groups in higher amounts than were present in 2 and 3. The absorption intensity of 3 at 7.25 microns was higher than the others indicating higher amounts of methyl groups than others. This also indicated Bitumen 3 had highly branched paraffinic chain. Absorption bands in 12.5 to 14.3 micron regions were not very prominent in any of the samples. Bitumen 3 showed high absorption at 9.71 micron which may be due to presence of C-O, S=O or Si-O groups(135). 1, 2 and 4 showed only about half this absorption intensity The absence of absorption between 5.95 and 6.25 micron was an indication that no olefinic structure was present.

5.2.1 - Infra-red spectra of thermally oxidised bitumens

On thermal oxidation all the bitumen samples showed a slight increase in absorption intensity at 2.95 micron suggesting a slight increase in OH groups. The appearance of distinct absorption bands in 2 and 4 at about 5.88 micron was due to increase in carbonyl groups (C=O). 1 and 3 in this region also showed the increase in band intensity suggesting the increase of these groups on oxidation. The increase in absorption intensity at 11.5 micron in all oxidised bitumens showed an increase in aromatic substitution.

The absorption bands at 9.7 micron increased in all oxidised samples suggesting an increase in C-O links.

It may be concluded that on thermal oxidation of bitumens aldehyde, ketone and/or acid groups, aromatic substitution, OH groups and C-O groups are formed or increased.

5.2.2 - Infra-red spectra of photo-oxidised bitumens

5.2.2 - Infra-red spectra of photo-oxidised bitumens 56) showed similar changes to those produced in thermally oxidised bitumens. The intensity of absorption bands at 5.88, 9.7 and 11.5 µ showed substantial increase in all samples suggesting increase in carbonyl, C-O and aromatic substitution respectively. Bitumen 3 showed highest intensity at 5.88 and 9.7 µ suggesting its higher rate of photo-oxidation than bitumen 1 and 2.

TABLE 17

ABSORPTION BANDS FOR VARIOUS FUNCTIONAL GROUPS

Position of absorption band microns	Functional group
2.66 - 2.98	$-OH$
2.88 - 3.28	$-NH$
3.0 - 3.5	$-CH_3$. $-CH_2$
5.4 - 5.56	C=O (anhydrides)
5.7 - 5.9	C=O (carbonyl)
5.7 - 5.9	Acids
5.7 - 5.8	Esters
5.8 - 5.9	Ketones
6.17 - 6.30	C=C (aromatic)
6.85	$-CH_2$
7.1 - 7.5	$-CH_3$
9.71	C-O (carbon-oxygen)
	S=O
	Si-O
10.3	Cycloparaffin
11.48	1,2,3 and 4 H atoms in aromatic structure
12.24	
13.1	
13.4	
13.3 - 13.9	$-CH_2$ in paraffins and paraffinic side chains

5.3 - Infra-red spectra of white oils

All white oil fractions gave identical infra-red spectra (Figure 57) except for a slight variation in the absorption intensities and aromatic contents. All fractions were predominantly paraffinic with or without slight aromatics. The infra-red spectra of white oils were identical to that of pure liquid paraffin suggesting very similar structures. 1 and 4 showed little aromatic content which was marked by the presence of ring vibration at 6.25 µ and weak absorption at 12.25 µ suggested the presence of paradisubstitution type of aromatic ring(113). Characteristic of saturated aliphatic hydrocarbons containing $-CH_3$ and $-CH_2-$ groups were strong absorption bands due to C-H stretching vibrations at 2.78 to 3.71 µ; there was also absorption at 6.85 and 7.28 µ due to deformation vibrations of the $-CH_2-$ and CH_3-C groups. A strong absorption band at 13.9 µ suggested long paraffinic chains of four or more carbon atoms. The intensity of this band was in decreasing order of 1, 2, 4 and 3. Longer wavelength absorption suggested the longer chains than absorption at shorter wavelengths.

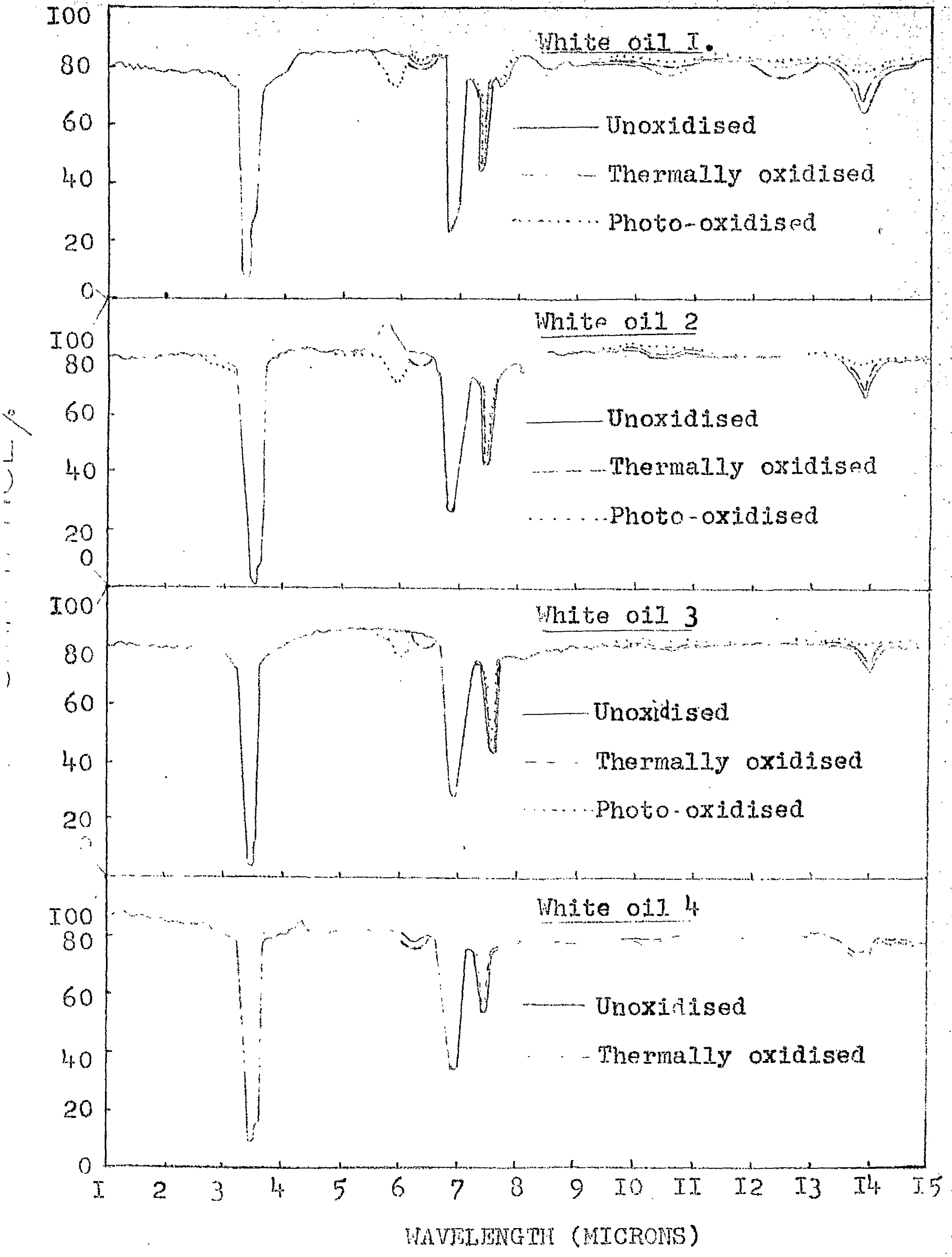
The weak absorption at 10.2 µ suggested the presence of small amounts of cycloparaffins. The absence of absorption band at 2.91, 5.88 and 9.77 µ region suggested the absence of oxygen containing groups.

5.3.1 - Infra-red spectra of thermally oxidised white oils

All oxidised samples showed identical infra-red spectra (Figure 57) to the unoxidised samples except for a slight

INFRARED SPECTRA OF WHITE OIL FRACTIONS OF BITUMENS I,2,3&4.

FIG. 57



change in absorption intensity. A slight increase at 6.25 and 12.25 μ suggested a slight increase in aromatic content which could be at the expense of cycloparaffins which showed a decrease in absorption at 10.2 μ. All showed a decrease in absorption intensity at 7.25 and 13.8 μ suggesting the reduction in paraffinic chain length and reduction in branching.

5.3.2 - Infra-red spectra of photo-oxidised white oil

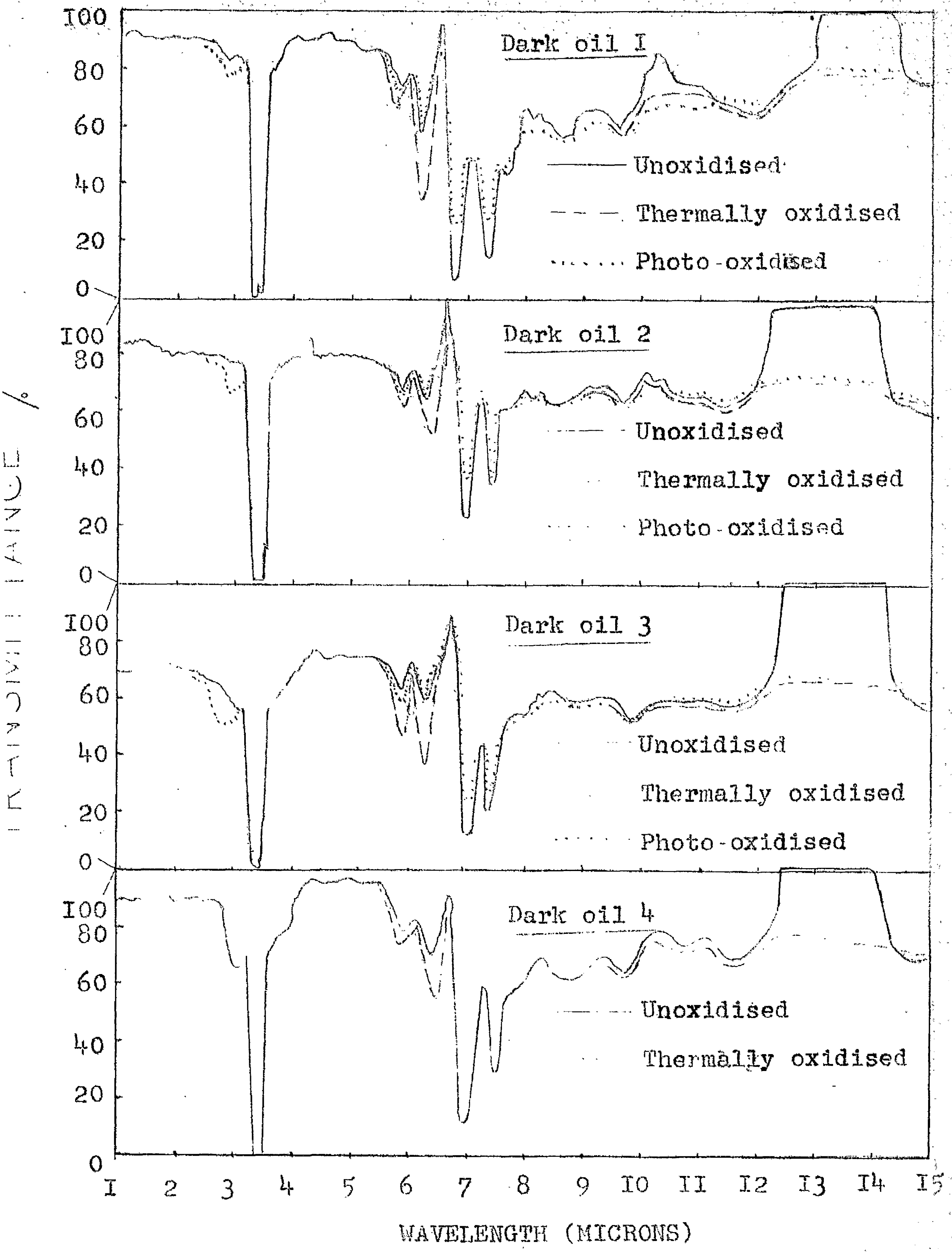
Photo-oxidised white oil fractions showed the formation of a new band at 5.88 μ (Figure 57). This suggested that photo-oxidation formed carbonyl groups i.e. aldehydes, ketones or acids which were not present in unoxidised white oils and were not formed on thermal oxidation. The absorption band at 13.8 μ decreased to a greater extent by photo-oxidation than by thermal oxidation. This implies that photo-oxidation has more deteriorating influence on white oil fractions than thermal oxidation. The absorption in the 9.50 to 11.2 μ region was not observed suggesting that cycloalkanes were lost on photo-oxidation. On photo-oxidation bitumen 1 showed decrease in absorption at 6.25 and 12.25 μ suggesting decrease in aromatic contents.

5.4 - Infra-red spectra of dark oil

Infra-red spectra of all four samples were identical (Figure 58) except for a slight variation in the intensity of bands. All were highly aromatic in nature as shown by the absorption bands at 6.25 and 11.5 micron regions. Aromaticity was high in 1 and 4 and low in 2 and 3. Absorption at 2.91 micron

INFRARED SPECTRA OF DARK OIL FRACTIONS OF BITUMENS I,2,3&4.

FIG.58.



in 1 and 4 showed the presence of -OH or -NH groups. This absorption band was not observed in 2 and 3. In all samples absorption band at 5.88 micron was observed with varying intensity suggesting a varying amount of aldehyde, ketone or acids present. This was greatest in 3 and lowest in 4.

Absorption at 11.5 is probably due to aromatic substitution. Absorption at 9.7 micron suggests the presence of C-O, S=O or Si-O group.

5.4.1 - Infra-red spectra of thermally oxidised dark oils (Figure 58)

On thermal oxidation the infra-red spectra of all dark oils showed a large increase in the absorption band intensity at 5.98 micron indicating an increase in carbonyl group; 1 and 3 showed a twofold, 4 and 2 a 50% increase in band intensity in this region. This suggested that 1 and 3 oxidised to a greater extent than 2 and 4. The absorption band intensity at 6.25 micron increased by a factor of 2 in oils 1 and 3, and one and a quarter times in 2 and 4 suggesting a respective increase in aromatics. The absorption band intensity at 9.6 micron increased in all cases suggesting increase in C-O links. Increase in absorption at 11.5 micron suggested the increase in aromatic substitution. It appears then that on thermal oxidation of dark oils increase in carbonyl and aromatics are considerable.

5.4.2 - Infra-red spectra of photo-oxidised dark oils (Fig.58)

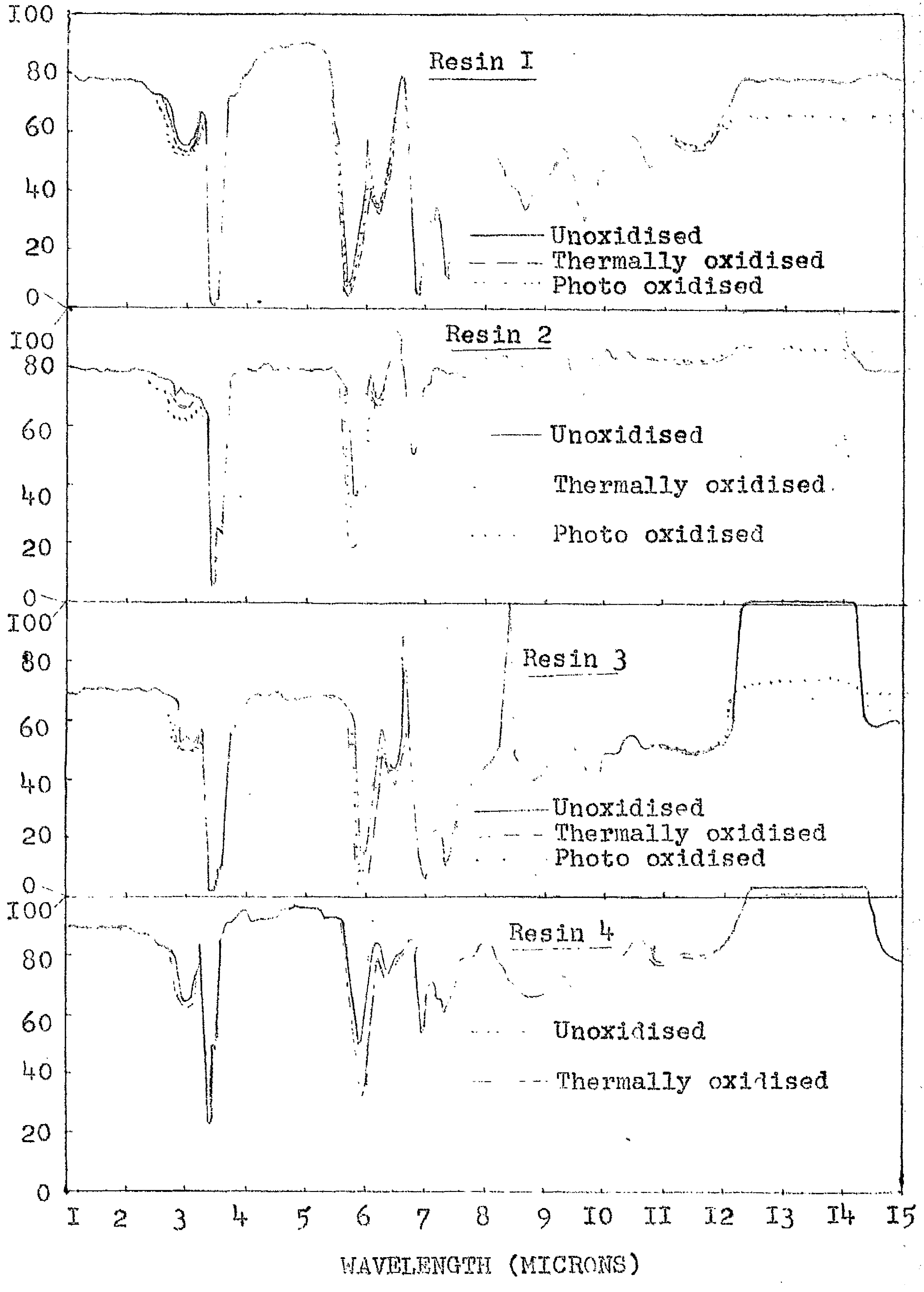
On photo-oxidation of dark oil fractions the infra-red spectra show little change in intensity of absorption bands. The absorption band intensity at 5.95 µ increased slightly showing a slight increase in aldehydes, ketones or acids. The absorption band intensity at 6.25 and 11.5 µ regions decreased to a large extent in 1 and 2 and to a lesser extent in 3 suggesting an overall decrease in aromatic content on photo-oxidation. Absorption at 2.95 µ was observed in all oils suggesting the formation of hydroxyl groups. Thus, on weathering, dark oils showed increase in hydroxyl and carbonyl groups and decrease in aromatic contents.

5.5 - Infra-red spectra of resins (Figure 59)

All resin samples show absorption at 2.95 micron suggesting the presence of -OH or -NH group. 1 and 4 showed higher absorption in this region. All showed strong absorption bands at 5.85 micron suggesting high acidity or high in aldehydes or ketones. Each spectrum showed distinct 6.25 micron absorption band which was highest in 1 and lowest in 2 confirming the aromatic character of resins. Resins were slightly more aromatic than dark oils according to the intensity of absorption band at 6.25 and 11.5 micron region. This is in agreement with Stewart's(113) views. All showed the same absorption intensity at 9.7 micron suggesting equal amount of C-O, S=O or Si-O group. Absorption bands of medium intensity at 3.40, 6.82 and 7.2 micron region suggested the presence of aliphatic chains.

INFRARED SPECTRA OF RESIN FRACTIONS OF BITUMENS I,2,3&4.

FIG. 59



5.5.1 - Infra-red spectra of thermally oxidised resins

On thermal oxidation, resins 2, 3 and 4 showed the carbonyl absorption band intensity at 5.85 region increased to a larger extent whereas 1 showed little change. The 6.25 u aromatic absorption band increased slightly in 1 and a little more in 2, 3 and 4. Slight increase in absorption at 11.5 and 12.2 indicates increase in aromatic substitution. A slight increase at 2.95 micron also suggests increase in -OH or -NH group.

5.5.2 - Infra-red spectra of photo-oxidised resin fractions

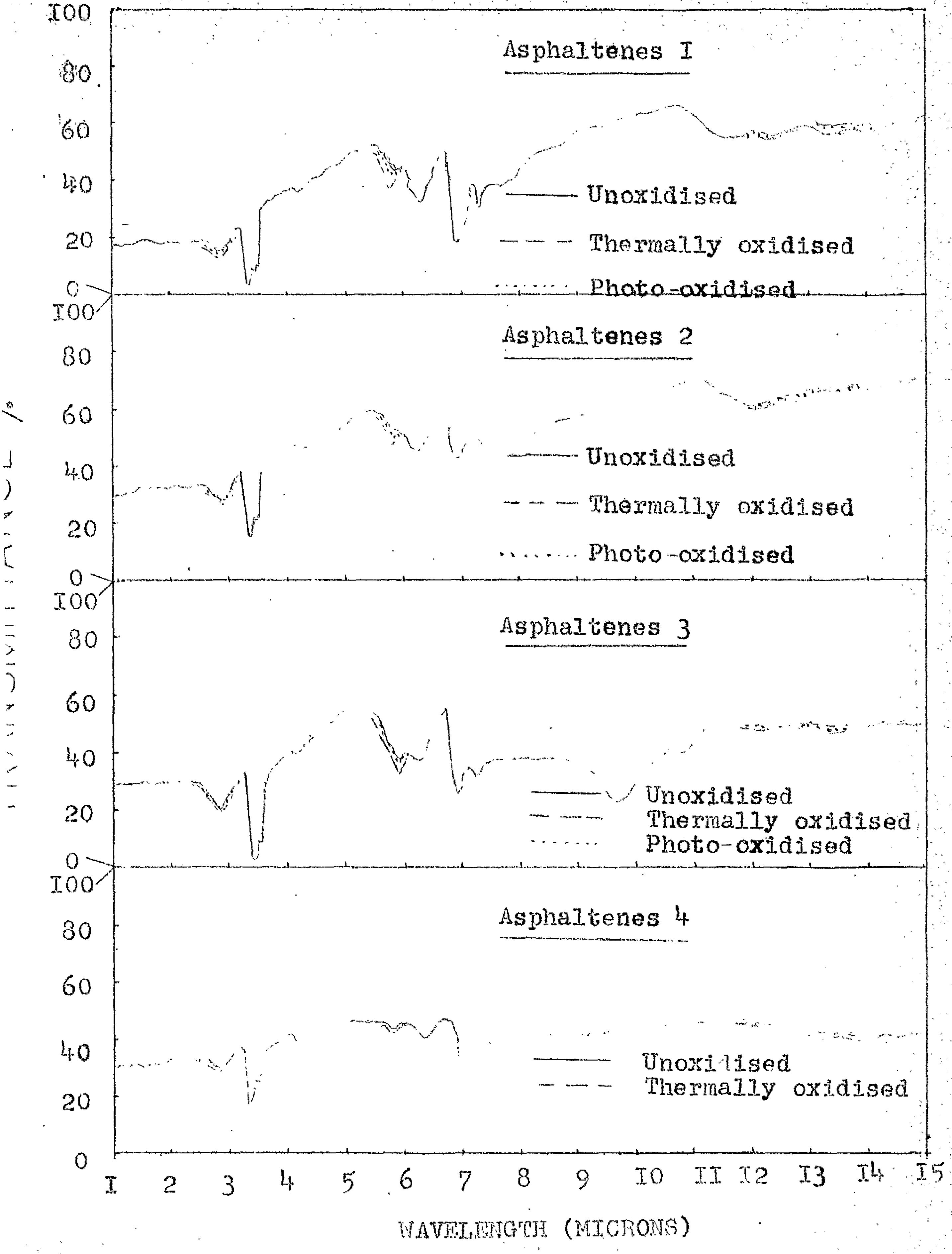
The infra-red spectra showed an increase in absorption intensity at 5.85 micron suggesting increase in aldehydes, ketones and/or acid group. 3 showed greater absorption than others in this region indicating greater oxidation. Other bands at 9.7 micron was unaltered, shows no change took place in C-O links. A slight increase at 6.25 and 11.5 micron observed in all cases showed increase aromatic content. Absorption at 2.95 also showed increase, suggesting an increase in hydroxyl group. Absorption decreased at 13.8 micron suggesting the increase in aromatics at the cost of paraffinics.

5.6 - Infra-red spectra of asphaltenes (Figure 60)

All unoxidised asphaltenes gave absorption bands at 2.85 and 5.85 μ region suggesting the presence of -OH or -NH groups and carbonyl groups. All showed absorption of high intensity at 6.25 μ and low intensity absorption at 11.5, 12.2 and 13.3 μ region suggesting the high aromatic

INFRARED SPECTRA OF ASPHALTENES FRACTIONS OF BITUMEN I,2,3&4.

FIG. 60



character of asphaltenes. Absorption bands of medium intensity at 3.40, 6.82, 7.2 and 13.8 µ suggest the presence of aliphatic groups. Boyd and Montgomery(139) used infra-red analysis for determining the methyl and methylene groups present in asphaltenes and resins using 7.28, 3.42 and 3.50 µ region. They also used absorption at 6.25 micron to determine the aromaticity. Considering and comparing the absorption band intensity at 6.25 micron with others at 3.40, 6.82, 7.2, 13.8 it could be concluded that asphaltenes are highly aromatic in nature. 3 showed an absorption band at 9.7 suggesting the presence of C-O, S=O or Si-O. This band was not observed in others.

5.6.1 - Infra-red spectra of thermally oxidised asphaltenes

On thermal oxidation each asphaltene fraction showed increase in carbonyl and -OH groups by the increase in absorption at 5.88 and 2.9 µ. The absorption band at 13.8 µ decreased slightly in intensity in all samples suggesting a decrease in paraffinic chain length. There was a slight increase in absorption at 12.2 µ suggesting an increase in aromatic substitution. Thus, it could be concluded that on thermal oxidation the carbonyl (aldehyde, ketone or acid) and hydroxyl groups increased at the expense of paraffinic chain length.

5.6.2 - Infra-red spectra of photo-oxidised asphaltene

Infra-red spectra showed little difference in absorption intensities on photo-oxidation of asphaltenes. Absorption increased slightly at 2.9, 5.85, 6.25 and 12.2 µ suggesting increase in OH, C=O, aromatic and aromatic substituted rings. Absorption decreased slightly at 13.8 showing a slight decrease in paraffinic group content.

Thus, on photo-oxidation asphaltenes showed little increase of OH, C=O and aromatics.

5.7 - Discussion

Examination of the original petroleum bitumens and Trinidad Lake Asphalt by infra-red spectroscopy has indicated that similar structural groups occur in all the bitumens used, although the amounts may vary. Petroleum bitumens are more aromatic in character and possess long paraffinic chains whereas Lake Asphalt would appear to have heavily branched chains attached to a less aromatic structure. Another difference in the higher content of carbonyl groups (plus C-O, S=O or Si-O groups) in LakeAsphalt, while the petroleum bitumens give indications of having higher amounts of OH and NH groups.

On both thermal and photo-oxidation all the bitumens studied showed an increase in aromatic content, carbonyl and hydroxyl groups, with the Lake Asphalt giving a greater increase in carbonyl groups than the others, in agreement with its higher rate of oxidation. Martin(144) has suggested that hydrocarbon complexes containing highly branched chain structures, oxygenated groups and naphthenes are likely to be most affected by weathering. This is in accord with the higher reactivity of Trinidad Lake Asphalt.

The various fractions were also examined by infra-red spectroscopy, before and after thermal and photo-oxidation. The results obtained are outlined as follows:-

White oil fractions. These fractions were predominantly paraffinic-naphthenic in all cases, with occasionally a trace of aromatic material retained.

Thermal oxidation appears to have caused formation of a small amount of aromatics with decrease in naphthenes and length of paraffinic chain. On photo-oxidation carbonyl groups were formed with more severe loss of naphthenes and paraffinic chains, suggesting more extensive deterioration of this formation in the presence of ultra-violet light.

Dark oil fractions of all the bitumens indicated a high aromatic character and the presence of carbonyl, hydroxyl and -NH groups. Thermal oxidation produced an increase in carbonyl groups with increase in aromatic content, while photo-oxidation showed increase in carbonyl and hydroxyl groups with decrease in aromatics.

Resin fractions in all cases gave indications of hydroxyl, carbonyl and -NH groups in a highly aromatic structure. Suggestions were that C-O and S=O or SiO were also present.

On both thermal and photo-oxidation carbonyl and hydroxyl content increased as did aromatic percentage. Photo-oxidation also reduced the amount of paraffinic chains.

Asphaltenes of all the bitumens were highly aromatic in nature with structural groups similar to the resin fractions. Both 'dark' and 'light' oxidation produced an increase in carbonyl and hydroxyl groups and a decrease in paraffinic content.

GENERAL DISCUSSION

6. GENERAL DISCUSSION

The analytical techniques described in Chapter 2 of the thesis provides the basis for the general characterisation of bitumens and their fractions from different sources. The compositions of various petroleum bitumens and of Trinidad Lake Asphalt differed considerable and the bitumens should, therefore, behave differently under weathering conditions. Trinidad Lake Asphalt contained more than twice the amount of asphaltenes than did the petroleum bitumens. Chromatographic separation by the modified Kleinschmidt technique gave good repeatability and the method is useful for simple fractionation.

Analysis by nuclear magnetic resonance gave an indication of the different types of the hydrogen distribution in bitumens and their fractions and suggested that the white oil fraction of all bitumens was paraffinic-naphthenic in character with straight or heavily branched chains. The dark oil fraction contained slightly more aromatic hydrogen than the resin fraction, whilst the asphaltene fraction was difficult to analyse due to its paramagnetic properties.

Infra-red analysis of petroleum bitumens and T.L.A. indicated the presence of similar structural groups in varying amounts. Petroleum bitumens were slightly more aromatic than T.L.A. and possessed long paraffinic chains with little branching, whereas T.L.A. contained short, heavily branched chains. Other notable differences between the bitumen types was that T.L.A. contained higher amounts of carbonyl and C-O, S=O or Si-O groups and less OH or NH groups than the petroleum bitumens. The white oil fraction of both the types of bitumens showed paraffinic-naphthenic characteristics with or without aromatics being present.

The I.R. spectrum of white oil compared with that for pure liquid paraffin, suggested identical structures. The dark oil fraction from all the bitumens had high aromatic contents and a considerable amount of hydroxyl and carbonyl groups. Resins also were highly aromatic and contained greater amounts of hydroxyl and carbonyl groups as well as indicating the presence of C-O, S=O or Si-O.

Asphaltenes were highly aromatic with hydroxyl and carbonyl groups.

Asphaltenes from T.L.A. in addition to the above groups showed the presence of high amounts of C-O, S=O, or Si-O groups. All the fractions and bitumens on oxidation gave infra-red absorption bands at 2.9, 5.88, 6.25, 9.7, 10.3, 11.5 and 13.8 micron regions suggesting changes in concentration of hydroxyl, carbonyl, aromatics, C-O (S=O or Si-O) cycloparaffins, aromatic substitution and paraffinic chains respectively. These changes were observed to a greater extent in T.L.A. than petroleum bitumens confirming that the former was more easily oxidised.

Sulphur determination by a modified bomb method gave good repeatability and average values indicated that asphaltenes contained the largest amount of sulphur (5.47%) with the white oils having the lowest content (1.44%). Dark oils showed a higher average sulphur (4.33%) content than the resins (3.68%). Trinidad Lake Asphalt had a higher percentage of sulphur (4.73%) than the average sulphur contents of petroleum bitumens (3.86%). Romberg et al(132) also found the highest concentration of sulphur in the asphaltic fractions and the lowest in the paraffinic fractions of bitumens. The relationship of sulphur content to the reactivity of the bitumens and their fractions is not easily understood. The white oil fraction containing a low amount of sulphur gave low rates of oxidations in the dark and high rates in the presence of ultra-violet light. On the other hand, asphaltenes containing a high amount of sulphur, were very reactive in dark oxidation but less so in the presence of ultra-violet light.

Jezl(143) had shown that sulphur compounds in mineral oils had a retarding effect on oxidation rates but this inhibiting effect was appreciably reduced by the presence of aromatics, particularly the mononuclear type. The individual fractions of the bitumens are of such complex structure that the influence of sulphur on reactivity could not easily be studied in any specific manner as it would have involved a study of the oxidation of model compounds.

The thermal oxidation method (Chapter 3) is a rapid method of measuring the oxygen absorbed by small amounts of bitumens and their fractions. The reactivities shown by the fractions were in the decreasing order of asphaltenes, resins, dark oil and white oil.

Thurston and Knowles(25) have also indicated asphaltenes oxidised most readily and oils were most resistant in dark conditions. Trinidad Lake Asphalt containing a much higher proportion of asphaltenes than the petroleum bitumens studied and in view of the fact that asphaltenes are so reactive it can be suggested as a simple explanation that Lake Asphalt is more reactive due to its higher asphaltene composition.

The theoretical rates of oxidation of the various bitumens calculated from the individual rates of oxidation of their fractions agreed well with the observed rates, except for Bitumen 1. This could be possibly due to the presence of a high amount of the low reactivity white oil providing a synergistic effect on the oxidation of the hydrocarbon complex. It is surprising that theoretical and observed rates are in such good agreement as it might have been expected that a more inhibiting or accelerating effect would have been evident. The effect of temperature on the thermal oxidation rates of bitumens and fractions showed that for every 10°C rise in reaction temperature, the reaction rate doubled.

A kinetic study of the oxidation of bitumens in the dark had shown that Trinidad Lake Asphalt was a moderately reactive bitumen with an overall activation energy of 13.97 k.cals/mole with the petroleum bitumens of low reactivity having overall activation energies ranging from 14.85 to 17.60 k.cals/mole. Bitumens of moderate reactivity are considered to be most suitable for road binders(12) and this had been confirmed in full-scale road experiments(11,14). Bitumens of low reactivity can be modified to the desired reactivity by either blending with suitable bitumens or bituminous fractions.

The photo-oxidation technique was developed to study (i) the rates of oxygen uptake, (ii) the rates of formation of water soluble degradation products and (iii) type of oxidation skin formed. Samples exposed to u.v. radiation were thin films of bitumens, synthetic bitumens, modified bitumens with photo-sensitisers and bitumen fractions. Photo-oxidation of Lake Asphalt gave a higher rate of oxygen uptake (4.75×10^{-3} cc/cm^2/hr) than petroleum bitumens 1 (4.25×10^{-3} cc/cm^2/hr) and 2 (3.75×10^{-3} cc/cm^2/hr. The natural asphalt also gave higher formation rates of water soluble products (3.25×10^{-3} mg/cm^2/hr) than petroleum bitumens 1 (2.75×10^{-3} mg/cm^2/hr) and 2 (2.62×10^{-3} mg/cm^2/hr). Trinidad Lake Asphalt developed a dull, rough skin with a network of hair checks whilst petroleum bitumens had a brighter and slightly wavy skin with a network of broader checks. These results confirm that T.L.A. is more reactive than the petroleum bitumens under the influence of oxygen and light.

The photo-oxidation of bitumen fractions showed the white oil fraction to be the most reactive fraction with an average oxygen uptake of 7.85×10^{-3} cc/cm^2/hr with the dark oil fraction least reactive at an average uptake of 1.85×10^{-3} cc/cm^2/hr. This indicates that the paraffinic-naphthenic white oil fraction would decrease resistance to weathering and the aromatic dark oil fraction would tend to increase the weather resistance.

Similar observations were made by Thurston and Knowles(26) and Corbett and Swarbrick(58). Martin(144) showed that hydrocarbons with aromatic groups, highly branched chain structures, oxygenated groups and also cycloparaffins were most reactive. Infra-red analysis showed Lake Asphalt to be aromatic with oxygen-containing groups such as carbonyl (acids, esters, aldehydes or ketones) and C-O, S=O or Si-O groups. Indications were also present of heavily branched paraffinic chains. These would appear to be some of the factors responsible for the high reactivity to oxygen of Lake Asphalt.

An investigation of the photo-oxidation of a series of synthetic bitumens produced by combining previously separated asphaltenes and maltenes in varying proportions produced some interesting results.

It was found that the rate of oxygen uptake and of formation of water soluble products increased, up to 15% asphaltenes in the case of the petroleum bitumens and up to 45% asphaltenes for Lake Asphalt. Increase in asphaltene content up to and beyond the natural contents produced a decrease in both rates. This may be due to any of the following reasons:

(i) increase in viscosity of bitumen with addition of asphaltenes

(ii) change in internal structure

(iii) asphaltenes in excess acting as antioxidants

(iv) formation of a hard skin on oxidation preventing diffusion of oxygen.

In all cases formation of water soluble products increased with oxygen uptake. Carbonyl and hydroxyl groups were found to be present in the acidic oxygenated products.

Photo-oxidation of Model bitumens containing varying amounts of photo-sensitisers such as anthracene, anthracene oil, anethole, eugenol, safrole and di-tert. butyl peroxide was studied. The rates of oxygen uptake and water solubles increased proportionally to the amount of photo-sensitisers added to the bitumen. The decreasing order of photo-oxidation rates are in the order di-tert. butyl peroxide, anthracene, anethole, safrole and anthracene oil. The oxidation skin formed by these bitumens plus additives varied from bright smooth to dull and rough depending on the amount of photo-sensitisers used. With a high percentage (5%) of these additives the films gave a dull, rough surface similar to those produced by T.L.A. Skin formation is probably important from the viewpoint of road surfacings in that it influences the final bitumen surface texture, either directly by producing a rough surface or indirectly by being abraded by traffic to expose aggregate. Anthracene oil is fairly cheap and easily available from coal tar distillation and could be used effectively to flux a hard bitumen to a required grade and produce skid-resistant properties. The use of other photo-sensitisers to produce the same effect would be uneconomical because of their high cost.

7. SUGGESTIONS FOR FUTURE WORK

In the present work it was not possible to examine certain interesting aspects and it is considered worthwhile to extend this investigation as follows:-

(1) Further fractionation of dark oils, resins and asphaltenes into mono-, di- and tri-nuclear aromatic rings employing chromatographic techniques. Determination of molecular weight, functional groups by I.R., hydrogen distribution by N.M.R. and elemental analysis. This study should be extended to unoxidised, thermally and photo-oxidised bitumens and fractions.

(2) Determination of viscosity of bitumens and fractions before and affer oxidation using a microfilm sliding plate viscometer.

(3) The photo-oxidation of bitumen/sand mixtures including surface texture measurements before and after oxidation.

(4) The chemical composition of water soluble degradation products of photo-oxidised bitumens and fractions employing I.R., N.M.R. analysis and thin layer chromatography.

(5) The effect of adding asphaltenes from petroleum bitumens to Lake Asphalt maltenes to investigate the possible increased susceptibility to oxidation.

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