STUDIES ON

THE OXIDATION OF MINERAL LUBRICATING OILS

A thesis presented to the University of Glasgow
in accordance with the regulations governing
the award of the Degree of Doctor of Philosophy
in the Faculty of Science

by

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SUMMARY

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The work carried out under this research programme was primarily concerned with the effect of the composition of a lubricating oil fraction on its oxidation behaviour. Before commencement of this work, however, it was first of all necessary to devise a method for the determination of resins and to modify methods for the determination of molecular weight and oxygen content.

The method used to determine the amount of resins produced on oxidation was their selective adsorption on Fullers Earth, the adsorption process being carried out in a petroleum ether solvent. It has been shown that this method can accurately determine the quantity of oxidised products remaining in an oil after oxidation and that the treatment does not affect the unoxidised part of the oil in so far as its average structural composition is concerned.

Molecular weight was determined by an ebullioscopic method involving the use of a thermistor sensing element. A modification was made in the condensing system of the apparatus. A removable cold finger condenser was replaced by a permanently fixed Leibig type condenser which has been shown to give more accurate results.

Modifications were made to the Unterzaucher oxygen determination apparatus and method and were concerned with the temperature used, the flow rate of nitrogen and the

time of analysis. The modified technique is satisfactory for use with oxidised oils.

It has been shown that the differences between oxidation behaviour of oils of different composition are principally ones of degree rather than of kind, the amount of total sludge, for instance, being a function of the aromatic content of the original oil. The total acidity produced on oxidation was found to be a function of the sludging tendency of the oil while the acidity of the non-sludging part of the oil was found to be a function of the paraffinic content of the original unoxidised oil.

The amount of deterioration of the lubricant and the effect of the oxidised materials on its properties was found to be related to the aromatic content of the original oil.

Under normal I.P. oxidation test conditions, the amount of material removed on oxidation and treatment with Fullers Earth was found to be fairly evenly spread over the various hydrocarbon types in the oil, with a slight tendency for the aromatics to be preferentially attacked. This effect was found to be emphasised with oils of higher aromaticity.

A stirring method of oxidation was devised which accelerated oxidation and under these conditions it was found that oxidation was more widely spread over the various structural types, with the tendency for preferential attack on aromatics much lessened.

A considerable amount of evidence has been obtained

indicating that the oxidative deterioration of the lubricants followed the pattern of:
hydrocarbons ---> resins ---> oil soluble sludge ---> oil insoluble sludge.
The extent to which this sequence of reactions is carried was found to be dependent upon the aromatic content of the original oils. Oils low in aromatics form only resins while oils high in aromatics form all the reaction products through to oil insoluble sludge.

Some evidence has been obtained indicating that the acidity of the oil insoluble sludge is related to its insolubility and it is suggested that this is due to the formation of hydroxy acids, produced by oxidation of aromatics present in the oil soluble sludge, which are known to be insoluble in petroleum oils.

INTRODUCTION

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Lubricants from petroleum oils are the only available materials, possessing all the required properties, which can be produced today in the quantity and with the economy required by modern industry. They serve many purposes such as conducting frictional heat away from bearings, acting as a seal, or as carriers for rust preventives, as anti-friction agents, and as extreme pressure additives and the like. However, their primary purpose is, in general to lubricate.

The specification for a lubricant is, of course, dependant upon the conditions under which it is required to perform. The main requisite, however, is that during operation it should undergo the minimum of change that may reduce its capability to carry out its function. Contamination due to extraneous materials such as dust, water, products of combustion of the fuel, metallic compounds from engine wear or leaded gasolines decrease the efficiency of the lubricant, but can be reduced or eliminated by careful design and operation. Much more important, however, is the change in the nature of the oil molecules themselves produced during service.

Increases in engine performance have led to much higher engine block and crankcase temperatures resulting in intimate contact of hot oil and air. Under these conditions the lubricant is subject to oxidative attack and the changes produced in the oil molecules lead to viscosity increase, acid and sludge formation causing bearing corrosion, laquer formation, piston ring sticking, stoppage of oil flow etc. The exact nature and extent of these individual changes is dependant upon the nature of the lubricant and the amount and temperature of the air with which it is brought into contact.

It does not appear sound to investigate the mechanism of oxidation in such engine systems where the complexity of variables is neither known nor understood, without an adequate knowledge of the oxidation in simple systems. Greater knowledge of the oxidation behaviour of oils in simple systems where the variables are few and subject to rigid control is necessary and the following work is an attempt to throw some light on the influence of the chemical nature of the oil on its oxidation in such simple systems.

CHAPTER 1

NATURE OF LUBRICATING OILS

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NATURE OF LUBRICATING OILS

Lubricating oils are composed entirely of paraffinic, aromatic and naphthenic hydrocarbons, Sachanen and Virobianz[1] having shown by the determination of addition iodine numbers that no olefins are present. Little can be said at the moment about the physical structure, except that the refined oils are substantially homogeneous mixtures of hydrocarbons, excluding solid paraffins, which are miscible in all proportions.

The proportions of each hydrocarbon type present will depend upon the source of the crude and its refining treatment. Both have a large effect on the ultimate composition. For instance, Fenske et al.[2] have shown that the narrow fractions of lubricating oils produced by fractional distillation have approximately the same chemical composition expressed in terms of ring analysis, or about the same distribution of aromatic and naphthenic hydrocarbons in each fraction. The same effect was reported by von Fuchs and Anderson[3] who found that the content of paraffinic side chains and rings is the same in oils S.A.E. 20 and 40 of the same origin.

Carnahan[4] however, obtained a completely different type of fractionation by reflux solvent/solvent extraction of a mid-

Continent neutral. The first extract fractions consisted of polycyclic aromatics with short paraffin side chains. The middle fractions contained a small proportion of naphthenes with moderately long paraffin side chains. The last fractions and residuum contained no aromatics but only naphthenes with long paraffin side chains.

Yet again Rossini[5], Leslie and Heuer[6], and Mair, Willingham and Streiff[7], solvent extracted a Ponca City crude and found that aromatic rings are combined with naphthenic rings producing aromatic-naphthenic hydrocarbons in varying ratios from 1:3 to 3:1. Another alternative explanation that the hydrocarbons consist of mixtures of aromatics and naphthenes must be ruled out since the means of separation of fractions for analysis would have easily differentiated between them.

Only highly branched paraffins boiling in the range of lubricating oil distillates have low enough melting points and are miscible enough with oils to be considered as separate constituents of lubricating oil fractions. However, Beilenberg[8] and Vlugter, Waterman and van Westen[9], and Müller and Neyman-Pilat[10] investigated the composition of various crudes and concluded that even dewaxed paraffinic type crudes were free from isoparaffins. Modern mass spectrometric evidence[11] indicates, however, the presence of isoparaffins and consequently the possibility of their presence even although only in minute amounts cannot be entirely excluded.

From evidence of this type it may be concluded that dewaxed lubricating oil fractions on the whole consist of three basic types:

a) Fractions in which there are aromatic-naphthenic rings with paraffin side chains, of approximately the same composition over the whole boiling range of the distillate.
b) Fractions in which aromatic rings and naphthenic rings are separate and with or without paraffin side chains.
c) Combinations of a) and b).

Thus oil properties will depend not only on the percentages of each hydrocarbon type present but also on the manner in which they are combined in the molecule.

<u>Structural Grouping</u>

Synthetic means has been used by Robinson[12] to determine the nature of the aromatic hydrocarbons present in lubricating oils. He added various synthetic high molecular weight aromatics to de-aromatised oils and compared the properties of these oils with those of the original oils. From this work he concluded that aromatics removed by de-aromatisation should be close to polycyclic aromatic hydrocarbons with comparatively short side chains, or to monocyclic aromatics with naphthenic rings on their side chains.

Removal of the aromatic hydrocarbons present in dewaxed lubricating oils leaves naphthenic hydrocarbons. Mabery, Buck, Zoule, Coats and Best[13,14,15,16,17,18] determined the empirical formulae of these naphthenes produced from lubricating oils of varying origin and found that they varied from C_nH_{2n-2} to C_nH_{2n-8}. Bestougeff[19] investigated the naphthenes of Russian lubricating oil fractions and gave formulae varying from C_nH_{2n-2} to C_nH_{2n-6}. For the aromatic hydrocarbons the same authors gave values from C_nH_{2n-8} to C_nH_{2n-44}. These empirical formulae correspond to hydrocarbons varying from two to five condensed rings.

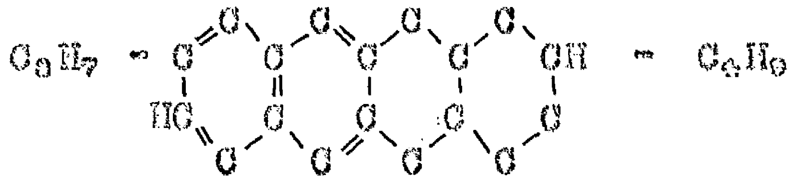
According to Kurtz and Lipkin[20,21] more than half of the rings in lubricating oil fractions are of the five carbon atom type: the average number being 5.3. In their method, however, the number of carbon atoms per ring for hydrocarbons of the condensed mixed ring type deviates from the actual number of rings by -0.4. If this deviation is significant, the average number of carbon atoms should be corrected to 5.7 indicating a greater number of six-carbon-atom rings per molecule. Although there seems to be some doubt as to the absolute relative proportions it must be definitely concluded that hydrocarbons composed of five membered rings are normally present in lubricating oil fractions. From investigations of optical exaltation of a large number of lubricating oil fractions Grosse[22] concluded that the presence of C_3, C_4, C_7, C_8, etc. hydrocarbon rings is highly improbable.

The length of paraffinic side chains is normally calculated on the basis of molecular weight and the number of rings. For instance, the fraction investigated by Rossini[5] was shown to have four aromatic and naphthenic rings and short paraffin side chains of from 5 to 7 carbon atoms. Bestougeff[19] calculated that the number of carbon atoms in paraffin side chains was 16 for naphthenes from a paraffinic crude and 11 for an asphaltic crude.

It would appear therefore that for oils of medium viscosity the number of carbon atoms in paraffin side chains varies from 5 to 20, long chains being associated with naphthenes and short ones with aromatics. These conclusions have been confirmed by comparison of synthetic hydrocarbons of varied viscosity index, short chains producing highly negative values and long chains values over 100.

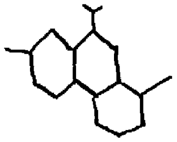
The occurrence of long paraffin side chains (C_{12} or over) in lubricating oils of low pour point seems improbable as derivatives of benzene, cyclohexane naphthalene etc. with long normal paraffin side chains have melting points above 10°C. Such hydrocarbons if present in the original oils would be removed by the dewaxing process. On the other hand, since Mikeska[23], Cosby and Sutherland[24] have shown that even a single branching, particularly in the middle, may be sufficient to lower the pour point to below -10°C., the presence of paraffin side chains of C_{12} with a branched chain structure is quite possible. The degree and character of the branching are as yet unknown.

Krämer and Spilker[25], and Spilker[26] synthesised lubricating hydrocarbons similar to those derived from petroleum by alkylation of polycyclic aromatics. Further investigations by Spilker showed that any cyclic hydrocarbon, aromatic or naphthenic, monocyclic or polycyclic, alkylated with one or more sufficiently long paraffin side chains will have lubricating properties. The specific gravity, viscosity, viscosity index and chemical composition of such hydrocarbons will be very close to those of petroleum lubricating oils. This agrees well with the formula given by Rossini[5] for an "extract" homogeneous fraction of mid-Continent origin of specific gravity 1.004, molecular weight 334.5 and boiling point 217° at 1mm. mercury.



Mikeska[23,27] investigated thoroughly the synthetic cyclic hydrocarbons possessing lubricating properties and found that the properties depended upon the number of rings, ratio of aromatic to naphthenic rings, ratio of rings to paraffins and the number, length, degree of branching and position of the side chains.

Mass spectrometric studies by Hood, Clerc and O'Neal[11] also point to the fact that lubricating oil fractions consist of polycyclic hydrocarbons to which are attached several short paraffin side chains (methyl in many cases) and one long chain with a short branch. A typical molecule may be represented as follows where the rings may be aromatic and/or naphthenic.



Characterisation of Lubricating Oils

The manner in which the constitution of mineral oils is expressed is dependant upon the choice of components. First, the composition can be expressed according to the amount of the various types of molecule present in the sample and the analysis leading to these figures is called "molecular type analysis". Secondly, atoms can be regarded as the components of the oil fraction and the amount of each type of atom present can be determined by "ultimate analysis". Finally, structural elements can be considered as the components of the mixture. The analysis leading to these figures is termed "structural group analysis", as the average proportion of the several structural groups are estimated irrespective of the manner in which the groups are combined in the molecules. This latter method has proved to be the most useful to date and it is by means of it that the composition of mineral oils is usually expressed.

Structural Group Analysis

In this method of analysis the hypothetical mean molecule in the fraction is considered and the distribution of the carbon atoms among the three types of hydrocarbon groups present given. Thus composition is expressed as the percentage of the carbon atoms in paraffinic, naphthenic and aromatic structure along with the number of naphthenic and aromatic rings per molecule.

All methods of structural group analysis evolved from the "direct method" which is based on molecular weight determination and ultimate analysis of the oil fractions before and after hydrogenation.

A paraffin molecule of a given molecular weight will have a definite and deducible percentage of hydrogen. When naphthenic rings are introduced the addition of each ring results in the loss of two hydrogen atoms. Therefore any saturated molecule containing naphthenic rings will have a lower hydrogen content than the paraffin of the same molecular weight. It is then possible to establish a direct relationship between hydrogen content, molecular weight and the number of rings per molecule in a saturated hydrocarbon, viz:

$$R_N = 1 + (8.326 - 0.5793H)\ M/100$$

where R_N is the number of naphthenic rings per molecule

H is the percentage of hydrogen

M is the molecular weight.

Where there are aromatic rings in the molecule and these are hydrogenated to saturated rings, then each aromatic carbon atom adds on a hydrogen atom. Thus the hydrogen taken up in the hydrogenation of double bonds is a measure of the number of aromatic rings present. Analysis of the saturated molecule produced can be completed as above with the exception that the percentage hydrogen is now a measure of the total number of rings present in the original molecule. The difference between total rings and aromatic rings gives naphthenic rings and from this picture of the hypothetical mean molecule the carbon distribution can be calculated.

In the derivation of structural group analysis methods it was found necessary to make certain assumptions regarding the number of carbon atoms per ring and the extent of ring condensation. The final choice has been kata condensed, six membered rings. The reasons for this choice have been discussed in some detail by van Ness and van Westen.[28]

The first method of structural group analysis published was by Vlugter, Waterman and van Westen[29] and is known as the "Waterman Ring Analysis". Additivity is a feature of hydrocarbon molecules and the authors noted that the Lorentz-Lorenz specific refraction

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

where n = refractive index at 20°C using the sodium D-line
d = density at 20°C.

was additive for increments of C and H, and thus "r" was proportional to the percentage of hydrogen in hydrocarbon molecules. Therefore by the measurement of specific refraction and molecular weight of a saturated oil sample the number of rings per molecule could be calculated.

The same authors gave a method based on the measurement of the aniline point for analysing oil samples containing aromatic rings. The aniline point for the sample under examination was measured and compared with the corresponding value for the completely hydrogenated sample of the same molecular weight and specific refraction, obtained from a graph. The difference in the two aniline points was then used by means of suitable factors to give the percentage of aromatic rings and to predict the specific refraction of the sample if it were completely hydrogenated.

A further refinement of the "direct method" was produced by Leendertse to give the "density method".[28] This dispensed with the rather difficult measurement of aniline point and replaced it by the measurement of density. The aromatic ring content and the specific refraction of the completely hydrogenated sample were estimated from the difference between the density of the sample and the density of the completely hydrogenated oil of the same molecular weight and specific refraction obtained from a graph.

At this stage analysis was reduced to the measurement of refractive index, density and molecular weight. The method has been further simplified by the evolution of equations from which the carbon distribution and ring content could be calculated from the above quantities. A summary of the methods used to derive these equations is given below.

n-d-M Method of Structural Group Analysis

Using the physical constants refractive index, (n), density, (d), and molecular weight(M), van Ness and van Westen[28] describe a method for the structural group analysis of mineral oil fractions based on the statistical analysis of a large number of samples from various sources. From general equations of the type,

$$C = \frac{a}{M} + b\Delta d + c\Delta n$$

$$R = a + bM\Delta d + CM\Delta n$$

where C is the percentage carbon in one type of structure

R is the mean number of rings per molecule

d is the difference between measured density(d) and the density of the limiting normal paraffin (hypothetical paraffin containing infinite CH_2 groups, in the liquid state) at the same temperature.

n is the similar quantity for refractive index.

M is the molecular weight.

and a, b, c, a, b, and c, are constants.

The percentage carbon in total ring structure (C_R), aromatic ring structure(C_A), the mean total number of rings per molecule(R_T) and number of aromatic rings per molecule(R_A) may be found.

Two equations are given for each quantity to be calculated, one for low range aromatics and one for the higher range.

The percentage carbon in paraffinic structures(C_P), naphthenic structures(C_N) and the mean number of naphthenic rings per molecule(R_N) are estimated by difference.

The method is intended for the Structural Group Analysis of olefin free petroleum distillates boiling above the gasoline range. It is based on samples whose molecular weight is above 194, those containing 75% carbon in ring structure where aromatic rings do not exceed naphthenic rings by more than 1.5 times, fractions having up to four rings per molecule with not more than half of them aromatic and is therefore eminately suitable for lubricating oil fractions.

The method can also be used for samples containing up to 2% sulphur and samples containing up to 0.5% nitrogen and oxygen.

The equations used to calculate the carbon distribution and ring content of an oil are as follows, where all symbols are as previously stated and S denotes the percentage sulphur present.

$$d = d - 0.8510$$

$$n = n - 1.4750$$

In turn two factors, v and w, used in subsequent calculations, are determined.

$$v = 2.51\ n - d$$

$$w = d - 1.11\ n$$

The percentage of carbon in aromatic structure is given by:

for v positive $\%C_A = 430v + \frac{3660}{M}$

for v negative $\%C_A = 670v + \frac{3660}{M}$

The percentage carbon in ring structure is given by:

for w positive $\%C_R = 820w + \frac{10,000}{M} - 3S$

for w negative $\%C_R = 1440w + \frac{10,000}{M} - 3S$

The percentage carbon in naphthenic structure and paraffinic structure is given by:

$\%C_N = \%C_R - \%C_A$

$\%C_P = 100 - \%C_R$

The mean number of aromatic rings per molecule is given by:

for v positive $R_A = 0.44 + 0.055Mv.$

for v negative $R_A = 0.44 + 0.080Mv.$

The mean total number of rings per molecule (naphthenic and aromatic) is given by:

for w positive $R_T = 1.33 + 0.146M(w - 0.005S)$

for w negative $R_T = 1.33 + 0.180M(w - 0.005S)$

The mean number of naphthenic rings per molecule is given by:

$R_N = R_T - R_A$

A similar series of equations is available for measurements of refractive index and density at 70°C when these are not available at 20°C. Van Nes and van Westen give a series of nomographs for rapid solution of the equations.

CHAPTER II.

OXIDATION OF HYDROCARBONS

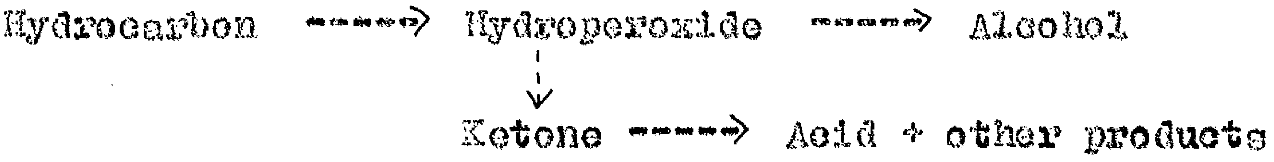
CHAPTER II

1. Hydrocarbon Oxidation

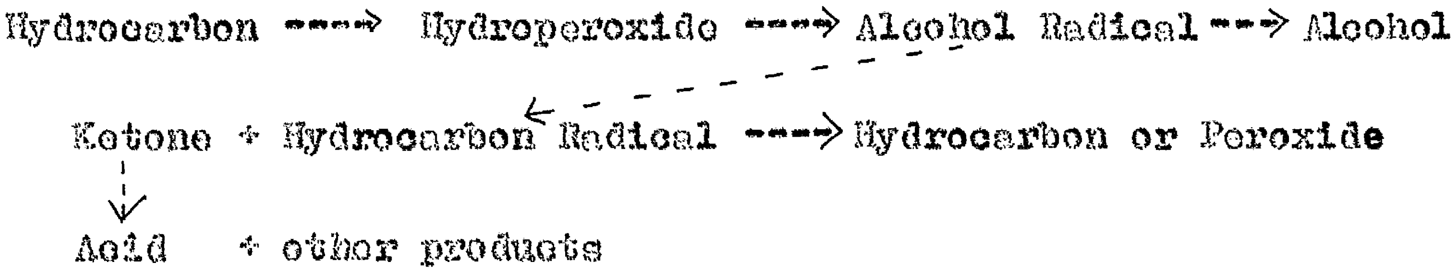
The major difficulty in early studies of the oxidation of hydrocarbons lay in the isolation of the primary reaction products. Bone and co-workers[30] believed that the first product was an alcohol and that subsequent products were formed by oxidation of the alcohol. Later work by George, Rideal and Robertson[31] has shown that alcohols are in general less easily oxidised than the corresponding hydrocarbon and that in certain cases the alcohols act as oxidation inhibitors. The basis of modern theory lies in the assumption that the primary reaction product between a hydrocarbon and oxygen is a peroxide. This view was first advanced by Bach[32] and Engler and Wild[33], subsequently developed in more detail by Callender[34] and Ubbelohde[35] and extended to olefins, aromatics and hydrocarbons as a whole by Farmer[36] and Chavanne[37] and Stevens[38].

George, Rideal and Robertson[39] found that C_{15} and C_{25} paraffins and alkylbenzenes are oxidised at 100-120°C to form hydroperoxides which account for 60-80 per cent of the oxygen absorbed by the alkylbenzenes, and which decomposed to give almost exclusively ketones in the case of paraffins. The presence of peroxides in high concentrations in the early stages of oxidation has been reported by Larsen[40], Balsbaugh and Oncley[41] with hydrocarbons and by Dornte[42] and by Denison[43] in the oxidation of white oils.

In the oxidation of hydrocarbons, therefore, it is the attack of oxygen on a C-H bond which is the predominant reaction, and accordingly it is the hydroperoxide decomposition products which are important in determining the subsequent reactions. The following scheme describes the course of the reaction when the chain fission reaction of the hydroperoxide does not take place:



George and Walsh[44] have shown that a chain fission reaction can occur especially with tertiary hydroperoxides, which involve the splitting of the O-O bond to give an alcohol radical followed by the breaking of the weakest adjacent C-C bond to give a ketone and a hydrocarbon radical. In this case the reaction scheme can be given as:



The position of initial attack has been established in many cases. Twigg[45] has found that the secondary carbon atoms of n-decane are attacked equally and preferentially to the primary carbon atoms. Chavanne and co-workers[37,46] studied n-decane, n-nonane and n-octane and found that attack of paraffins is at the CH$_2$ adjacent to the terminal CH$_3$ group. This is consistent with the views of Burwell[47] who states that the beta carbon atom is involved primarily, the gamma secondarily and so on to the centre of the molecule, so that formic, acetic, and propionic acids would be expected in order of decreasing concentration in the reaction products. Fenske et al.[48,49] found this to be the case in the analysis of the products of oxidation of lubricating oil fractions. Hoffmann and Boord[50] give the following order of preference for the initially oxidised carbon atoms of ethyl cyclohexane:

Tertiary > Secondary of ethyl group > Secondary of nucleus > Primary

The carbon atoms in the cyclohexane ring are not attacked with equal facility: those adjacent to the ethyl group being more readily attacked.

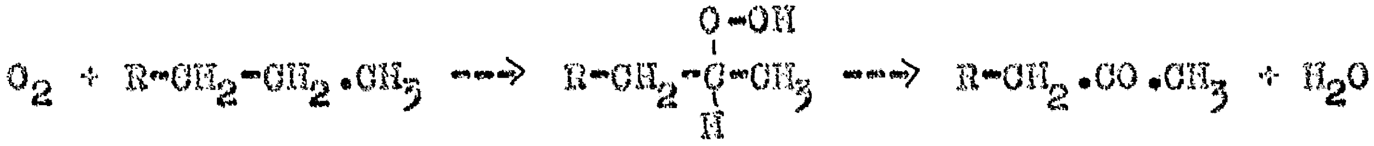
In comparison with normal paraffins the branched chain hydrocarbons are usually oxidised much more easily and in general a tertiary C-H bond is the preferred site of attack i.e. 2-methyl heptane.

In aromatic and hydroaromatic molecules oxidation attack is at the weakest C-H bond. The oxidation of side chain aromatic hydrocarbons occurs preferentially at the side chain -CH$_2$ rather than in the ring, whereas in hydroaromatics attack concentrates at the -CH adjacent to the double bond.

On the basis of information of this kind reaction mechanisms for the various types of hydrocarbons have been put forward and are summarised below.

a) **Paraffins**

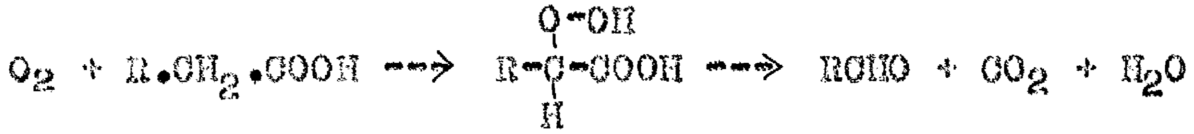
Zuidema[51] has put forward the following mechanism for the oxidation of a straight chain paraffin.



$$O_2 + R-CH_2-CH_2.CH_3 \longrightarrow R-CH_2-\overset{O-OH}{\underset{H}{C}}-CH_3 \longrightarrow R-CH_2.CO.CH_3 + H_2O$$

Hydroperoxide   Ketone

$$O_2 + R-CH_2.CH_3 \longrightarrow \underset{\text{Carboxylic Acid}}{R.CH_2.COOH} + \underset{\text{Formaldehyde}}{HCHO}$$

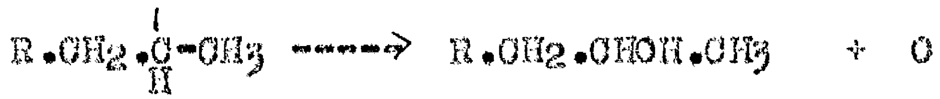


$$O_2 + R.CH_2.COOH \longrightarrow R-\overset{O-OH}{\underset{H}{C}}-COOH \longrightarrow RCHO + CO_2 + H_2O$$

Thus alternate formation of acid and carbonyl groupings may eventually lead to complete breakdown of the paraffin chain.

In addition there would be some primary attack on the gamma rather than the beta carbon atom. This would result in the formation of a ketone of the same number of carbon atoms but with the carbonyl group shifted one carbon atom toward the centre of the molecule.

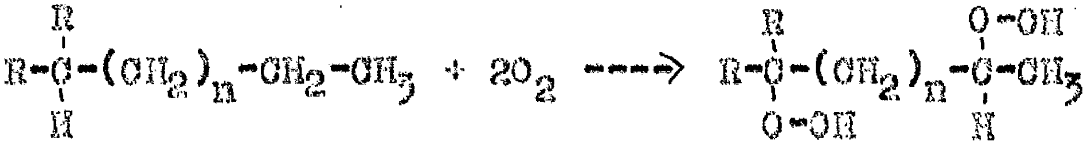
The formation of alcohols requires a reducing action on the hydroperoxide, the latter losing one atom of oxygen in acting as an oxidising agent, thus:



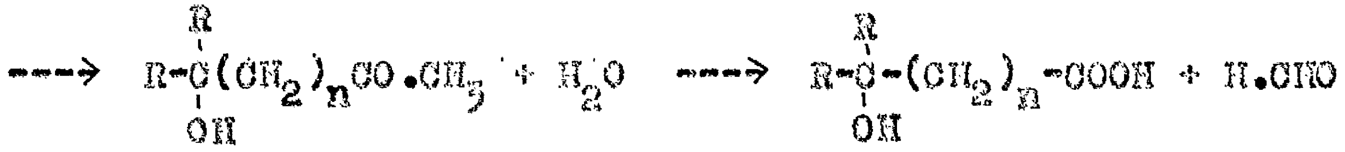
$$R.CH_2.\overset{O-OH}{\underset{H}{C}}-CH_3 \longrightarrow R.CH_2.CHOH.CH_3 + O$$

Alcohol

With a branched chain paraffin there are two sites of attack, a tertiary and a secondary hydrogen atom. Attack may proceed simultaneously or in stages depending upon the conditions of oxidation.



$$R-\underset{H}{\overset{R}{C}}-(CH_2)_n-CH_2-CH_3 + 2O_2 \dashrightarrow R-\underset{O-OH}{\overset{R}{C}}-(CH_2)_n-\underset{H}{\overset{O-OH}{C}}-CH_3$$

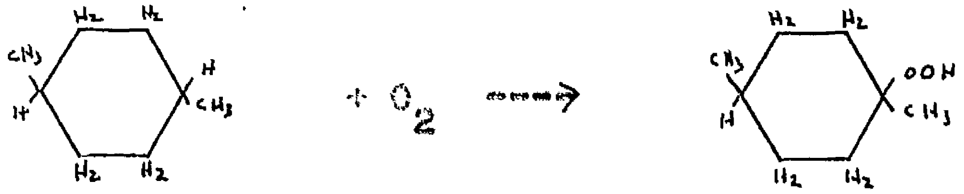


$$\dashrightarrow R-\underset{OH}{\overset{R}{C}}(CH_2)_nCO.CH_3 + H_2O \dashrightarrow R-\underset{OH}{\overset{R}{C}}-(CH_2)_n-COOH + H.CHO$$

Hydroxy Acid.

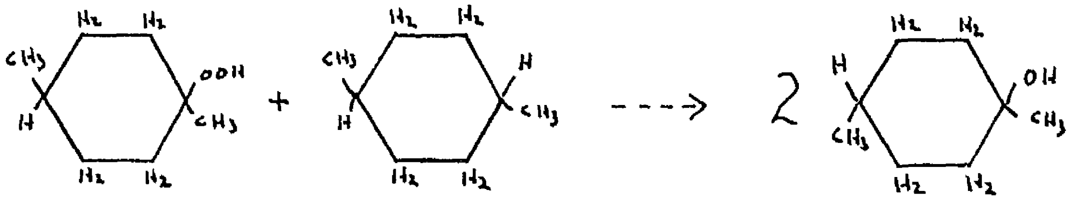
b) <u>Naphthenes</u>

Chavanne and Bode[37] have made an extensive study of the oxidation of 1:4 dimethylcyclohexane and postulated the following mechanism of oxidation:



1:4 dimethylcyclohexane

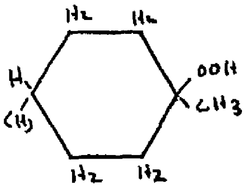
Hydroperoxide



1:4 dimethylcyclohexanol

The diol may be formed in a similar manner.

Instead of reduction of the hydroperoxide to form an alcohol, further oxidation can occur resulting in rupture of the ring.



$\longrightarrow CH_3.CO.CH_2CH_2.CH(CH_3).CH_2.COOH + H_2O$

β-methyl-δ-acetyl. valeric acid.

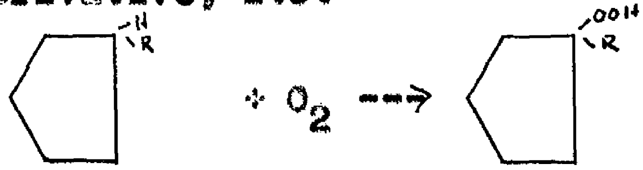
$\longrightarrow CH_3.CO.CH_2.CH_2.C.(CH_3)CH_2.COOH \longrightarrow CH_3.CO.CH_2.CH_2.CO.CH_3$

Acetonyl Acetone

$+ CH_2OHCOOH$

Glycolic Acid

Dupont and Chavanne[46] studied the oxidation of three cyclopentane derivatives and found that the mechanism differed from that of the six membered ring. Whereas cyclohexane derivatives produced ketones containing one carbon atom less, the cyclopentane derivatives produced a straight chain ketone containing the original number of carbon atoms. The reaction in this case probably proceeds through the decomposition of the hydroperoxide by reduction to an aliphatic ketone rather than to the cyclic alcohol as in the case of the cyclohexane derivative, i.e.



$+ O_2 \longrightarrow \quad \longrightarrow CH_3CH_2CH_2CH_2.CO.R + O$

Thus the end product resembles that formed from a paraffin.

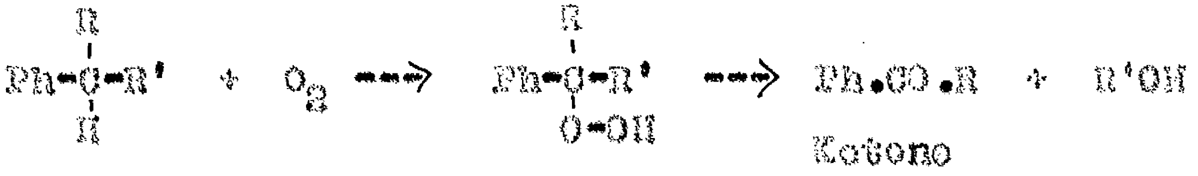
The reason for this difference in behaviour is not clear, though it could be possibly due to the presence of two tertiary groups in the cyclohexane derivatives and only one in that of the cyclopentanes, or by the difference in ring size or side chain length.

Chain rupture by further oxidation of the hydroperoxide may also take place in a manner similar to that of the six carbon atom ring.

c) Aromatics

Stevens[38] and Stevens and Roduta[38] studied the oxidation of a series of benzene derivatives and found that oxidation always centres about a carbon atom attached to the benzene ring. Methyl benzenes all formed aldehydes containing the same number of carbon atoms as the parent molecule, while larger groups all formed ketones containing a phenyl group plus the other group attached to the benzene ring, or the smaller of the two groups in the case where two groups are present. Acids resulting from the further oxidation of aldehydes or ketones were also formed, as well as acids of low molecular weight which formed from the fragments split off in the formation of ketones from secondary compounds. No traces of alcohols were ever detected in the final products.

Considering the general case where R is smaller than R' the reaction mechanism may be postulated as:



$$Ph{-}\overset{R}{\underset{R}{C}}{-}R' + O_2 \longrightarrow Ph{-}\overset{R}{\underset{O-OH}{C}}{-}R' \longrightarrow \underset{\text{Ketone}}{Ph.CO.R} + R'OH$$

The two fragments then oxidise as follows:

$Ph.CO.R + O_2 \longrightarrow Ph.COOH + RCHO$

$R.CHO + \frac{1}{2} O_2 \longrightarrow R.COOH$

Aldehyde Acid

and

$R'.OH + \frac{1}{2} O_2 \longrightarrow R'.COOH$

Alcohol Acid

2. Influence of Structure on Oxidation

a) Pure Hydrocarbons

Larson, Thorpe and Armfield[52] have made an extensive study of the oxidation rates of a number of pure hydrocarbons. They classified the compounds according to the time taken to absorb 2000cc. of oxygen per gramme mole and the type of oxygen absorption curve. These curves are of four types, namely, autocatalytic, autoretardant, linear, and the combination type in which autocatalysis prevails first then autoretardation. Unfortunately, these types of curve apply only under a given set of conditions, von Fuchs and Diamond[53] having shown that a given oil may exhibit autocatalysis or autoretardation depending upon the temperature of oxidation.

The most rapid oxidation was shown by hydrocarbons containing a partially hydrogenated condensed ring or a benzene ring with a long paraffin side chain. Surprisingly, these compounds did not give an autocatalytic type curve showing that autocatalysis is not a requisite for rapid oxidation. The naphthalene derivatives were as a class the most stable and most of their curves were of the linear or autoretardant type.

Hydrogenation of long side chain alkylbenzenes to the corresponding cyclohexane derivative resulted in an increase in stability, whereas hydrogenation of a naphthalene derivative resulted in a marked loss in stability, particularly if the naphthalene ring was only partially hydrogenated. Thus in the stability scale adopted naphthalene was 1600 times more suitable than tetrahydronaphthalene (tetralin) and 89 times more stable than decahydronaphthalene (decalin). The influence of a paraffin side chain was shown by comparing the octadecyl derivatives of naphthalene, tetralin and decalin respectively when the factors relating stability were reduced from 1600 to 210 in one case and from 89 to 22 in the other.

The influence of the structure of aromatic side chains was illustrated by a comparison of the primary, secondary and tertiary amyl derivatives of benzene. According to the mechanism of oxidation of an alkylbenzene the primary compound would form the hydroperoxide at the alkyl carbon attached to the ring. The peroxide would then dehydrate to phenyl autyl ketone. The secondary compound would likewise form the peroxide but since there would be only one hydrogen atom on the carbon in question, initially propyl alcohol rather than water would split off and acetophenone be the other product. Since the tertiary compound cannot form a hydroperoxide at the carbon attached to the ring but must oxidise at other positions it is the most stable of the three. A similar trend was noted by Stevens and Roduta[38] who found that the tert-butyl derivative was much more resistant to oxidation than any of the other alkylbenzenes.

Larsen, Thorpe and Armfield[52] attributed the extreme stability of naphthalene aromatics in comparison with the benzene homologs to the difference in the effect of their oxidation products as inhibitors. They oxidised n-amylbenzene to which had been added 9.8% of preoxidised α-methyl naphthalene and found that the curve was almost coincident with that for α-methylnaphthalene.

Chernozhukov and Krein[54] studied oxidation stability by the analysis of the saponification values after a constant fixed time oxidation in a bulb. From their results they concluded that chainless polynuclear aromatics are very stable, that the introduction of side chain, particularly long side chains, decreases stability and that the beta derivatives of naphthalene are more reactive than the alpha. These conclusions are in agreement with those of Larsen[52] except that regarding the relative stability of α and β -methyl naphthalenes. Chernozhukov and Krein[54] found as did Larsen that benzene derivatives are less stable than naphthalene homologs and that the higher alkyl compounds are less stable than those of lower molecular weight.

Hock and Lang[55] oxidised cyclopentene, cyclohexene, hydrindene and tetralin by means of oxygen and ultra-violet light. They concluded that a five membered ring is less easily readily oxidised than a six membered ring but since their conditions of oxidation were different from those used by others quoted above their results cannot be compared with the others without some reservations.

b) Mixtures of Pure Hydrocarbons

In the oxidation of hydrocarbons the subsequent course of the reaction is dependant to some extent on the products of oxidation. With a single hydrocarbon this results in a wide variety of oxidation products, but with mixtures of hydrocarbons the effect of the oxidation products of one hydrocarbon upon the rate and extent of another is rather unpredictable.

This is readily illustrated by the work of Booser and Fenske[56] who compared oxidation rates of single hydrocarbons and mixtures. With hexadecane and cis-decalin they found that the mixture oxidised at the same rate as the pure cis-decalin, suggesting that the more readily oxidised hydrocarbon in the mixture is preferentially attacked. With a mixture of hexadecane and 1-methylnaphthalene, however, the oxidation rate was similar to that of the pure 1-methylnaphthalene and very much slower than the rate for the oxidation of hexadecane alone. This slow rate of oxidation of 1-methyl naphthalene is believed to be due to the formation of α-naphthol, which inhibits further oxidation so that this inhibiting effect is observed in mixtures containing this and similar hydrocarbons.

A further illustration of the unpredictable character of the oxidation of mixtures was shown by comparing the rate of oxidation of a neutral fraction of Pennsylvania oil with the paraffin-naphthene portion and aromatic portion of the same oil separated by silica gel. The original neutral oil was oxidised more slowly than either of the constituent fractions, and despite the greater stability of the aromatic portion there were indications that it was preferentially oxidised in the composite neutral.

A similar effect was noted by Larsen et al.[52] who found that in blends of 25 to 50 per cent of diamylnaphthalene in white oil, the former was oxidised preferentially even though white oil by itself was fifty eight times as reactive as diamylnaphthalene.

c) Lubricating Oil Fractions

It was seen in the previous section that even in simple mixtures the oxidation products of one component could have a drastic effect on the oxidation rate of another. In lubricating oils where there is a complex of components whose individual structure is unknown the oxidation process becomes so complicated as to defy all but a general approach. Many workers have studied a wide variety of lubricants and the generalisations that can be made are summarised below.

Larsen et al.[40] determined functional groups in the oxidation products of a number of Californian oils extracted in stages by furfural and oxidised at 150°C. They found that as aromatics were removed there was a decrease in sludge formation, an effect which is consistent with the conclusions based upon the work of pure hydrocarbons to the effect that aromatics give dark insoluble condensation products.

Extraction also resulted in a higher conversion of oxygen to water and slightly less to carbon dioxide and to volatile acids, with no trends apparent in free or combined acids, nor in alcohols and carbonyls. No peroxides were found in the oxidation products of the oils indicating that any peroxides formed were immediately decomposed into further reaction products.

Dornte and co-workers[42,57,58] studied oxygen absorption of white oil at 135°C and found that peroxides were the principal oxidation products, with carbonyls, water and acids next and only a trace of carbon dioxide. With lubricating oils at a temperature of 175°C they found that about 40 per cent of the oxygen was converted to water and 8 to 10 per cent to carbon dioxide.

Fenske et al.[48,49] working under similar conditions with Pennsylvania oil at 170°C gave the following distribution of oxygen in the oxidation products: water, 44 to 70 per cent: carbon dioxide, 3 to 9 per cent: carbon monoxide, 0.6 to 3.2 per cent: volatile acids, 1 to 7.5 per cent: fixed acids, 2 to 2.5 per cent: and 2 to 7 per cent isopentane insolubles (They assumed the latter contained 15 per cent oxygen). They found that the distribution of oxygen is influenced little by temperature over the range 150 to 180°C provided the amount of oxygen consumed remains constant, but that it varies as oxidation proceeds.

Hicks-Bruun, Ritz, Ledley and Bruun[59] also made similar studies at a temperature of 175°C and found that 34.5 to 43.5 per cent of the oxygen could be accounted for as water and 3.1 to 7.5 per cent as carbon dioxide. They compared an oil containing 19 per cent aromatic rings by Waterman analysis with one containing 5 per cent and found that the former produced three to four times as much "soluble sludge" and "insoluble sludge" as the latter. Other trends agreed with those found by Larson.

von Fuchs and Diamond[55] examined in detail the effect of varying the concentration of bright stock aromatics on the time required for absorption of 1800 cc. of oxygen per 100 gm. of motor oil in the presence of iron as a catalyst. They found that the curve relating absorption time to concentration of added aromatics passed through a distinct maximum in the vicinity of 5 per cent, dropping off to absorption times less than half of the maximum at 0 and 10 per cent showing that the oil had a definite "optimum aromaticity".

This concept of "optimum aromaticity" with respect to oxidation stability was also illustrated by Fenske et al.[48] who separated a Pennsylvania oil containing 9 per cent aromatic rings into 124 fractions by a combination of vacuum distillation and solvent extraction. At a temperature of 140°C in a conventional oxygen absorption apparatus they oxidised seven fractions varying from 0 to 40 per cent aromatic rings and found that none of the fractions examined was as stable as the original oil. The most stable of the fractions were those with 15 and 25 per cent aromatic rings, the least stable those of zero aromaticity.

An "optimum aromaticity" for insulating oils is also indicated in the work of Clark[60] who found by measurement of di-electric stability that the oils showed a maximum stability in the vicinity of six per cent aromatic rings.

These results show that the oxidation of aromatics is a process independent of the oxidation of naphthenes and paraffinic side chains. In lower concentrations the aromatics retard the oxidation of saturated hydrocarbons, oxidation of aromatics themselves being an insignificant factor. At higher concentrations, oxidation of the aromatics is superimposed on that of saturated hydrocarbons and may reverse the retarding effect of oxidations.

3. Purpose of Research

Products of oxidation may be divided into three broad groups depending upon their solubility in the oil. These are "oil insoluble sludge", "oil soluble but isopentane insoluble sludge" and the remaining oil soluble oxygen containing material, loosely termed "resins". Each of these fractions will have its own individual effect on oil properties and the extent to which this occurs will depend upon the amount of each fraction and its chemical nature, both of which are dependent upon the chemical nature of the base oil.

The purpose of the following work may be summarised as follows.

(1) To investigate the effect of oil composition on:

  a) The extent of oxidation.
  b) The effect of the oxidation products on oil properties.
  c) The properties of the oxidation products.

(2) Removal of all oxidised materials and the comparison of the properties of the reclaimed oil with those of the original oil.

Before commencement of the research programme it was first necessary to devise a method for the determination of the resins present in the oxidised oils. This is described in Chapter V. It was also necessary to modify the methods of determination of molecular weight and oxygen content and these are described in Chapter XI.

CHAPTER III

DATA ON LUBRICATING OILS USED

CHAPTER III

DATA ON LUBRICATING OILS USED

Three mineral oil fractions in the lubricant viscosity range were used in the present investigation. All had been refined to some extent but were free of additives.

The sample number, source of supply and information regarding refining history is given in Table I. In Table 2 are given the constants which were measured by the methods described later in Chapter XI, viz., refractive index, density, molecular weight and kinematic viscosity.

None of the samples used contained any appreciable quantity of sulphur and for the purposes of the present investigation the sulphur content of the oils is ignored.

The n-d-M method of analysis was used to determine structural groups and the results obtained are shown in Table 3.

TABLE I

OIL SAMPLES USED

SAMPLE	SOURCE	HISTORY (refining treatment)
1	Mid-Continent	Acid refined, solvent dewaxed and filtered.
2	Middle East	Compounded distillate oil and bright stock: solvent extracted, solvent dewaxed and clay finished: bright stock also underwent propane deasphalting.
3	Lagunillas, Venezuela.	Naphthenic feed stock: vacuum distilled, caustic soda treated and redistilled.

TABLE 2

CONSTANTS OF OIL SAMPLES USED

Sample No.	Refractive Index 20°C	Density 20°C	Molecular Weight	Viscosity 100°F C.S.	Ramsbottom Carbon Residue %
1	1.4911	0.8890	550	254.4	0.422
2	1.5019	0.9057	530	228.9	0.854
3	1.5280	0.9408	326	227.0	0.420

TABLE 3

n-d-M ANALYSIS OF OILS USED

Sample No.	% C_A	% C_R	% C_N	% C_P	R_A	R_N	R_T
1	7.58	34.74	27.16	65.23	0.505	2.445	2.95
2	12.33	39.37	27.04	60.63	0.807	2.45	3.26
3	29.8	56.1	26.3	43.9	1.21	1.60	2.81

CHAPTER IV

OXIDATION TESTS

CHAPTER IV

OXIDATION TESTS

Over the years a number of test methods have been developed for the determination of the oxidation characteristics of a lubricant. These are of two basic types, namely, laboratory tests and engine tests. The former give useful information, but are limited in their scope, while the latter are of practical value but provide little fundamental information.

Laboratory oxidation tests are generally of two types. First there are tests in which air or oxygen is bubbled through a sample of the oil at elevated temperature. Examples of this are the I.P.[61] test, the oxidation test described by Dornte[62] in which the amount of oxygen absorbed is continuously recorded, the Indiana oxidation test[63] and the modified Indiana stirring test[64] in which high speed stirring provides the aeration. Secondly there are tests in which the hot sample is surrounded by an atmosphere of oxygen and absorption takes place at the surface of the static sample, e.g. the Sligh oxidation test.[65]

Each test has its own criterion by which it determines the extent of oxidation. Viscosity increase, carbon residue increase, or the amount of precipitable material formed are generally utilised.

Controlled engine tests are used in the laboratory to simulate true operating conditions and several measurements may be made to estimate lubricant efficiency. Lacquer deposits on components, sludge deposits on filters and in oil lines, corrosive and abrasive wear, all may be measured.

A great many engine tests have been devised and many of these have been standardised by the Co-ordinating Research Council of America.[66] Little information, however, may be found on the correlation of laboratory and engine tests. Larsen, Armfield and Whitney[67,68] have shown that three oils could be placed in any of the six possible orders of merit by variation of the catalyst in a laboratory oxidation test. Matthews and co-workers[69] have shown, however, that an oxidation test can provide a good indication of how an oil will behave in an engine test, but stress that the catalytic conditions used should be as close as possible to those existing in an engine.

With such a wide variety of empirical and semi-empirical tests to choose from, the choice of test must depend upon the information required. In the following work it was desirable to oxidise different samples of oils for varying periods of time under strictly controlled conditions, without attempting in any way to predict the behaviour of the oils in an engine system. Consequently the test chosen was the Institute of Petroleum Test I.P.48.[61] which has the advantage both of being a standard test and providing operating conditions which are subject to easy control.

The Institute of Petroleum Oxidation Test

The standard oxidation test for lubricating oils in Britain is that of the Institute of Petroleum - I.P. 48, which was originally the British Air Ministry test for aviation engine oils. Garner and co-workers[70] examined this test from the point of view of reproducibility of results and the effect of variations in the specified conditions.

In this test air is passed at a rate of 15 litres per hour through a 40 ml. sample of oil at 200°C. for 6 hours, leaving for 12 to 18 hours and oxidising for a further 6 hours to give a total oxidation time of 12 hours.

Kinematic viscosity at 100°F. (I.P. 71) and Ramsbottom carbon residue (I.P.14) are measured before and after oxidation. The ratio of viscosity after oxidation to viscosity before oxidation, and the increase of the percentage carbon residue are taken as measures of oil oxidation.

This test was created primarily to enable oils to be arranged in order of stability to oxidation, but for the purposes of this work the test was used to oxidise the oils for varying periods of time under standard conditions. At the outset experiments were carried out which showed that no essential differences were produced by oxidising the oil for one prolonged period or in periods of 6 hours as laid down in the official test.

Details of Apparatus

The boiling tube in which the oxidation was carried out was constructed of heat resistant glass 25 cm. long, 2.5 cm. in diameter and fitted with a ground glass top. Into this top was fitted a heat resistant glass cap which contained a glass inlet air tube reaching to 4 mm. from the bottom of the boiling tube and an outlet air tube. This boiling tube was marked at a height corresponding to 40 ml. at room temperature.

The heating bath consisted of a copper vessel 9 in. in diameter and 12 in. in height filled with a heavy duty heating oil. At the required depth in the bath there was a perforated brass plate which contained five specially drilled holes, one in the centre for the stirrer shaft and the other four spaced so as to serve as supports for four oxidation cells. The top of the bath was sealed by an asbestos cover with four holes for the cells, one in the centre for the stirrer shaft and two other smaller holes through which passed respectively, a thermometer and the element of a Sunvic thermostatic control. The bath was heated by two electric heaters fitted externally to the bottom of the bath, one of 1000 watts and the other of 800 watts. The two heaters were used for initial heating of the bath, the larger being switched off when the correct temperature was reached. The heat losses were just balanced by the remaining heater and fine temperature control resulted.

Stirring was provided by a single bladed propeller mounted vertically above the bath.

Insulation of the bath was provided by 1 in. fibre glass sheathing.

Air was provided by means of a "Proctor" diaphragm pump which was capable of providing a non-pulsating flow of up to 300 cubic inches per minute. Sensitive flow control was obtained by means of a stopcock with V-notches cut at either end of the hole in the cock. The flow rate was measured on a normal type U-tube manometer flowmeter with capillary tubing as orifice. Four flowmeters were used, each connected by a stopcock to a common manifold from the "Proctor" pump but with individual lead offs to the oxidation cells. The flowmeters were calibrated by means of a rotary gas meter.

A view of the bath with two cells in position is shown in Fig. 1.

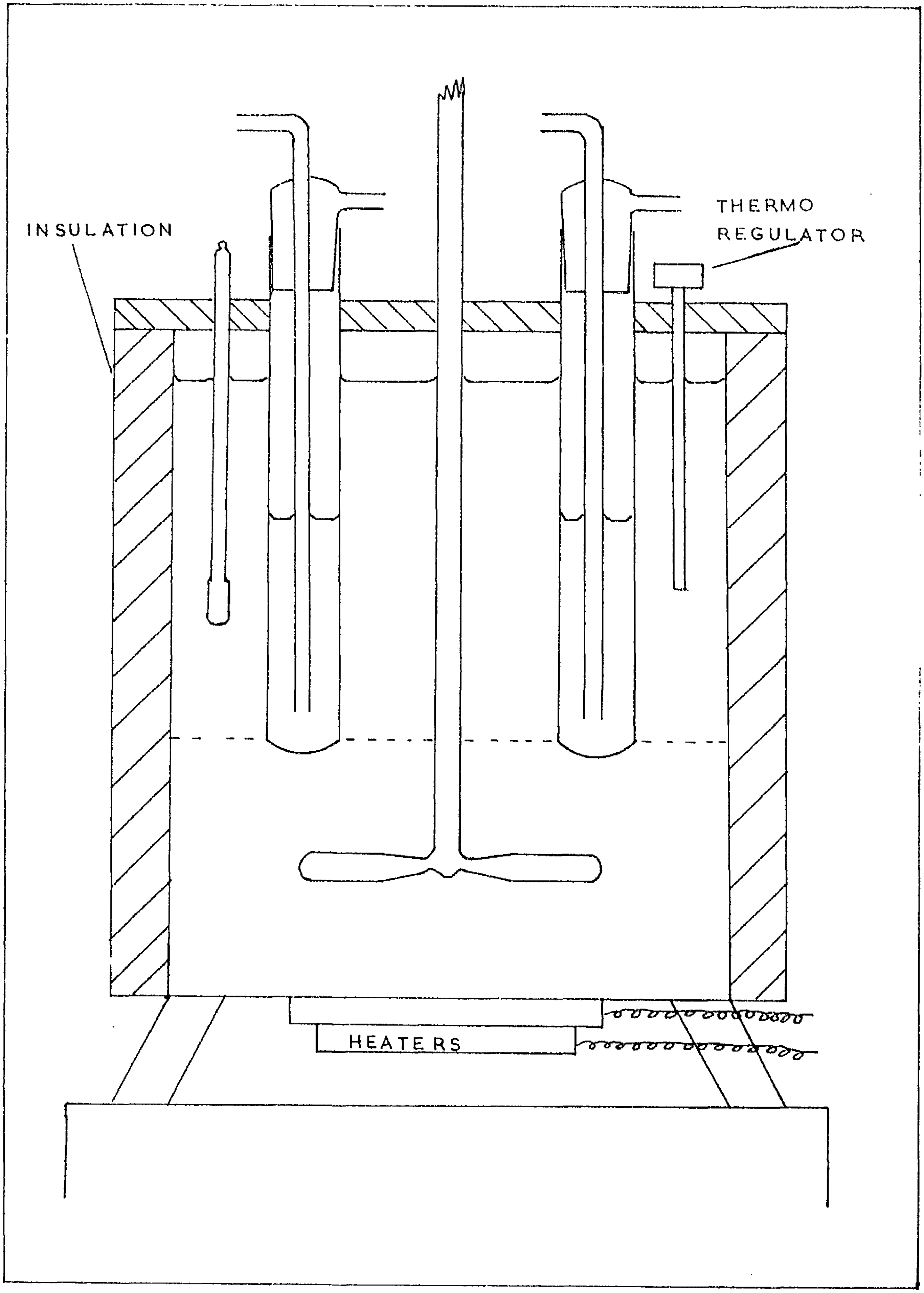


FIG. 1

CHAPTER V

SLUDGE AND RESIN DETERMINATION

CHAPTER V

SLUDGE AND RESIN DETERMINATION

1. Determination of Sludge and Preparation of Desludged Oil

a) The term "sludge" considered in connection with used oils, usually refers to insoluble materials of hydrocarbon origin thrown out of solution during oil oxidation. This definition neglects other degradation, polymerisation or oxidation products which may be dissolved in the oil. These latter materials may be considered as oil soluble sludge since they are not present in the original oil but produced during oxidation. Such dissolved sludge must be considered to be just as objectionable as insoluble sludge as it represents alteratio products of the oil and may be thought of as potential insolubl sludge.

The method used for sludge determination was a modified version of that described by Levin and Towne,[71] which consisted of the direct determination of soluble sludge and the indirect determination of insoluble sludge.

Direct determination of insoluble sludge was not considered since difficulties arise in the treatment of the filtered sludge to remove all traces of oil, most hydrocarbon solvents either dissolving part of it or precipitating soluble sludge from the remaining oil.

Paraffins are poor solvents for sludge or asphaltic materials, the lower boiling paraffins being the poorest of the series. Thus Levin and Towne[71] used a commercial pentane mixture for precipitation, pentane being the lowest molecular weight paraffin which can be conveniently handled. Experiment showed that it did not dissolve material originally undissolve in the oil itself.

It is obviously very arbitrary to classify as "oil soluble sludge" that portion of a clarified oil which is insoluble in commercial pentane. The use of pentane, however, was considrred more desirable than liquid propane as used by Hall, Levin and McMillan[72], as this tends to precipitate material normally present in the unoxidised oil.

The advantage of using pentane, although quite empirical, was that it did not precipitate material from the unoxidised oils, but did precipitate sludge at very short oxidation times with the more aromatic oils.

b) Experimental Procedure

A well stirred, representative sample of the oxidised oil was filtered as rapidly as possible through a Gooch crucible, tightly packed with asbestos to half its depth and kept at 75°C. by means of a heating tape.

On this clarified sample, as well as on an unclarified portion, the pentane insoluble matter was determined as follows:

A 10gm. sample was weighed into a suitable Erlenmeyer flask and to it was added a 100 ml. of pentane, maximum solution being affected by agitation. The solution was allowed to stand overnight, then filtered through a Gooch crucible packed as above. The contents of the crucible were washed with 100ml. pentane, sucked dry and dried in an oven for one hour at 110°C. From the difference in the weights of the pentane insoluble matter the insoluble sludge was calculated as follows:

$$C = \left\{ A - \left(B. \frac{10 - A}{10 - B}\right) \right\}$$

where A = sludge not dissolved in pentane,
original oil sample (g/10gm)
B = sludge not dissolved in pentane,
clarified sample (g./10gm.)
C = oil insoluble sludge (wt.%)

From this calculation it may be seen that 10A gives "total sludge" (wt.%), 10B oil soluble sludge (wt.%) and C gives oil insoluble sludge (wt.%).

The filtrate from both samples was collected and the bulk of the pentane solvent removed by evaporation at low pressure and room temperature. Final traces of pentane were removed under vacuum at 60°C and the resulting "desludged" oil kept for analysis.

2. Determination of Resins and Preparation of Deresined Oil

a) After removal of oil insoluble and oil soluble sludge, there remains in the oil oxidised material which is not precipitable by hydrocarbon solvents. This material is not very highly oxidised or polymerised and is loosely termed "resins". The resins, along with the more highly oxidised material, contain oxygen and therefore being more polar than the hydrocarbons from which they are derived can be adsorbed on to active clays or earths such as Fullers Earth. Sachanen[73] states that the adsorption of resins is not entirely selective; some high molecular weight aromatic hydrocarbons being adsorbed almost as readily as some resins. On the other hand the data of Haus[74] show that the separation of resins from hydrocarbons is unexpectedly sharp.

Before Fullers Earth was adopted as an adsorbent for the quantitative determination of resins, it was thought desirable to carry out some preliminary work using oxidised and unoxidised samples of the naphthenic oil fraction. The principles of the method used are those put forward by Matthews.[75]

The oxidised oil was dissolved in petroleum ether solvent in the ratio, solvent/oil = 25 ml./1gm., and then agitated with Fullers Earth. The Fullers Earth was removed by filtration and the solvent by evaporation.

The following points were then investigated:

(1) The amount of Fullers Earth required to remove a given amount of oxygen at room temperature and the derivation

of an equation relating the quantity of oxygen removed to the amount of Fullers Earth used at constant agitation time.

(2) The effect of agitation time on oxygen removal.

(3) The effect of Fullers Earth on the unoxidised oil.

Solvent Removal from Petroleum Ether Solution of Oil

It was necessary for the subsequent study of the oxygen free oil that the removal of the petroleum ether solvent should be as complete as possible.

The solvent used has a boiling range of 100-120°C. at Atmospheric Pressure, a density of 0.7290 gm./cc., a refractive index of 1.4130 and a molecular weight of 106.

Effect of Solvent on n-d-M Analysis

The n-d-M values of a mixture of unoxidised oil and solvent can be calculated from the following formulae:

where, Subscript (1) refers to oil
(2) refers to solvent
and (av) refers to average of (1) and (2).

w = respective weights
x = mole fraction
$[R]$ = molar refraction

$$d_{av} = \frac{w_1 + w_2}{\frac{w_1}{d_1} + \frac{w_2}{d_2}}$$

$$M_{av} = x_1 M_1 + x_2 M_2$$

n_{av} is calculated from:

$$[R]_{1,2} = \frac{n_{av}^2 - 1}{n_{av}^2 + 2} \cdot \frac{M_{av}}{d_{av}}$$

where $[R]_{1,2} = x_1 R_1 + x_2 R_2$

and $$[R]_1 = \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{d_1}$$

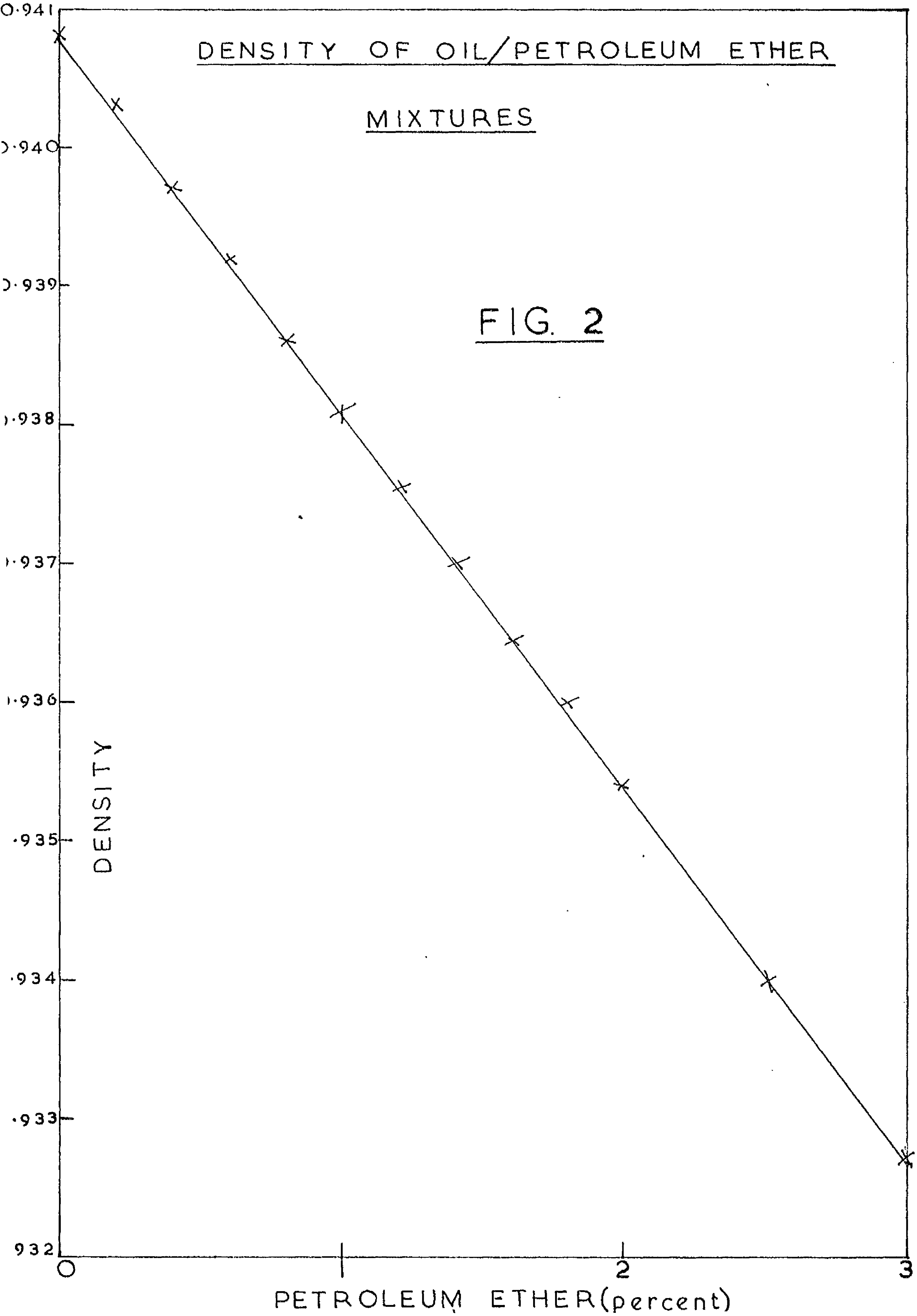
Using the above equations the n-d-M values of solvent/oil mixtures containing 0 - 3% by weight solvent were calculated and the carbon distribution obtained.

TABLE 4

Pet. Ether % (w/w)	n	d	M
0	1.5280	0.9408	326
0.2	1.5291	0.9403	325
0.4	1.5290	0.9397	323
0.6	1.5281	0.9392	322
0.8	1.5272	0.9386	321
1.0	1.5282	0.9381	319
1.2	1.5272	0.9375	318
1.4	1.5263	0.9370	317
1.6	1.5273	0.9364	315
1.8	1.5269	0.9360	314
2.0	1.5259	0.9354	313
2.5	1.5250	0.9340	310
3.0	1.5240	0.9327	307

When the density of the mixture is plotted against the percentage solvent (Fig.2) a relationship is obtained which enables the solvent residue left after evaporation to be obtained from a density determination.

The percentage error in carbon distribution values caused by the presence of solvent in the oil were then calculated (Table 5) and plotted against the percentage solvent (Fig.3).



DENSITY OF OIL/PETROLEUM ETHER MIXTURES

FIG. 2

PERCENTAGE ERROR IN CARBON DISTRIBUTION DUE TO PRESENCE OF PETROLEUM ETHER

FIG. 3

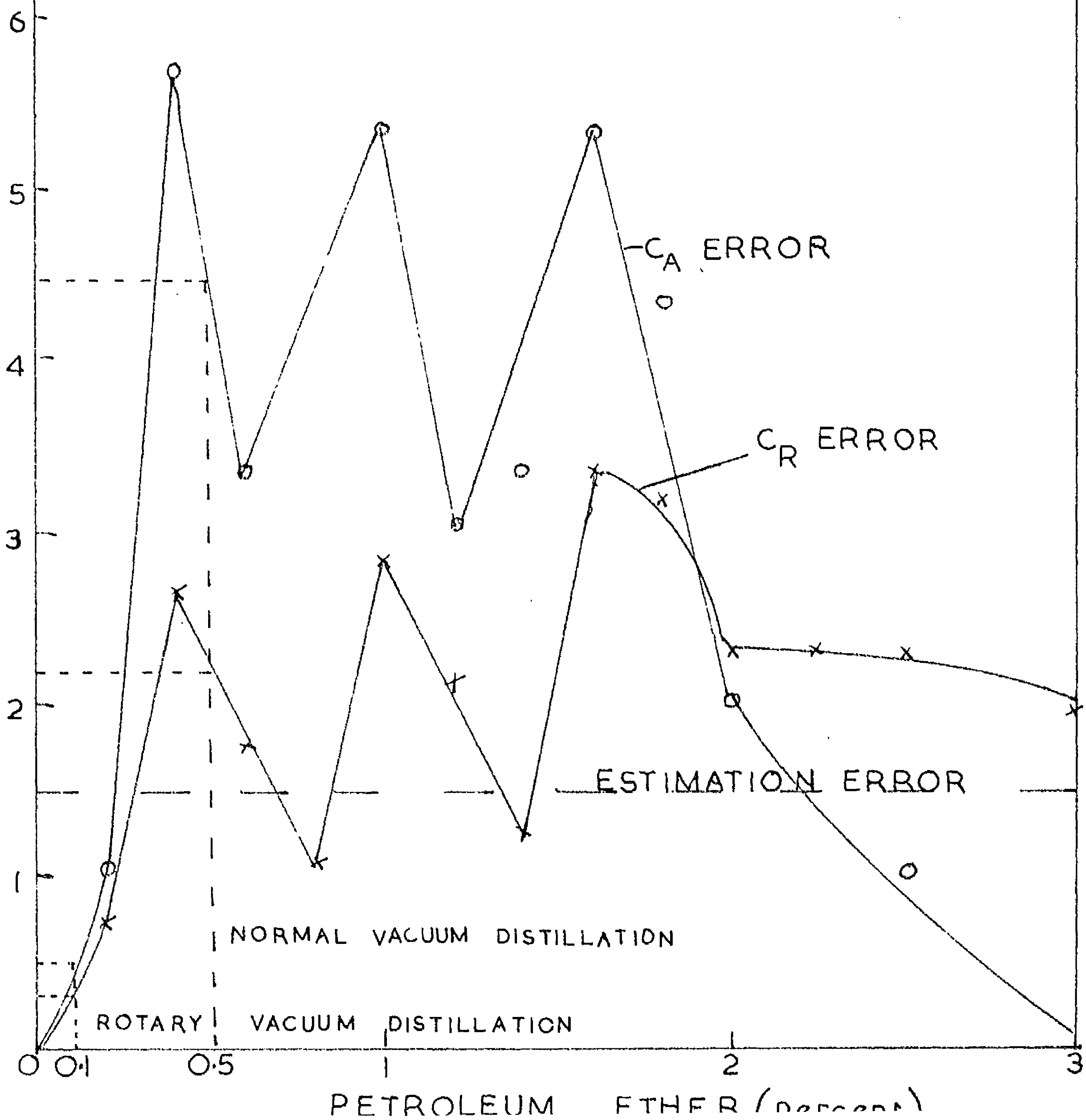


TABLE 5

Pet. Ether %	% C_R	% Error	% C_A	% Error
0	56.1	0	29.8	0
0.2	55.7	0.713	30.1	1.01
0.4	54.6	2.67	31.5	5.70
0.6	55.1	1.78	30.8	3.36
0.8	55.5	1.07	30.1	1.01
1.0	54.4	2.85	31.4	5.37
1.2	54.9	2.14	30.7	3.02
1.4	55.4	1.25	29.9	0.336
1.6	54.2	3.39	31.4	5.37
1.8	54.3	3.21	31.1	4.36
2.0	54.8	2.32	30.4	2.01
2.5	54.8	2.32	30.1	1.01
3.0	55.0	1.96	29.7	0.336

Thus by utilising Figs. 2 and 3 the effectiveness of solvent removal and the error in the carbon distribution values caused by the remaining solvent may be readily obtained.

Methods of Solvent Removal

Vacuum Distillation

A normal vacuum distillation unit heated by an "isomantle" was employed. The bulk of the solvent was first distilled off the oil in a large flask with gentle heat to prevent frothing and the residue transferred to a small flask. Distillation was then continued with an extra heating tape wrapped round the neck of the flask to facilitate solvent removal.

For 5gm. of unoxidised oil and 125 ml. of solvent the time required to remove the limiting amount of solvent at a distillation temperature of 27-35°C. and a vacuum of 28 inches of mercury was 90 minutes.

The density finally reached was 0.934 corresponding to a solvent content in the oil of 0.5% and errors of 2.2% and 4.5% in C_R and C_A respectively.

Rotary Vacuum Distillation

The evaporator used was manufactured by Towers Ltd. (Cat. No.1480). In this case the rotating flask was bathed in liquid paraffin at 100°C. and the bulk of the solvent distilled off in 2-3 minutes without any frothing. The solvent in the receiving flask was then removed to reduce the amount of vapour in the unit and distillation continued until solvent removal was completed. Water had been rejected as a heating bath medium since on releasing the vacuum water vapour entered the apparatus and adversely affected the subsequent oxygen analysis.

The time required for limiting solvent removal was 45 minutes at 100°C. and a vacuum of 28 inches of mercury. The final density obtained was 0.9405 corresponding to a solvent concentration of 0.1% and errors of 0.3% and 0.5% in C_R and C_A respectively.

Discussion

In the determination of the carbon distribution of an oil from an n-d-M analysis a total error of 1.5% is to be expected. With the first distillation technique the errors in C_R and C_A are above this value; with the second method both C_R and C_A errors are below this estimation error. The rotary vacuum distillation method is therefore faster, decreases chances of local overheating and produces a final concentration of solvent which will not affect the accuracy of the n-d-M results.

b) Removal of Oxygen Containing Bodies from the Oil

Experimental

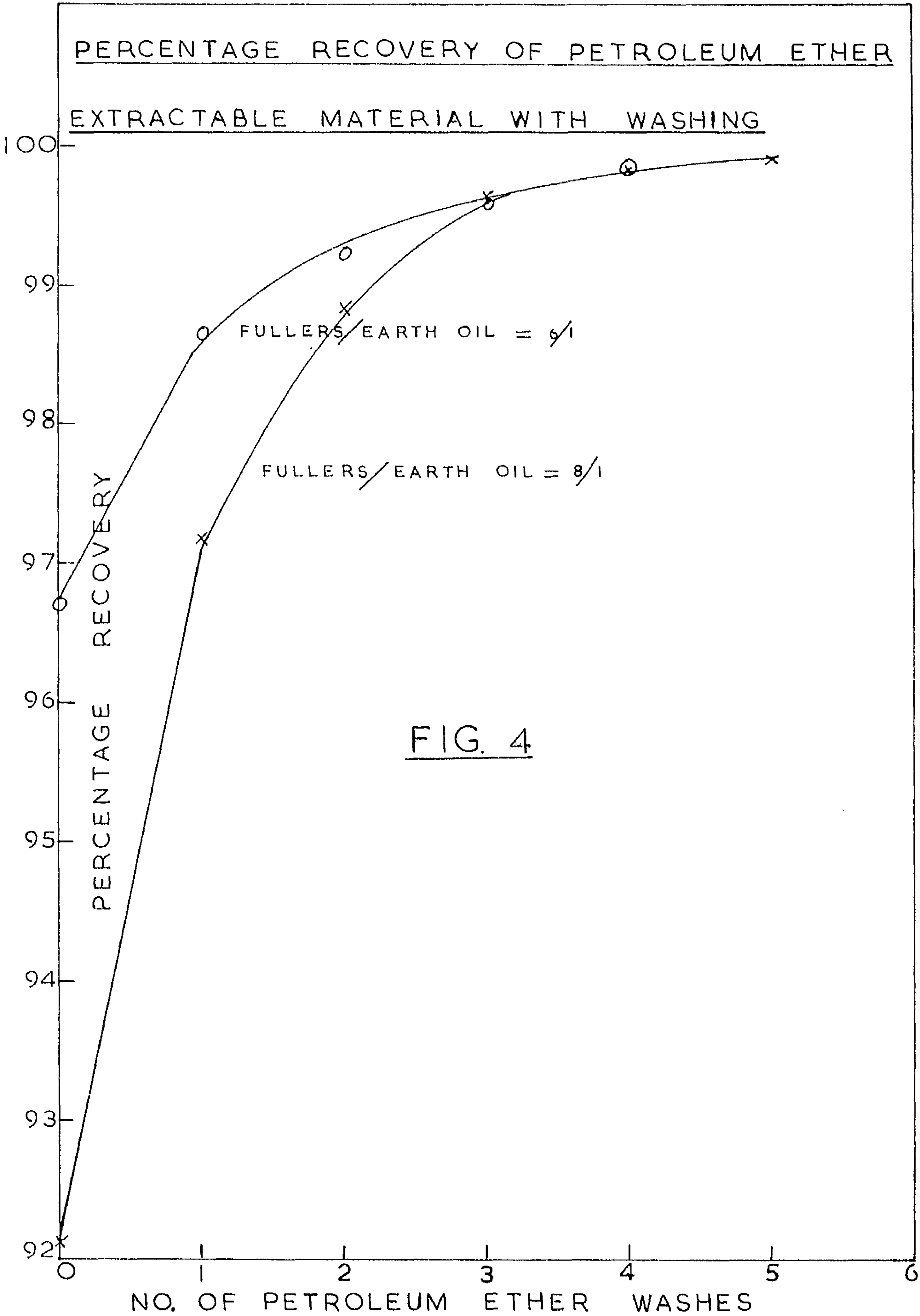
5gm. of oxidised oil were dissolved in 125ml. of petroleum ether and Fullers Earth added. The solution was then agitated, filtered through a cellulose-asbestos filter pad sold under the name "Sterimat", and the Fullers Earth washed with more petroleum ether. A sample of the filtrate was taken for an optical density analysis, as described below, and the solvent removed by evaporation. Finally, the oxygen content of the residual oil was determined by the Unterzaucher method[105].

Washing

When an oxygen containing oil is treated with Fullers Earth, the oxygenated molecules are preferentially adsorbed, along with smaller amounts of non-oxidised compounds which are not so firmly associated with the Fullers Earth and may be removed by washing with an excess of petroleum ether. Now for an n-d-M analysis to be carried out on an oil the oxygen content should be below 0.5% and as this percentage is reached the Fullers Earth begins to adsorb more of the non-oxidised compounds. These losses must be recovered if any reliability is to be placed on any subsequent quantitative analysis based on the amount of oxidised compounds removed by the treatment.

The recovery was achieved by agitating the filtered off Fullers Earth with a further 125 ml. of petroleum ether for 15 minutes, when an oil of the same oxygen content as the first extract could be recovered. Several washings of this nature were found to be necessary to complete recovery of non-oxidised oil when an excessive amount of Fullers Earth is used (Fig.4).

The weight of each subsequent extract was determined by evaporating off the solvent in the rotary evaporator and then transferring the oil residue to a small weighing scoop by means of 30/40°C. petroleum ether and allowing this solvent to evaporate off in a drying chamber kept at 50°C.



PERCENTAGE RECOVERY OF PETROLEUM ETHER EXTRACTABLE MATERIAL WITH WASHING

FIG. 4

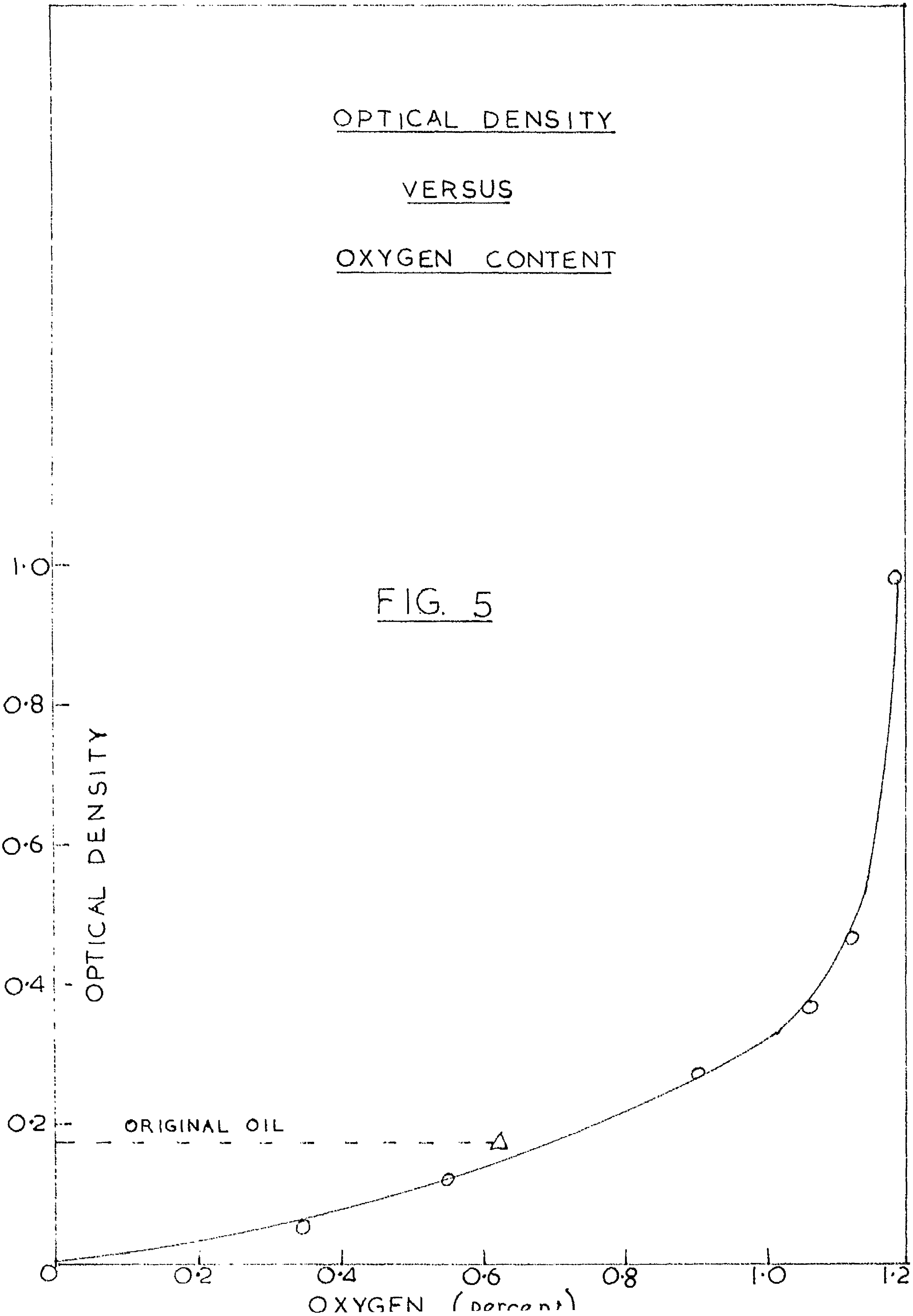
c) Optical Density and Oxygen Content

The optical density of an oil depends both upon its chemical nature and its oxygen content. This can be seen from Fig. 5 where the optical density is plotted against the oxygen content of petroleum ether solutions. The original oil shows a slight difference in optical density from a recovered oil of the same oxygen content but this difference is not marked and is perhaps due to the effect of oxidation on the chemical nature of the oil.

When the oxygen content of the petroleum ether solutions was plotted against the log. optical density a straight line was obtained (Fig. 6). This may be used to estimate the amount of oxygen in the oil dissolved in petroleum ether, remembering that varying degrees of oxidation may effect the chemical nature of the oil with a corresponding variation in optical density. However, even with this reservation matching with prepared samples provides a useful guide to enable an estimate to be made of the extent of oxygen removal.

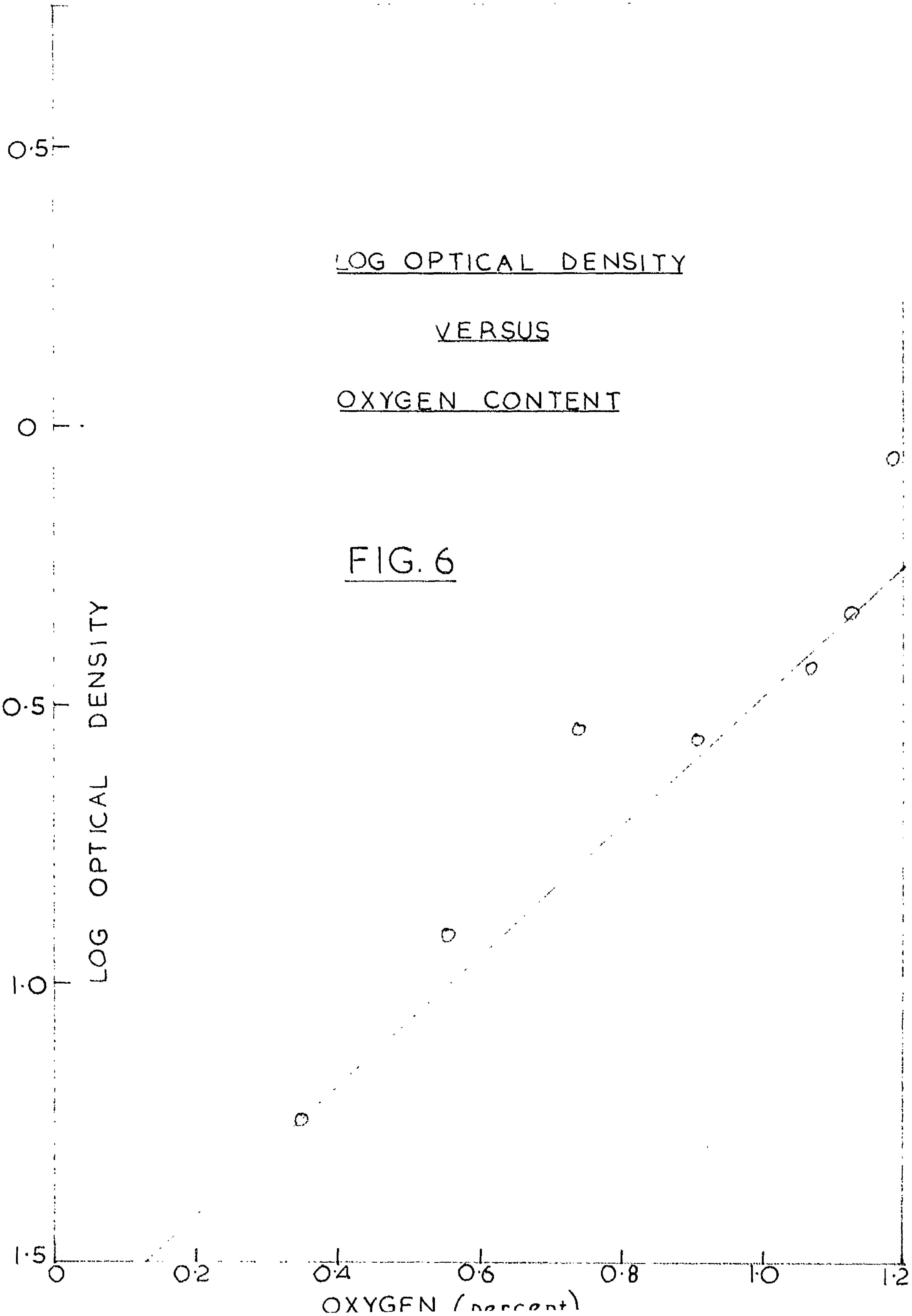
d) Factors Affecting Oxygen Removal

For a given oil/solvent ratio the removal of oxidised material from the oil depends upon the quantity of Fullers Earth used and the time required for equilibrium to be reached. The agitation time required to gain equilibrium decreases with increasing amounts of Fullers Earth (Fig. 7) and correspondingly the amount of Fullers Earth required decreases with increasing



OPTICAL DENSITY VERSUS OXYGEN CONTENT

FIG. 5



LOG OPTICAL DENSITY

VERSUS

OXYGEN CONTENT

FIG. 6

EFFECT OF AGITATION TIME ON OXYGEN CONTENT WITH CONSTANT FULLERS EARTH TO OIL RATIO

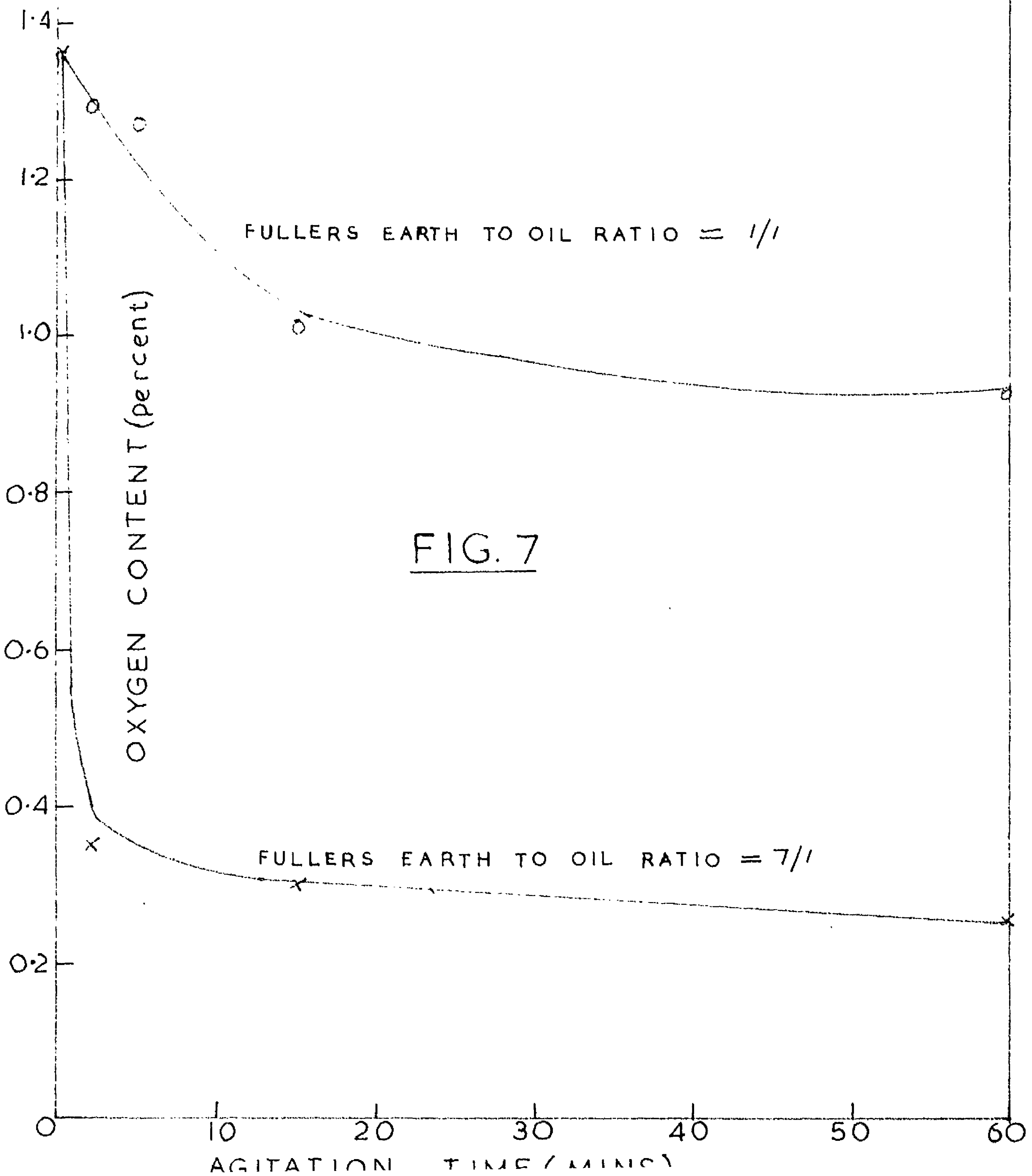


FIG. 7

agitation time although this effect is considerably less with an excess of Fullers Earth (Fig. 8).

Optimum conditions for removal of oxygen from 1.35% to 0.44% was 15 min. agitation time and a Fullers Earth/oil ratio of 6/1. Further extraction was limited by the amount of washing required to recover oil losses and is unnecessary if an n-d-M analysis is required.

If x_1 represents the original O_2%,
x represents the oxygen removed (%), and
C represents the Fullers Earth/oil ratio, (w/w).

When log. $\frac{x}{x_1}$ was plotted against log. C a straight line was obtained (Fig. 19). This is in agreement with the Freundlich isotherm for adsorption from solution and would appear to indicate an even distribution of oxygen over the oxidised material.

From this graph the equation:

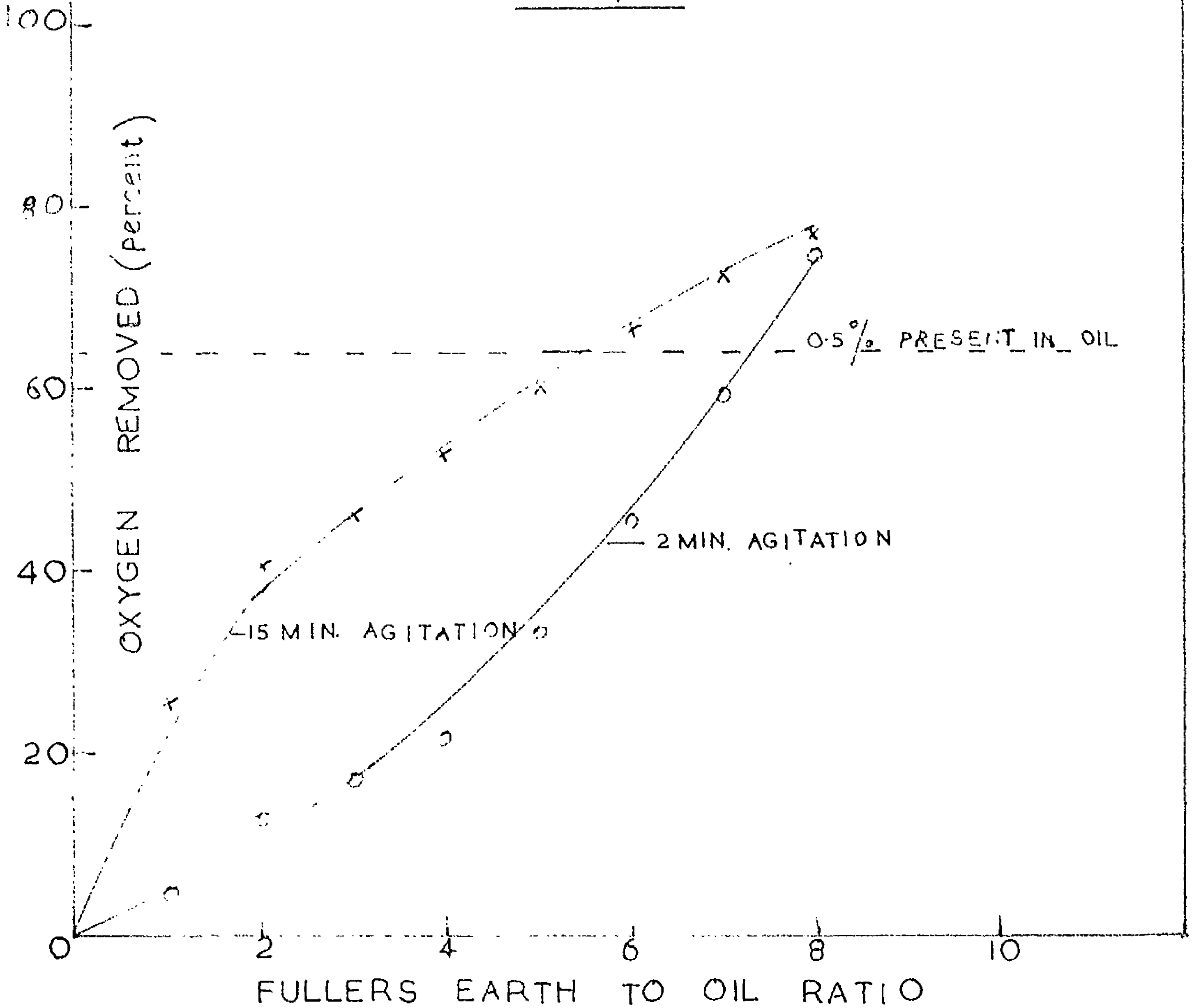
$$\log.\frac{x}{x_1} = \log.K + \frac{1}{n}\log.C$$

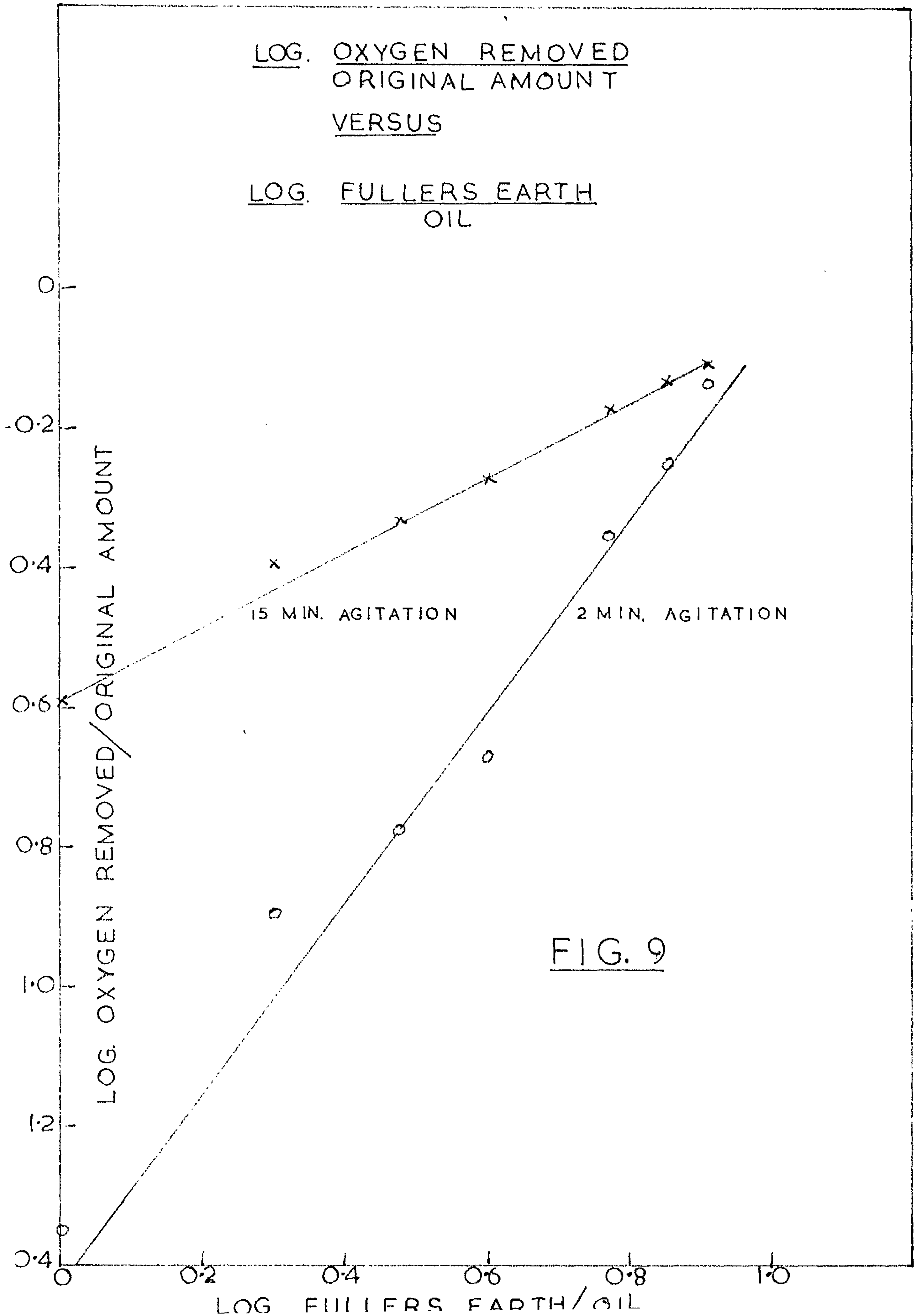
holds where K and n are constants.

From this equation the amount of Fullers Earth required to reduce the oxygen content from one percentage to another may be calculated. This allied with colour matching makes the Fullers Earth treatment fast and simple and prevents excessive oil losses due to an excess of Fullers Earth being used.

PERCENTAGE OF ORIGINAL OXYGEN IN OIL REMOVED VERSUS FULLERS EARTH TO OIL RATIO

FIG. 8





LOG. OXYGEN REMOVED / ORIGINAL AMOUNT
VERSUS
LOG. FULLERS EARTH / OIL
0
-0·2
0·4
0·6
0·8
1·0
1·2
·4
LOG. OXYGEN REMOVED/ORIGINAL AMOUNT
15 MIN. AGITATION
2 MIN. AGITATION
0
0·2
0·4
0·6
0·8
1·0
LOG FULLERS EARTH/OIL

FIG. 9

c) Effect of Fullers Earth on Unoxidised Oil

The procedure used for the treatment of oxidised oil was repeated with the unoxidised oil with Fullers Earth/oil ratios varying from 1/1 to 8/1. The original oil has an oxygen content of 0.625% and this is progressively reduced with increasing amounts of Fullers Earth although oil losses are much greater due to the much smaller amount of oxygen present.

When the n-d-M values were examined it was noticed that refractive index, density and viscosity decreased slightly as the Fullers Earth/oil ratio was increased, the accuracy of the molecular weight determinations not permitting a similar examination.

TABLE 6

F.E./Oil Ratio	n	d	M	V_K	O_2%
0	1.5280	0.9408	326	227	0.625
1	1.5232	0.9365	326	207	0.572
2	1.5250	0.9399	326	192	0.554
3	1.5245	0.9391	326	184	0.513
4	1.5235	0.9374	326	180.8	0.471
8	1.5220	0.9349	326	179	0.288

Although individual changes in properties occur no appreciable change in carbon distribution and ring content was brought about by this treatment.

TABLE 7

F.E./Oil Ratio	% C_A	% C_R	%C_N	% C_P	R_A	R_T	R_N
0	29.8	56.1	26.3	43.9	1.21	2.81	1.6
1	26.5	56.9	30.4	43.1	1.08	2.85	1.77
2	27.0	58.1	31.1	41.9	1.10	2.92	1.82
3	26.8	57.9	31.1	42.1	1.09	2.91	1.82
4	26.4	57.4	31.0	42.6	1.07	2.88	1.81
8	25.9	56.7	30.8	43.3	1.05	2.84	1.79

The changes in physical properties were directly related to the decrease in oxygen content (Fig.10) and the changes were such as to tend towards a constant carbon distribution for oxygen contents less than 0.5%.

Thus at this low concentration of oxygen, oil losses if any were unimportant as far as the n-d-M analysis is concerned.

The effect of Fullers Earth on unoxidised samples of Oils 1 and 2 was also examined and it was found that the changes in properties produced was much lower than that for the naphthenic type oil, as was to be expected since they did not contain any oxygen.

Davis, Lincoln, Byrkit and Jones[76] have removed the oxidised portion of an oil by means of an active clay. They then contacted the new oil with 100 per cent by weight of clay: and an apparent resin content of 0.4 per cent was

EFFECT OF FULLERS EARTH TREATMENT ON PROPERTIES OF UNOXIDISED OIL

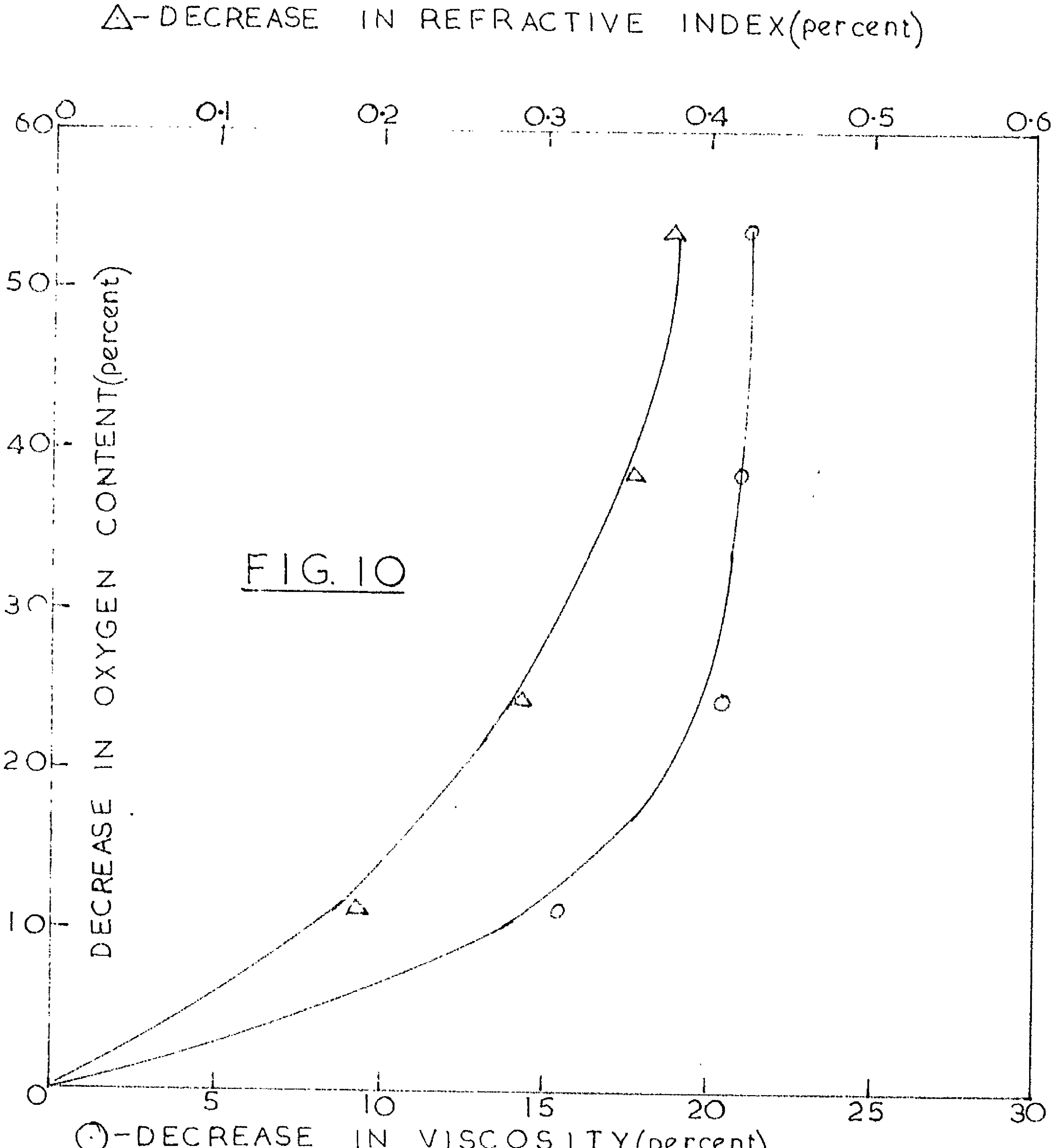


FIG. 10

found. The removal of this resin made practically no difference in the oil characteristics, thus bearing out the conclusions made above on the basis of the Fullers Earth treatment. Thus any possible effect of the Fullers Earth on the n-d-M analysis of the unoxidised oil may be neglected.

f) Determination of Resins

About 20 gm. of oxidised oil was accurately weighed out into a flask and the required amount of petroleum ether solvent added. From a knowledge of the period of oxidation of the oil and its oxygen content the approximate quantity of Fullers Earth required was estimated. This amount was added to the solvent/oil mixture and agitated for 15 minutes. A small sample was then filtered and colour matched with a previously prepared sample of unoxidised oil and solvent. If extraction was not complete small amounts of Fullers Earth were added until a filtered sample matched with the prepared sample. The solvent and unoxidised oil mixture was then filtered. To the filtered Fullers Earth was then added the same amount of fresh solvent as was originally used and the mixture agitated for 15 minutes. This mixture was then filtered and the filtrate combined with the original solvent/oil filtrate.

Solvent was then removed by evaporation and the residue of unoxidised oil transferred to a weighed bottle by means of 30/40°C. petroleum ether. After evaporation of this solvent at 60°C. the bottle and contents were weighed and the weight of the recovered oil obtained. From this the total weight of oxidised materials was obtained and from a knowledge of the quantity of total sludge the amount of resins was obtained by difference and expressed as a percentage. At the same time a sample of deresined oil was obtained which was kept for further analysis.

CHAPTER VI

THE EFFECT OF OIL COMPOSITION ON THE EXTENT OF OXIDATION.

CHAPTER VI

THE EFFECT OF OIL COMPOSITION ON THE EXTENT OF OXIDATION

The Institute of Petroleum oxidation apparatus, described in Chapter IV, was used at the outset to oxidise samples of the three oils for periods ranging from 1 hour to 24 hours. The oxidised oils so obtained were then treated by the procedures described in Chapter V, to determine the amounts of sludge and resins produced and at the same time obtain samples of sludge and resin free oils. On these samples of oxidised, sludge free and resin free oils various analysis were carried out in order to establish the effect of oxidation time on the production of the different types of oxidation products. Also from these analysis figures, information was obtained which enabled the nature of the oxidised products to be deduced, and the nature of the unoxidised portion of the oil to be determined. The last two points will be discussed in Chapters VII and VIII respectively.

Sludge and Resins Produced

Davis, Lincoln, Byrkit and Jones[76] have suggested that owing to the much greater proportion of resins than sludge produced on the oxidation of a lubricating oil, the resins formed are a truer measure of the extent of oxidation. On examining Fig. 11, the effect of oil composition on the extent of oxidation can be observed. Oil No.1, the lowest

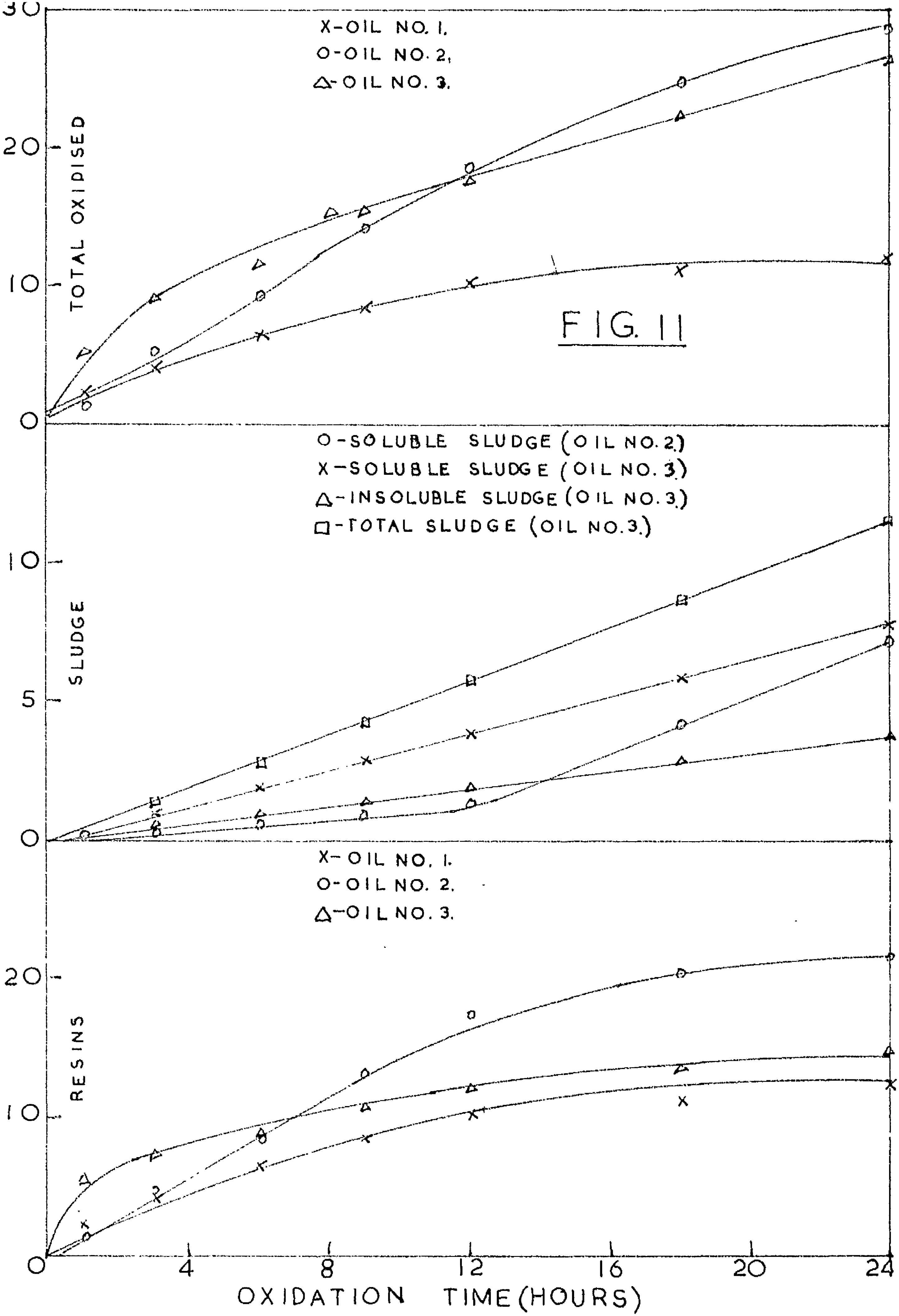

X-OIL NO. 1.
O-OIL NO. 2.
△-OIL NO. 3.
TOTAL OXIDISED
30
20
10
0
O-SOLUBLE SLUDGE (OIL NO. 2)
X-SOLUBLE SLUDGE (OIL NO. 3)
△-INSOLUBLE SLUDGE (OIL NO. 3)
□-TOTAL SLUDGE (OIL NO. 3)
SLUDGE
10
5
0
X-OIL NO. 1.
O-OIL NO. 2.
△-OIL NO. 3.
RESINS
20
10
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 11

in aromatics, formed as expected the smallest amount of retained oxidation products (as distinct from the gaseous products of oxidation). It would have been expected that Oil No.3, containing by far the greatest amount of aromatics would have produced the largest amount of retained oxidation products. This was indeed the case up to about 12 hours oxidation (cf. the standard oxidation test time). After this time the amount produced by Oil No.2 was greater due to a more constant rate of formation, while the rate for Oil No.3 fell after an initially high value.

No insoluble sludge was produced by Oils No.1 and 2 and no soluble sludge by Oil No.1 during the oxidation periods selected, as might be expected from the aromatic contents of the oil. Oil No.3 formed far more total sludge than Oil No.2, but while the rate of formation of insoluble and soluble sludge for Oil No.3 was linear, the rate of formation of soluble sludge of Oil No.2 increased rapidly after 12 hours and although it did not quite reach the extent of soluble sludge in Oil No.3 at 24 hours its rate of formation at this stage was much higher, but at approximately the same level as that for total sludge in Oil No.3.

In all cases the rate of formation of resins fell after about 12 hours oxidation time. In this respect Davis et al.[76] noted that in an engine test, the decrease in resin content occurred approximately concurrently with the increase in pentane insolubles, suggesting that resins after formation oxidised further to sludges. A similar effect was noted in the present work and is illustrated in Fig.12, where it is particularly noticeable with Oil No.2. The rate of formation of sludges in Oil No.3 was linear and had no corresponding increase with the decrease in resin formation, but this is again consistent with the work of Davis[76] who found that in less refined oils, the resin content reached a constant quantity and the sludges produced at a constant rate. In this respect it should be noted that Oil No.3 contained a very high percentage of aromatics, indicating a low degree of refining, as one of the effects of refining a crude is to reduce the amount of aromatics present.

Davis et al.[76] noted that the decrease in resins was not equal to the increase in sludge formation and they attributed this discrepancy as being due to further oxidation to oil insolubles which they did not measure. In this respect they seem to have ignored the fact that a very large amount of the oxygen absorbed by the oil can be accounted for in the gaseous products of oxidation such as water and carbon dioxide and therefore part of the decrease in resin formation could be quite easily explained by an increase in the rate of formation of these gaseous products. Haus[74] considers the precipitation process cyclic. He suggested that sludges were produced from resins until the limit of their solubility was reached, when they precipitate and carry adsorbed resins with them. The resin content of the oil would then increase to

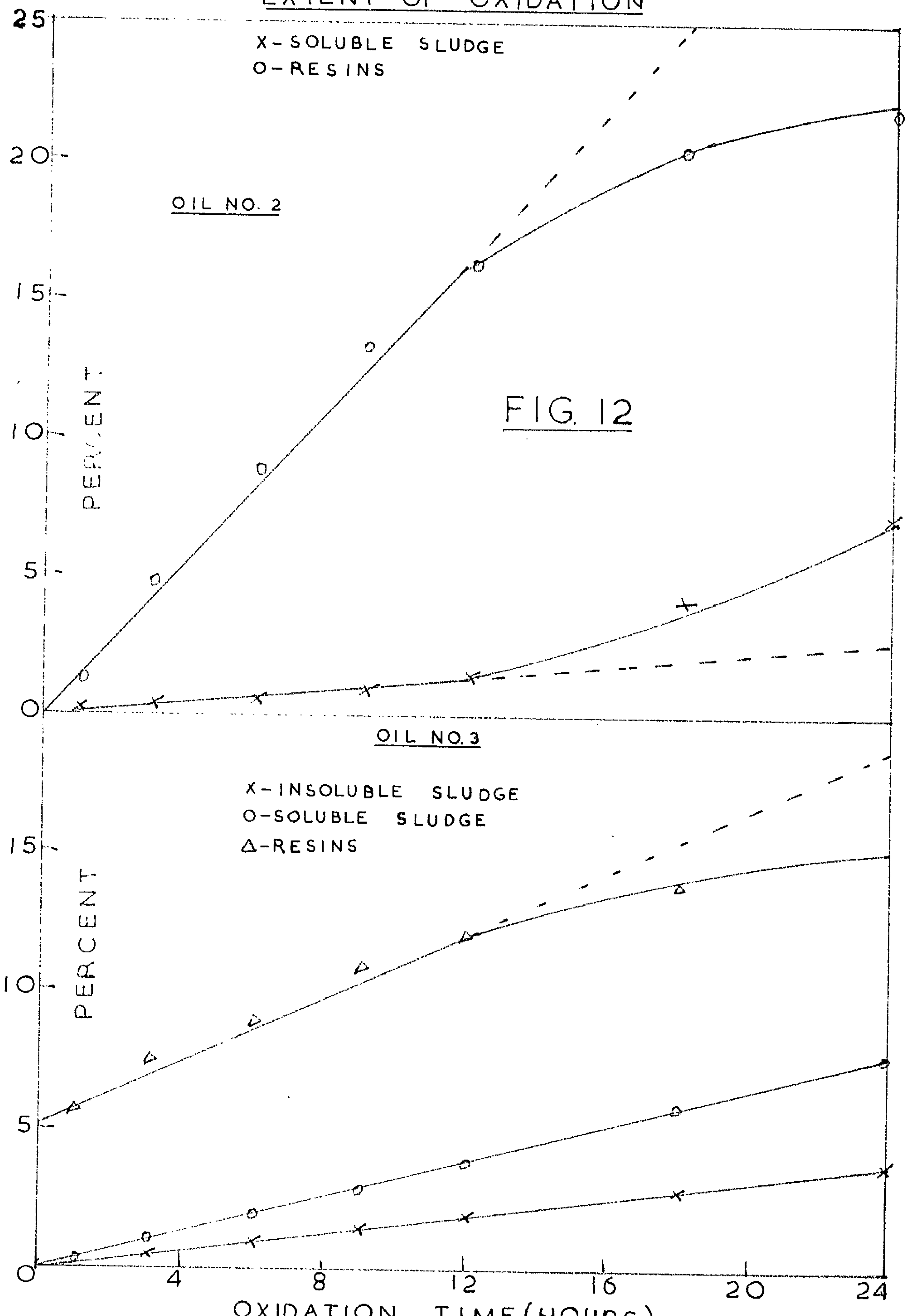

EXTENT OF OXIDATION
X-SOLUBLE SLUDGE
O-RESINS
OIL NO. 2
PERCENT
25
20
15
10
5
0
OIL NO. 3
X-INSOLUBLE SLUDGE
O-SOLUBLE SLUDGE
Δ-RESINS
PERCENT
15
10
5
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 12

a new maximum and the cycle repeat. This effect was not noted in the present work.

Oxygen Contents of Oxidised Oils

As was mentioned earlier in Chapter II, the work of Dornte,[42,57,58] Fenske et al.[49] and Hicks-Bruun et al.,[59] has shown that the bulk of the oxygen adsorbed by an oil could be accounted for in the gaseous products of oxidation. The measurement of the amount of oxygen remaining in the oil was not, therefore, a measure of the total oxygen reacting with the oil. It was important, however, to determine how the oxygen retained by the oil varied with oxidation time and oil composition.

It can be seen from Fig. 13, that the curves for oxygen versus oxidation time are similar in type for the two oils of higher aromatic content, while that of the low aromatic oil is dissimilar. The former two oils showed an increase in oxygen content first, followed by a decrease and then finally an increase again, whereas the latter showed a steady increase in oxygen content with time. This increase then decrease in oxygen content was most marked with Oil No.3, a very rapid increase taking place in the first hour of oxidation. The extent of this increase was verified by repeated oxidations for periods less than sixty minutes.

Larsen, Thorpe and Armfield[52] have determined quantitatively the products of oxidation of five classes of hydrocarbons. Although peroxides did not appear to constitute

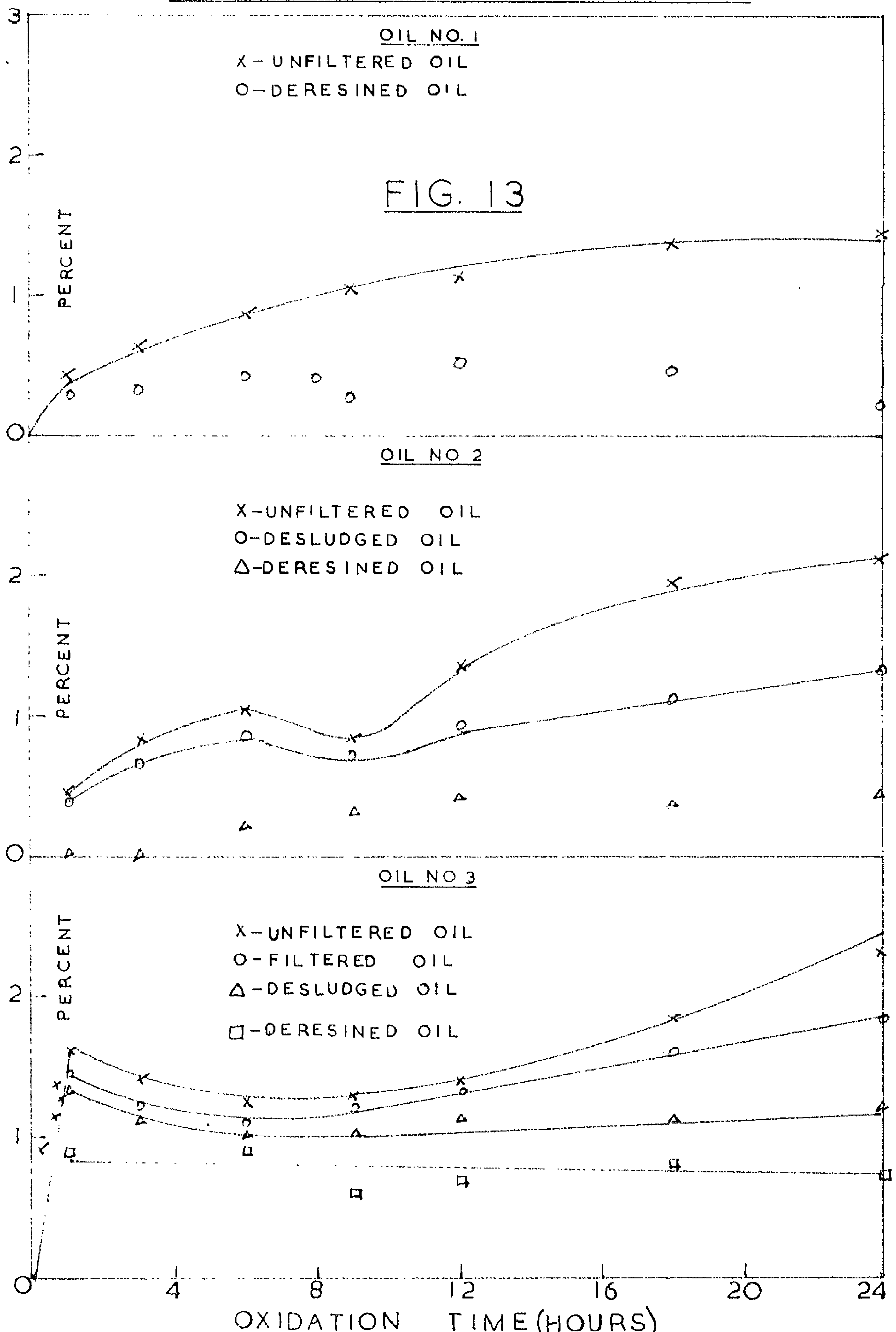


FIG. 13
OIL NO. 1
X – UNFILTERED OIL
O – DERESINED OIL
OIL NO 2
X – UNFILTERED OIL
O – DESLUDGED OIL
Δ – DERESINED OIL
OIL NO 3
X – UNFILTERED OIL
O – FILTERED OIL
Δ – DESLUDGED OIL
□ – DERESINED OIL
PERCENT
3
2
1
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

a major oxidation product Larsen et al.[40] have shown that peroxide content rises sharply in the early stages of oxidation and then falls. Dornte and co-workers[42,57,58] observed the formation of peroxides in the oxidation of while oils, but no peroxides were detected in the oxidation of other less refined oils. Fenske et al.[49] doubt that peroxides may be found in measurable amount.

These oxidised oil samples were analysed for peroxides but no trace was detectable. It may be assumed therefore, that the rise and fall in oxygen content cannot be directly due to the formation and decomposition of peroxides, but rather to other primary products of the decomposition.

In cases where sludges and resin were present the effect of their removal was to reduce the amount of oxygen but not the shape of the oxygen versus oxidation time curve. Since resins represent the bulk of all the retained oxidation products it is the form of this oxygen versus oxidation time curve which determines that of all the others. The values of oxygen content of the deresined Oil No.3 was higher than that expected from the extent of the Fullers Earth treatment, but this was found to be due to the presence of water formed during oxidation and retained in the oil as an emulsion.

From the above results it would then appear that after the initial absorption of oxygen to form peroxides and then, extremely rapidly, the primary decomposition products of the peroxides, the cracking and degradation processes forming the gaseous /

products used up more oxygen than was being absorbed by the oil. Thereafter this reaction reduced in extent and the loss of oxygen was more than counterbalanced by the amount absorbed.

With oil of greater paraffinicity the time required to reach equilibrium in the formation and decomposition of compounds to form the gaseous products of oxidation becomes much less until it is negligible in the case of Oil No.1. This may be due to the greater availability of paraffinic type hydrocarbons, which will be involved in the formation of gaseous products. This conclusion is supported by the work done elsewhere on the oxidation of pure hydrocarbons.

Carbon Residue

The carbon residue of an oil is dependant both upon its carbon/hydrogen ratio and the amount of oxygen present in it. On oxidation the carbon/hydrogen ratio will tend to increase due to condensation and polymerisation type reactions and thus increase the carbon residue value, while the oxygen content also increases and reduces the carbon residue. The final balance will then depend upon the nature of the oil before oxidation and its oxidation behaviour.

For the three oils under consideration, it can be seen (Fig. 14) that the carbon residues of the oils tended to increase with oxidation time. With Oil No.1, the rate of increase was linear at first but then increased, possibly due to the corresponding reduction in rate of the oxygen retention of the oil (Fig. 13). With Oil No.2, the carbon residue of

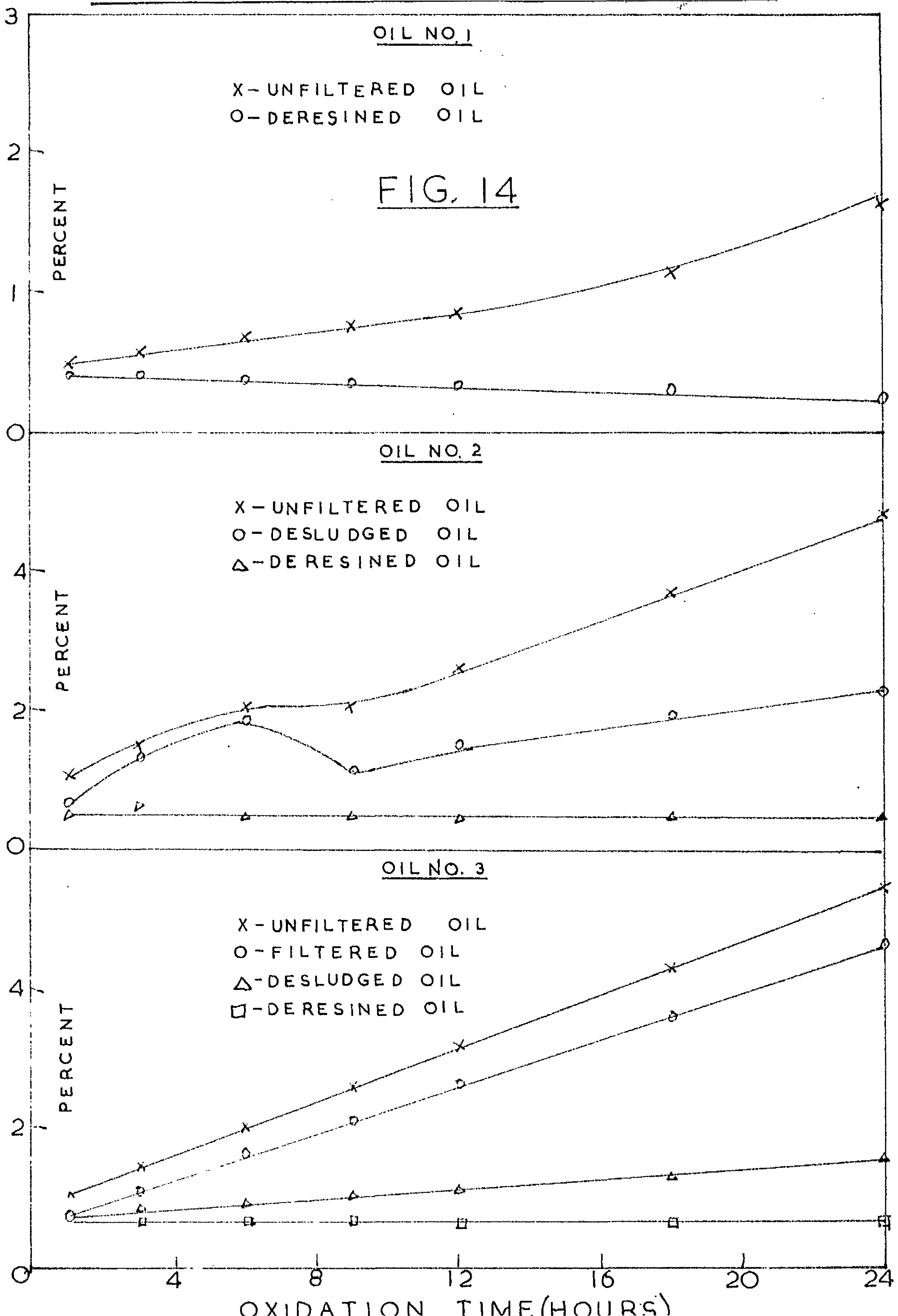

OIL NO. 1
X - UNFILTERED OIL
O - DERESINED OIL
OIL NO. 2
X - UNFILTERED OIL
O - DESLUDGED OIL
△ - DERESINED OIL
OIL NO. 3
X - UNFILTERED OIL
O - FILTERED OIL
△ - DESLUDGED OIL
□ - DERESINED OIL
PERCENT
PERCENT
PERCENT
3
2
1
0
4
2
0
4
2
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 14

the oxidised portion of the oil followed the same pattern as that of the oxygen versus oxidation time curve. This effect was more noticeable on the desludged oil and is contrary to what would be expected in the relationship between oxygen content and carbon residue. It must be assumed then, that the decrease in oxygen content of the oil was allied with a far greater decrease in the carbon/hydrogen ratio.

It would appear that the structure of the oxidised part of the oil and the reactions leading to the formation of those structures were far more important in this oil in determining the carbon residue than was the oxygen content of the oil. The results given by Oil No.3 agree with this in that the carbon residues of the oxidised parts of the oil increased linearly with time and independently of the oxygen content of the oil.

The carbon residue of the oil increased with increasing amounts of aromatics as can be seen from Fig. 14. A similar effect was noted by Gibson[77] who found that above 9% C_A, the carbon residue increase was a function of % C_A. This is to be expected from the high carbon/hydrogen ratio of aromatics.

When the carbon residue was broken down into the contribution of sludges and resins to the total value, it was found that this was dependant on the composition of the oil, as can be seen from Table 8.

TABLE 8

	Contribution to C.R. at 24 Hours Oxidation			
Oil No.	Insoluble Sludge	Soluble Sludge	Resins	Hydrocarbons
1	0	0	85%	15%
2	0	52.2%	37.5%	10.3%
3	15.2%	55.8%	18.3%	10.7%

It can be seen that as the aromatic content of the oil increased the contribution of the more heavily oxidised part of the oil increased while that of the resins decreased and that of the hydrocarbon portion of the oxidised oil was small and tended to a constant value.

This agrees with Smith[78], who suggested that the carbon residue of a crude is roughly proportional to its resin content, since hydrocarbons do not form an appreciable amount of coke under the conditions of the Ramsbottom and Conradson carbon residue tests.

Vassilieff[79] has shown that resins in crude oils produced 20% and sludges 70% of the coke in the Conradson test. It can be seen that the values for the above oxidised samples of oil tend to this value with increase in aromatic content.

Viscosity

TABLE 9

Oil No.	Viscosity of Unoxidised Oil		Viscosity Doubles at		Viscosity Ratio at 12 and 24 Hours			
	20°C	50°C	20°C after	50°C	20°C	50°C	20°C	50°C
1	933	127.9	Over 24 hrs.		1.2	1.2	1.6	1.5
2	807.1	113.3	17	16	1.4	1.4	4.4	3.2
3	1083	98.8	10	12	2.2	1.8	4.4	2.6

From Figs. 15 and 16 and Table 9, the effect of oxidation on the viscosity of the oil and the effect of the temperature of measurement can be seen. As is to be expected the rate of increase of viscosity at both 20°C. and 50°C. was in the order of increasing aromaticity. Aromatics tend to polymerise on oxidation to produce very viscous materials. The time taken for the viscosity to double may be used to determine the initial rate of increase of viscosity and this is shown in Table 9. This figure, however, must be considered as only giving an indication of the initial rate of increase in viscosity and not as a direct measurement of the rate of change of viscosity as it can be seen from Figs. 15 and 16 that the rate of change of viscosity increased with increasing oxidation time.

In this respect it should be noted that the Institute of Petroleum test uses the viscosity ratio after 12 hours oxidation to classify an oil with respect to oxidation stability.

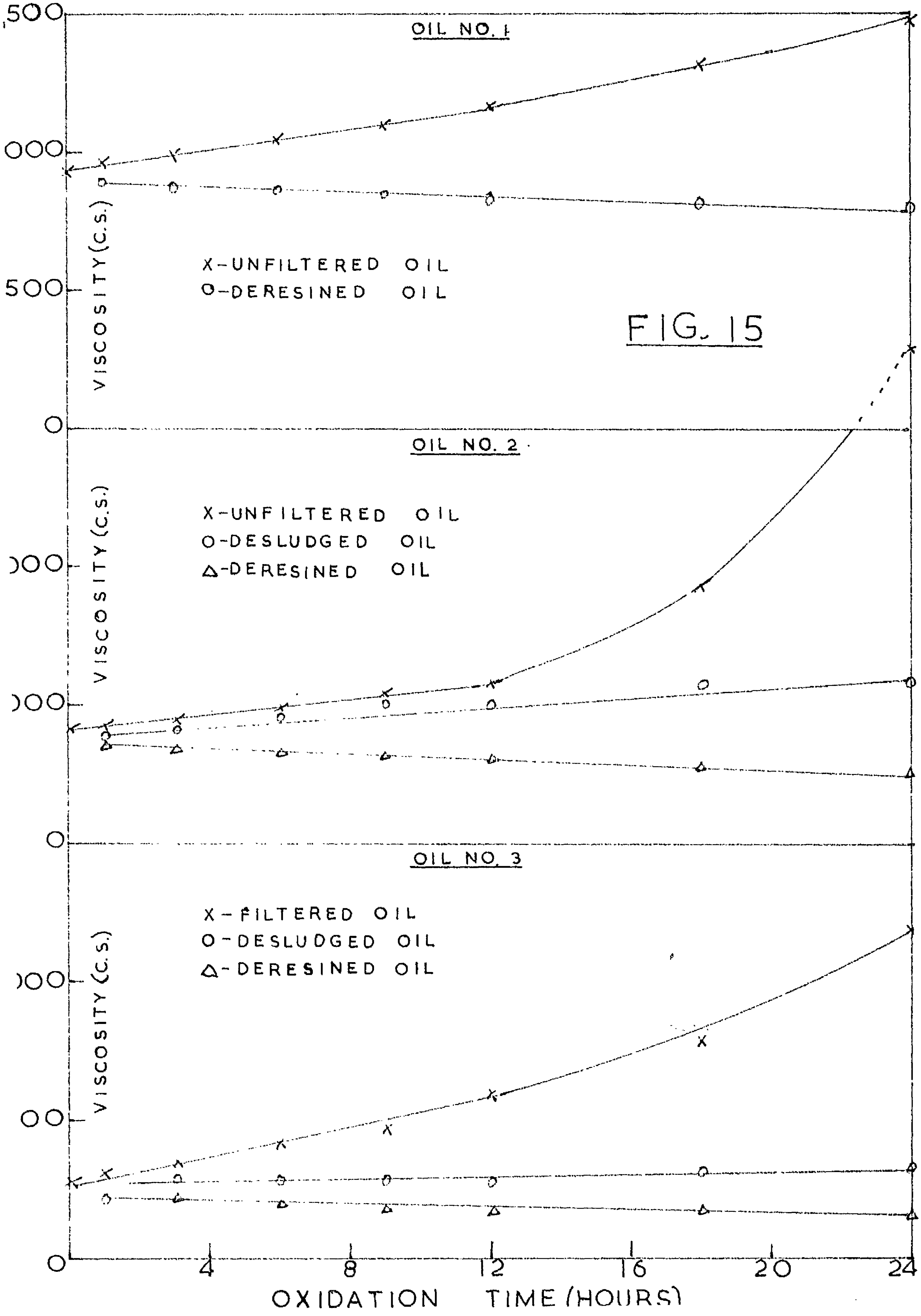


FIG. 15

OIL NO. 1
X-UNFILTERED OIL
O-DERESINED OIL
OIL NO. 2
X-UNFILTERED OIL
O-DESLUDGED OIL
Δ-DERESINED OIL
OIL NO. 3
X-FILTERED OIL
O-DESLUDGED OIL
Δ-DERESINED OIL
VISCOSITY (C.S.)
VISCOSITY (C.S.)
VISCOSITY (C.S.)
500
000
500
0
000
000
0
000
00
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

VISCOSITY OF OXIDISED OILS AT 50°C

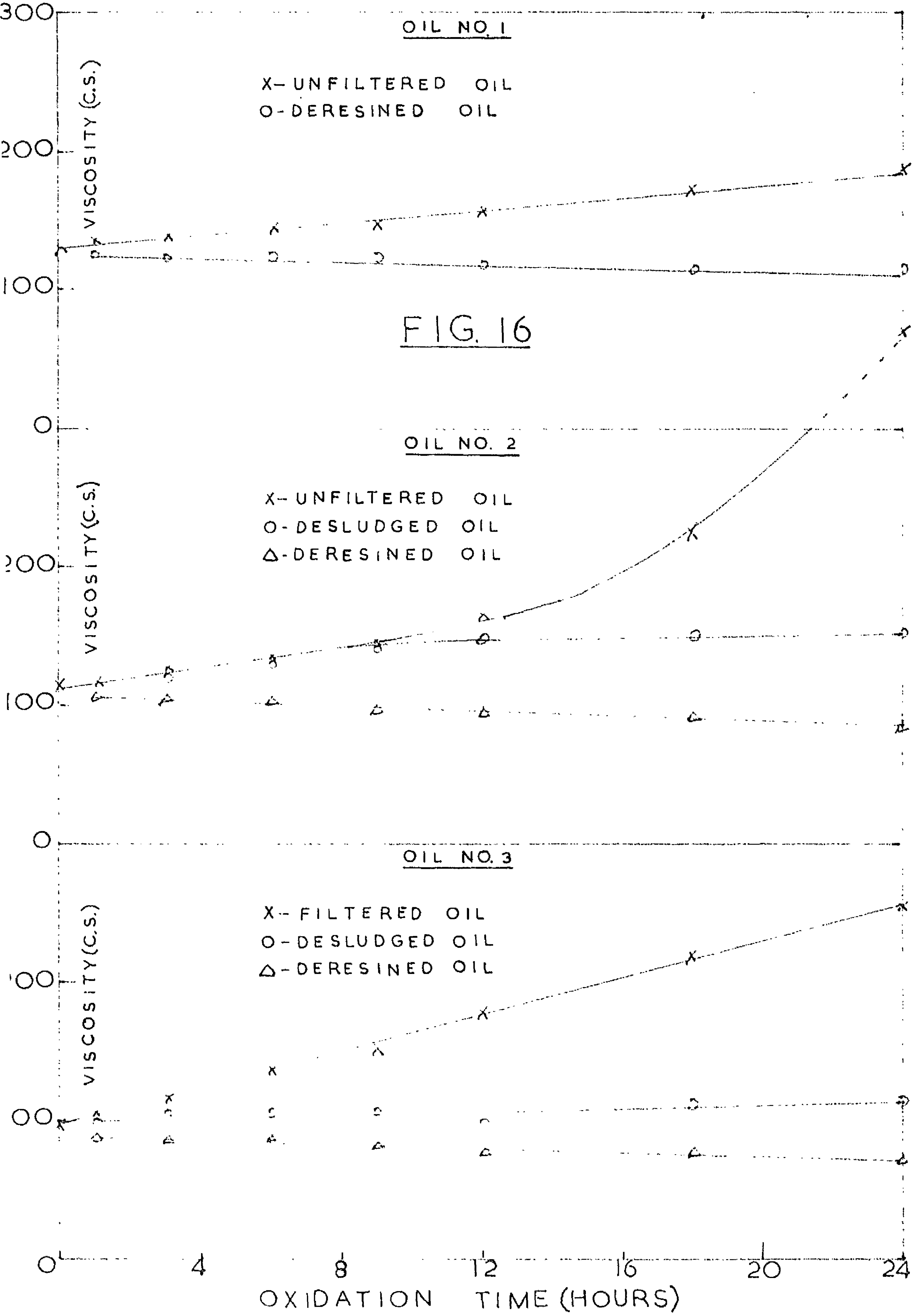


FIG. 16

It can be seen how this classification can lead to errors from the determination of viscosity ratio at 20°C. and 50°C. after 12 and 24 hours oxidation. After 12 hours the oils would be classified as having a lower oxidation stability in order of increasing aromaticity at 20°C. and 50°C. However after 24 hours, the viscosity ratio of Oil No.1 had not substantially increased whereas those of Oils 2 and 3 had. In fact Oils 2 and 3 had the same viscosity ratio at 20°C. but at 50°C. Oil No.2 had a higher ratio than Oil No.3, thereby reversing the situation as regards those two oils after 12 hours oxidation.

On removal of sludge the viscosities of the oils decreased to values just above that of the original oil, the difference becoming greater with increasing oxidation time. With Oil No.3 the similarity between the viscosity of the original oil and the desludged oil was very great, the difference only becoming apparent at higher oxidation times.

On removal of resins the viscosity fell below that of the original oil, the difference increasing with increasing oxidation time. The rate of change of decrease with increasing oxidation time for all three oils was linear at 20°C and 50°C.

Hicks-Bruun et al.[59] working with two oils containing 19% and 21% of carbon in aromatics found that 80% and 90% respectively of the viscosity increase was caused by the resins. In this work it was found that for the two oils which produced both sludge and resins, the contribution of each varied with the time of oxidation (Fig. 17). With Oil No.2 the resins produced the bulk of the increase up to 18 hours oxidation time and then the contribution of the sludge began to play an increasingly greater role. With Oil No.3 the resins played the mayor role up to 5 hours and then the sludge took over. It would seem from this that the aromatic content of the oil and the time of oxidation are the two important factors. Since the two oils used by Hicks-Bruun et al.[59] were higher in aromatics than Oil No.2 their finding that resins played the mayor role may well have been due to less severe oxidation conditions.

From results given it can be calculated that the

From results given it can be calculated that the
visc

viscosity contribution of the resins from all three oils lies between 6 and 8 cs./gm. for oxidation times varying from 1 to 24 hours. The sludge viscosity contribution tended on the whole to increase slightly after 4 hours oxidation to about ten times those of the resins (Fig. 18). It should be noted that Fenske et al.[49] had already expressed the view that viscosity increase was a rough measure of the total quantity of oxidation products. In this respect it would appear a far more satisfactory criterion of the extent of oxidation than the viscosity ratio.

Acidity

Burwell[80] has shown that the alkali consuming products present in an oxidised oil are more complex than simple acids and esters and include lactones and polyhydroxy compounds.

VISCOSITY INCREASE DUE TO SLUDGE AND RESIN

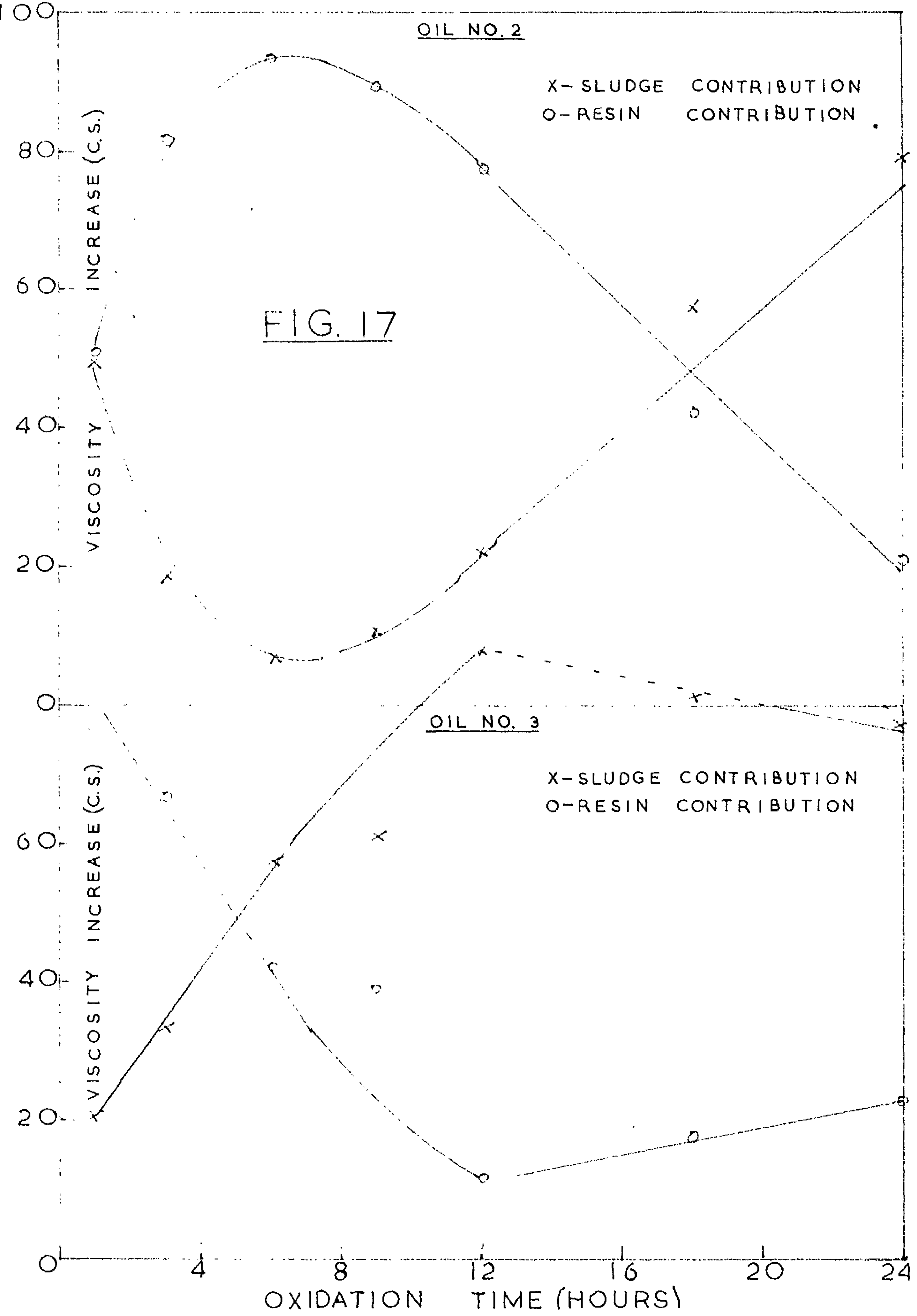


FIG. 17

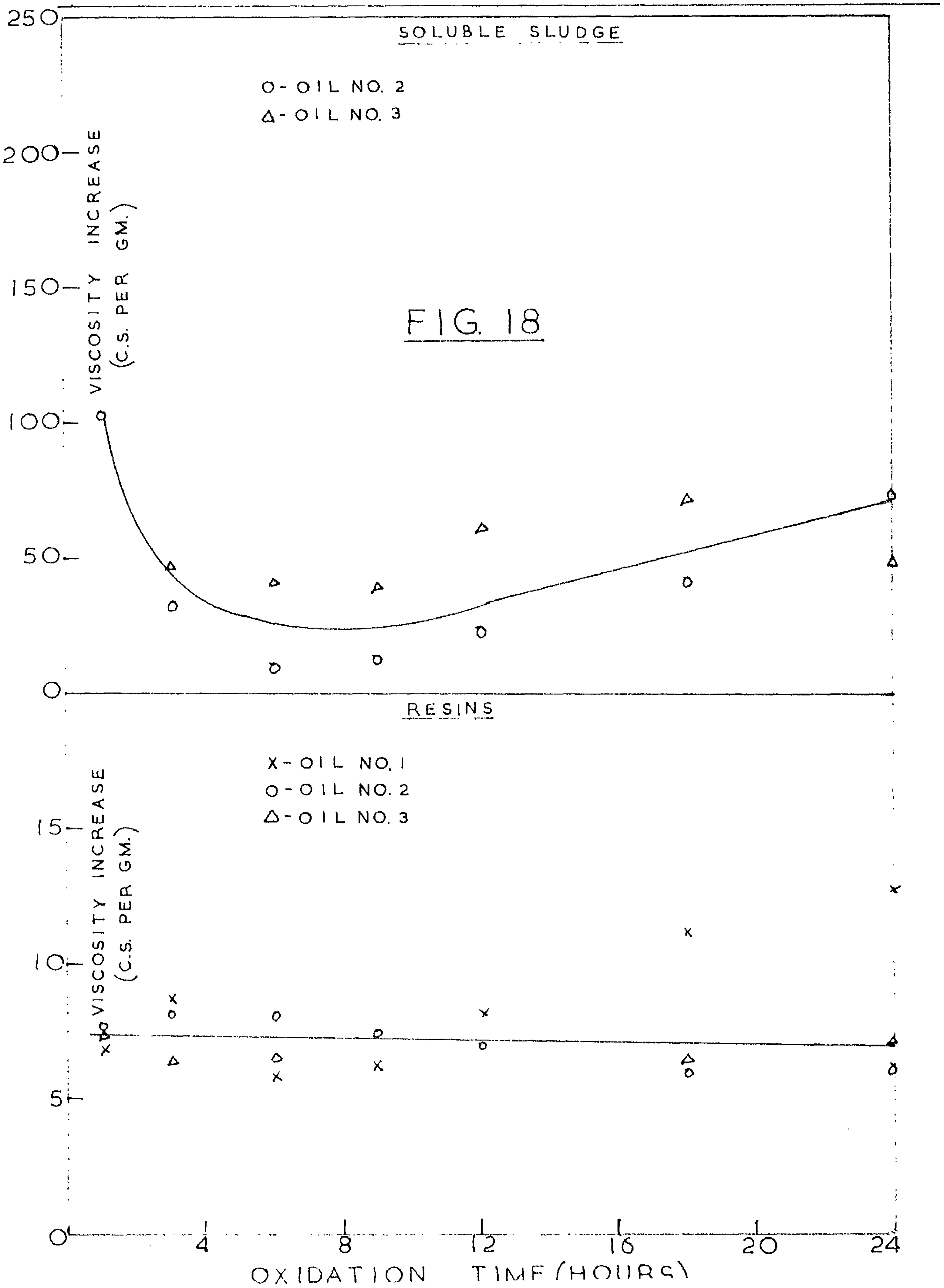

SOLUBLE SLUDGE
O - OIL NO. 2
Δ - OIL NO. 3
VISCOSITY INCREASE (C.S. PER GM.)
250
200
150
100
50
0
RESINS
X - OIL NO. 1
O - OIL NO. 2
Δ - OIL NO. 3
VISCOSITY INCREASE (C.S. PER GM.)
15
10
5
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 18

He also showed that there was no relation between metallic corrosion and the acids as determined by the neutralisation number. Consequently, for the purpose of this work the term "acids" will be used to donate those oxy-compounds capable of producing a hydrogen ion and not as a measure of the amount of carboxyl groups present.

From Fig. 19 it can be seen that the acidity of all three oils increased approximately linearly with oxidation time, with the more aromatic oils tending to produce the greater acidity. In this respect Larsen[81] found that lubricating oils derived from different crudes produced upon oxidation almost identical quantities of water and carbon dioxide: but showed no trends in the total acidity developed. Gibson[77] has, however, shown that there is a linear relationship between the Log Acid No. of the desludged oil and the percentage carbon in paraffinic structure. When the three oils under consideration were desludged it was noted (Fig.19) that the acidity decreased considerably, especially with the more aromatic oil. Removal of resins decreased the acidities to their original values before oxidation: in the case of Oils 1 and 2 this was zero and with Oil No.3 about an Acid NO of 0.2.

When the Log Acid NO of desludged oils was plotted against the percentage paraffin (Fig. 20), then it was found that the relationship was approximately linear. This would appear to lead to the conclusion that the development of

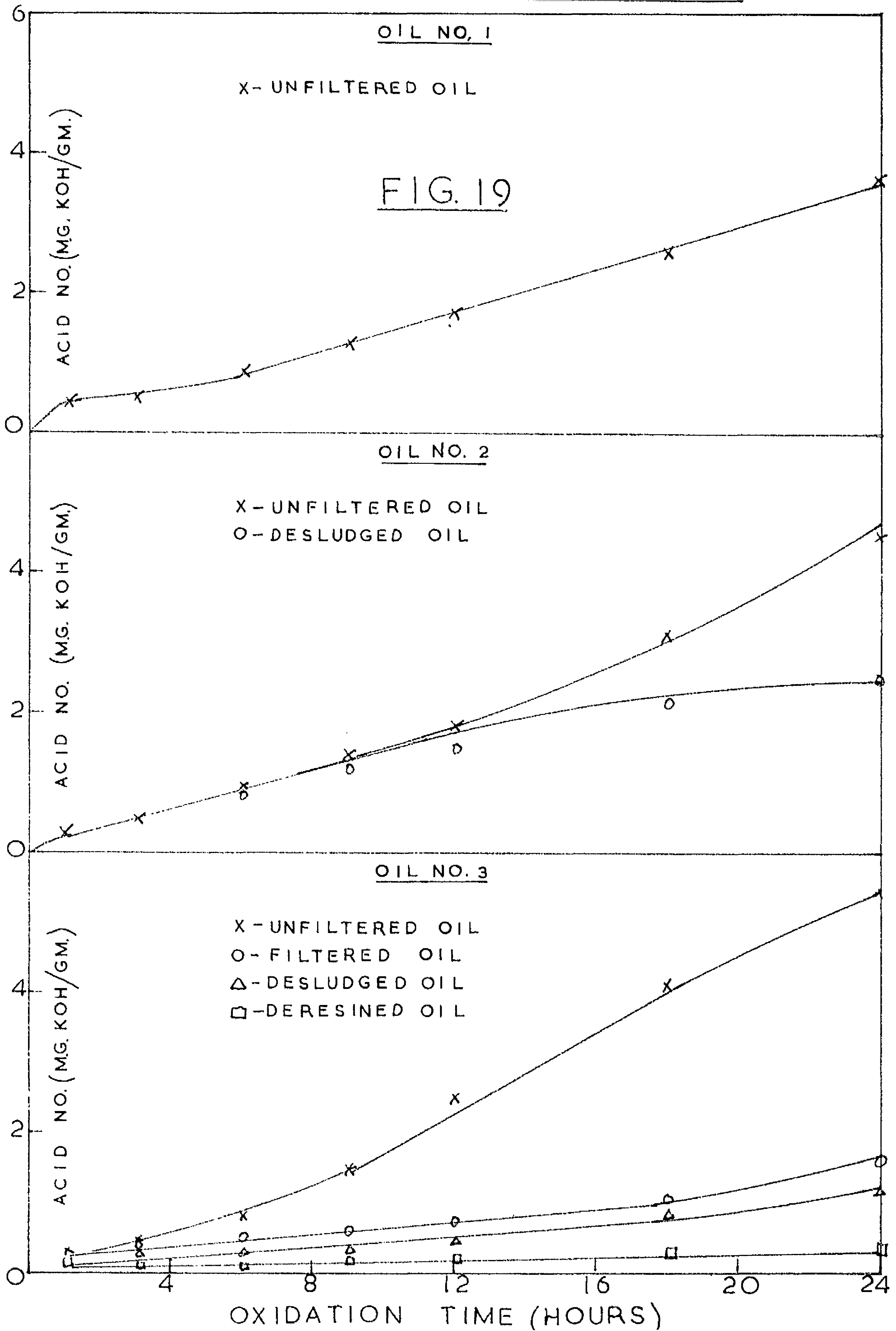
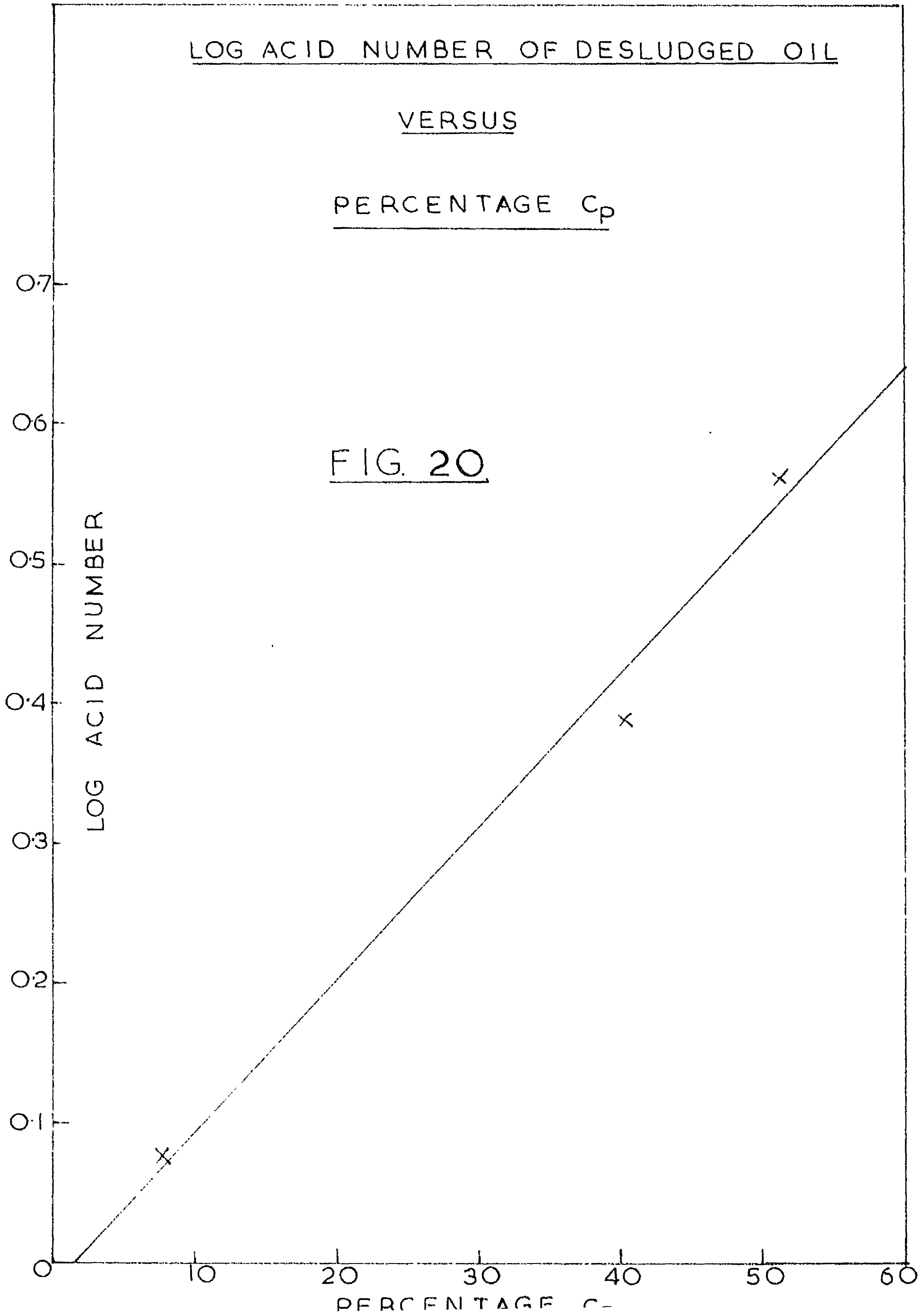


FIG. 19

OIL NO. 1
X - UNFILTERED OIL
OIL NO. 2
X - UNFILTERED OIL
O - DESLUDGED OIL
OIL NO. 3
X - UNFILTERED OIL
O - FILTERED OIL
△ - DESLUDGED OIL
□ - DERESINED OIL
ACID NO. (MG. KOH/GM.)
ACID NO. (MG. KOH/GM.)
ACID NO. (MG. KOH/GM.)
6
4
2
0
4
2
0
4
2
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)



LOG ACID NUMBER OF DESLUDGED OIL

VERSUS

PERCENTAGE C_p

FIG. 20

acidity in the non-sludging part of the oil is related to the paraffinic content of the unoxidised oil: while the development of total acidity is connected with the tendency of the oil to produce sludge on oxidation.

Density

The density of the oxidised oils at any degree of oxidation will depend on the relative rates of formation of compounds of higher and lower density than that of the original oil. From Fig. 21 it can be seen, that on the whole, the density of the oils tended to increase on oxidation, but in an irregular manner indicating that the formation of oxidised products was not a uniform process. The total increase in density was related to the aromatic content of the unoxidised oils, the percentage increase after 24 hours being a linear function of the aromatic content (Fig. 22).

The removal of sludges and resins decreased the density: that of the sludges to values just above that of the original oil, while the removal of resins tended, on the whole, to reduce the density to values below that of the original oil, this tendency increasing with increasing oxidation time.

Molecular Weight

Increase in the average molecular weight of an oil on oxidation may be due either to the removal of lower molecular weight hydrocarbons as cracked products of oxidation, or polymerisation of hydrocarbon molecules. Decrease in molecular

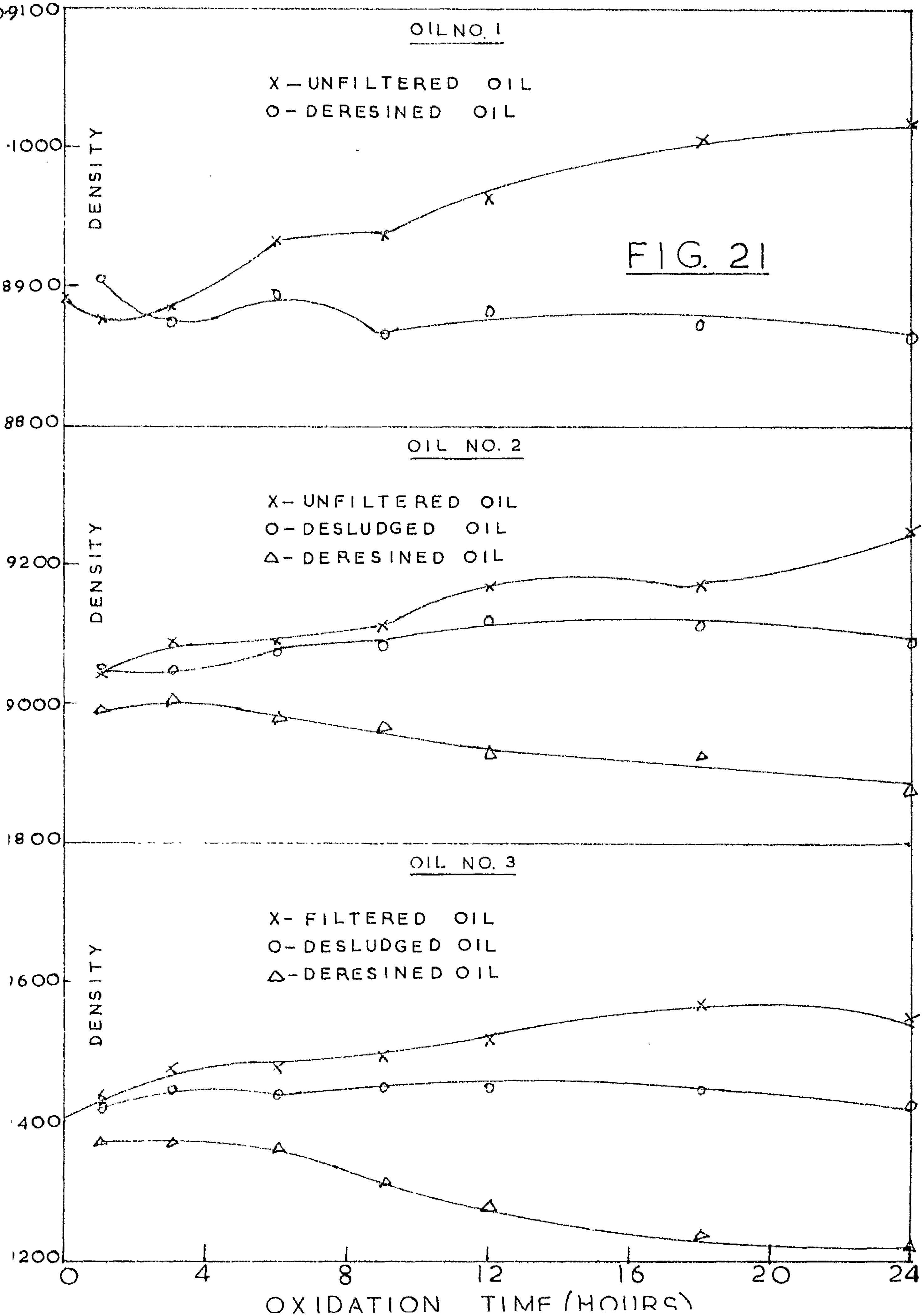
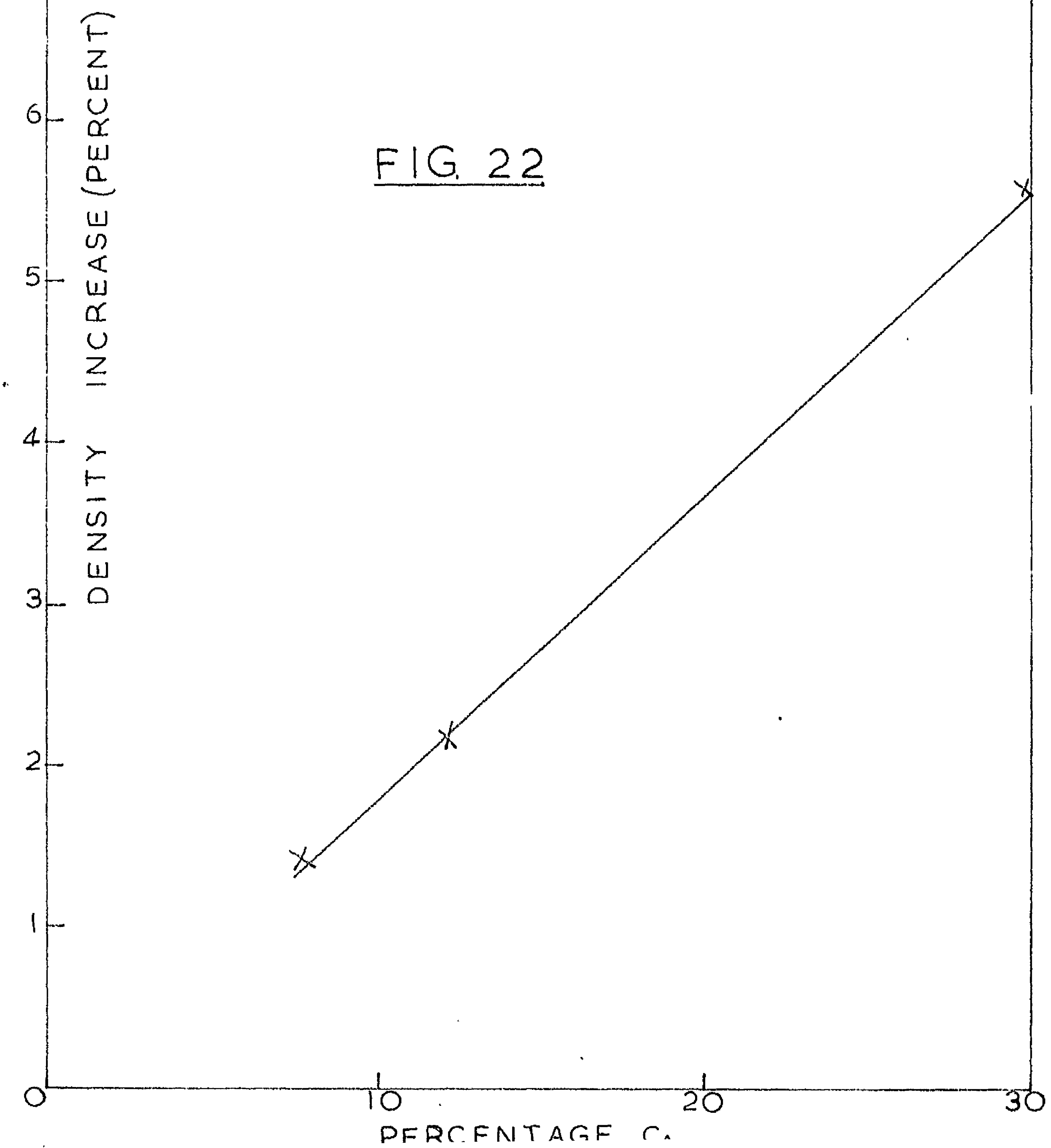

OIL NO. 1
X — UNFILTERED OIL
O — DERESINED OIL
DENSITY
·9100
·1000
·8900
·8800
OIL NO. 2
X — UNFILTERED OIL
O — DESLUDGED OIL
△ — DERESINED OIL
DENSITY
·9200
·9000
·8800
OIL NO. 3
X — FILTERED OIL
O — DESLUDGED OIL
△ — DERESINED OIL
DENSITY
·8600
·8400
·8200
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 21

PERCENTAGE INCREASE IN DENSITY OF
OXIDISED OILS
VERSUS
PERCENTAGE C_A

FIG. 22



weight on the other hand may be due either to the cracking of high molecular weight hydrocarbons or precipitation of high molecular weight compounds from solution in the oil. A study, therefore, of the molecular weight of the oxidised oils before and after the removal of sludge and resins could well give an indication of the type of molecule being primarily attacked.

With Oils 1 and 2 the form of the molecular weight versus oxidation time curve was very similar to that of the oxygen content versus time, while for Oil No.3 the curve took the opposite form up to 9 hours oxidation and was then similar to the oxygen content/time curve. Thus for the first two oils the formation of oxygen containing molecules would appear to be directly responsible for the increase in molecular weight and a decrease in oxygen content accompanied by a decrease in molecular weight would indicate a predominance of cracking type reactions. In Oil No.3 this tendency was initially reversed and a loss in oxygen accompanied by an increase in molecular weight would indicate the predominance of condensation type reactions with oxygen being lost as water (Fig. 23).

When the molecular weight of the unoxidised part of the oil was examined it was found that both Oils 1 and 2 showed an initial decrease in molecular weight up to 1 hour oxidation and this was then followed by an increase, greater in the case of Oil No.2. Thus the larger hydrocarbons initially bore the brunt of the oxidative attack and as they were removed the attack became concentrated on the lighter hydrocarbons. With

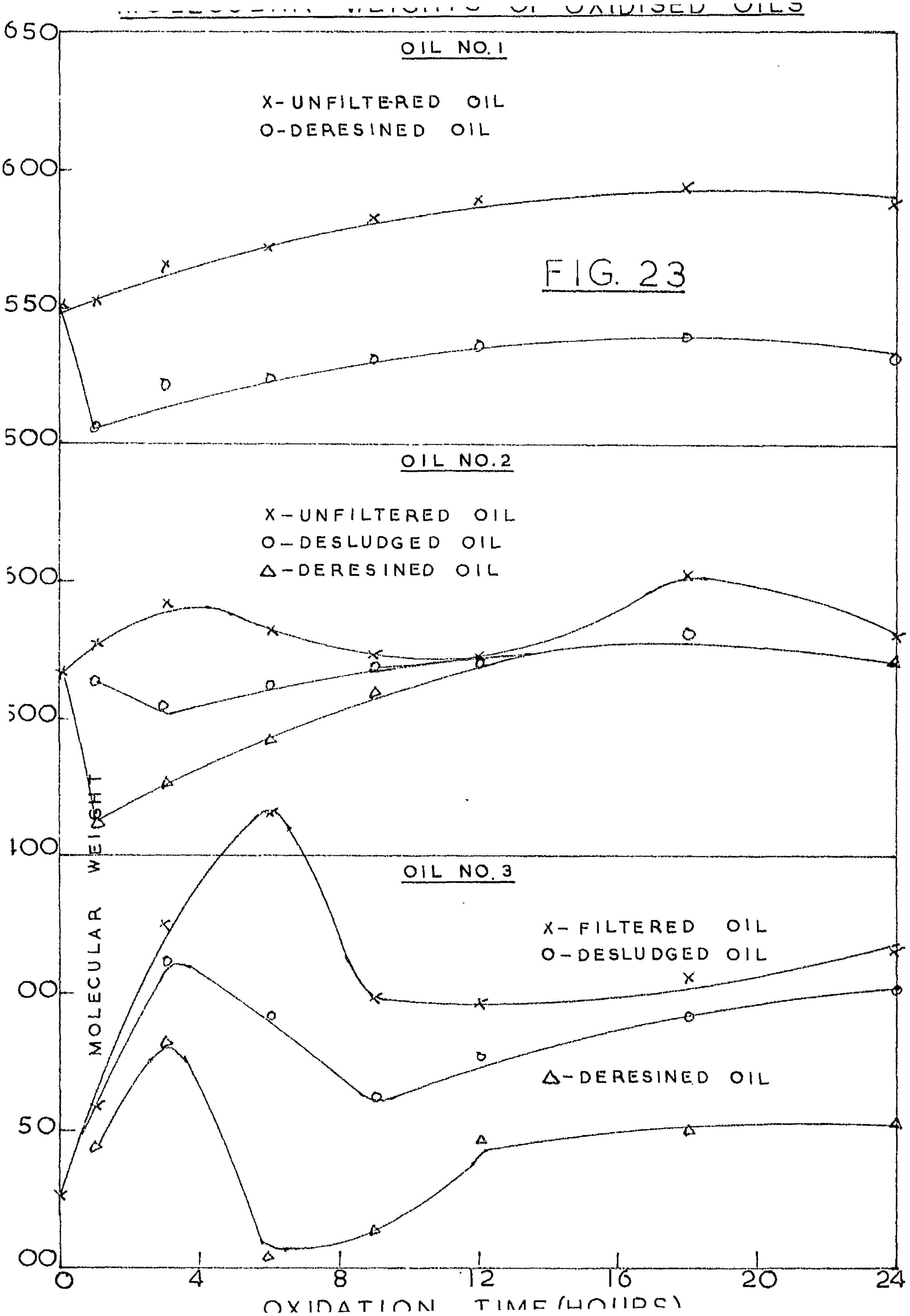

OXIDISED OILS
OIL NO. 1
X - UNFILTERED OIL
O - DERESINED OIL
OIL NO. 2
X - UNFILTERED OIL
O - DESLUDGED OIL
Δ - DERESINED OIL
OIL NO. 3
X - FILTERED OIL
O - DESLUDGED OIL
Δ - DERESINED OIL
MOLECULAR WEIGHT
650
600
550
500
500
500
100
00
50
00
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 23

Oil No.3 attack varied initially between lighter and heavier hydrocarbons and this must have been due to differences in the rates of oxidation of the two, presumably since they may in this case have represented two hydrocarbon types. Once this initial variation ceased little change was noted in the molecular weight as was also the case at the higher stages of oxidation of the other two oils. In the unoxidised oils the bulk of the hydrocarbons present must therefore be of approximately the same molecular weight, with a small percentage of material of more diverse molecular weight and structure which bear the brunt of the initial oxidative attack. This effect was more noticeable in oils of higher aromaticity.

In Chapter VIII will be discussed the hydrocarbon types involved in these molecular weight changes of the unoxidised part of the oil.

CHAPTER VII

THE EFFECT OF OIL COMPOSITION ON THE NATURE OF OXIDISED MATERIALS.

CHAPTER VII

THE EFFECT OF OIL COMPOSITION ON THE NATURE OF OXIDISED MATERIALS

Theoretically the simplest method of examining the properties of the sludges and resins produced on the oxidation of lubricating oil fractions is to separate and analyse them. However, for this method to produce accurate results it is necessary that no change in the nature and properties of the sludge and resins is brought about by the means used to separate them. In the case of the resins there would appear to be no fundamental change brought about by the separation process as they will redissolve in the oil giving it once again its original physical properties. Unfortunately the means of separating the sludge from the oxidised oils involves their peptisation and aggregation and in this process there is no guarantee that no further polymerisation of the sludge will take place. In order to test this, sludge was precipitated from oxidised samples of the oils by the addition of petroleum ether which was then evaporated from the oil at room temperature and under vacuum. It was found that the bulk of the precipitated sludge would not redissolve in the oil. Davis, Lincoln, Byrkit and Jones[76] also found that when sludges and resins were separated, the resins went back into solution whereas the sludges did not. Owing to this difficulty the method used to determine the properties of the sludge and resins was to examine the properties of the oil before and after their removal and from a knowledge of the amounts of sludge and resin produced to calculate their properties. When random samples of sludge and resins were taken and their properties compared with those obtained by this difference method it was found that for the resins there was reasonably close agreement in all cases, while the sludges showed widely divergent values.

Due to the nature of the oil insoluble sludge and its insolubility in most hydrocarbon solvents it was not possible to calculate or determine its properties except in a limited number of cases.

Oxygen Content

Fig. 24 shows the variation in the percentage oxygen in sludges and resins with oxidation time and oil composition. Oxygen content of the insoluble and soluble sludge from Oil No.3 decreased rapidly at first, particularly that of the insoluble sludge, after an initial high value, and then increased. The rate of increase of oxygen in the insoluble sludge was fairly rapid while, after the initial decrease, that of the soluble sludge increased gradually to a value of about 10% after 24 hours oxidation. The oxygen in the soluble sludge from Oil No.2 was initially much higher than that from Oil No.3 but decreased fairly rapidly to a value of about 15% after 23 hours oxidation.

The change in value of the percentage oxygen present

OXYGEN CONTENT OF SLUDGE AND RESIN

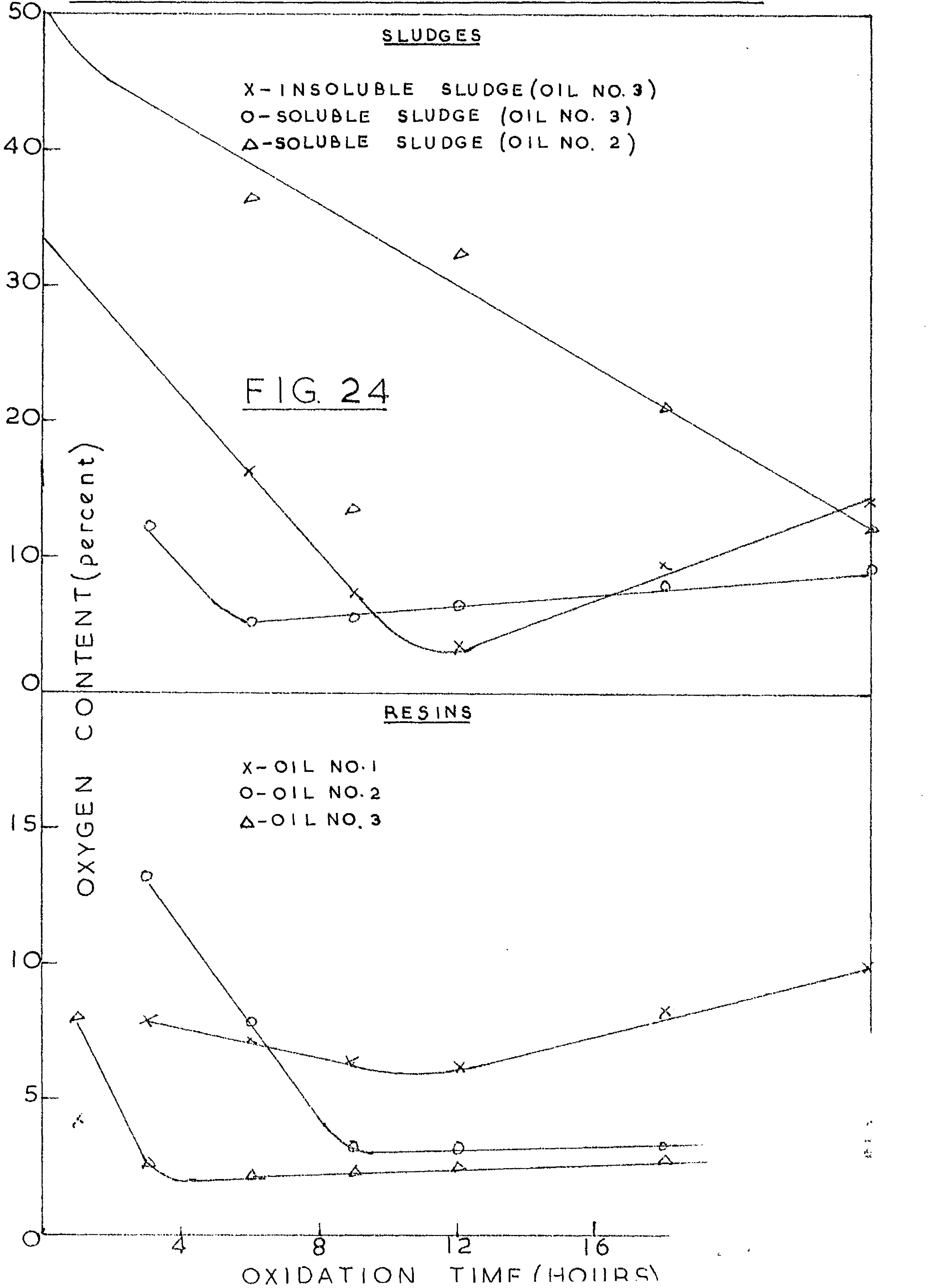


FIG. 24

in the resins was similar for all three oils. This was an initial increase followed by a decrease then finally a more gradual increase. The points at which the changes in rate took place were different for the three oils, being earliest for Oil No.3 and latest for Oil No.1. The resins from Oils 2 and 3 in the later stages of oxidation had very similar values of oxygen content, being 3-4% at 24 hours oxidation, while that of Oil No.1 was rather higher being about 10% at 24 hours. These values for oxygen content compare with those obtained by Hicks-Bruun et al.^{59} which were 9-15% for resins and over 20% for sludges. Davis et al.^{76} suggested that a value of 15% for oxygen present in "total pentane precipitables" was a reasonable average for such materials. It can be seen from the above results, however, that the percentage oxygen in either the sludges or resins will depend on the extent of oxidation of the oil.

When the weight of oxygen present in sludges and resins per 100 gm. of oxidised oil was considered it could be seen that the lower the aromatic content of the oil, the greater the weight of oxygen present in the sludges and resins (Fig. 25). With Oil No.2 it was noted that there was initially a greater weight of oxygen in the resins than in the sludges but that this was reversed after 12 hours oxidation time, after which the weights present in each were about similar.

With Oil No.3 the greater weight of oxygen was initially

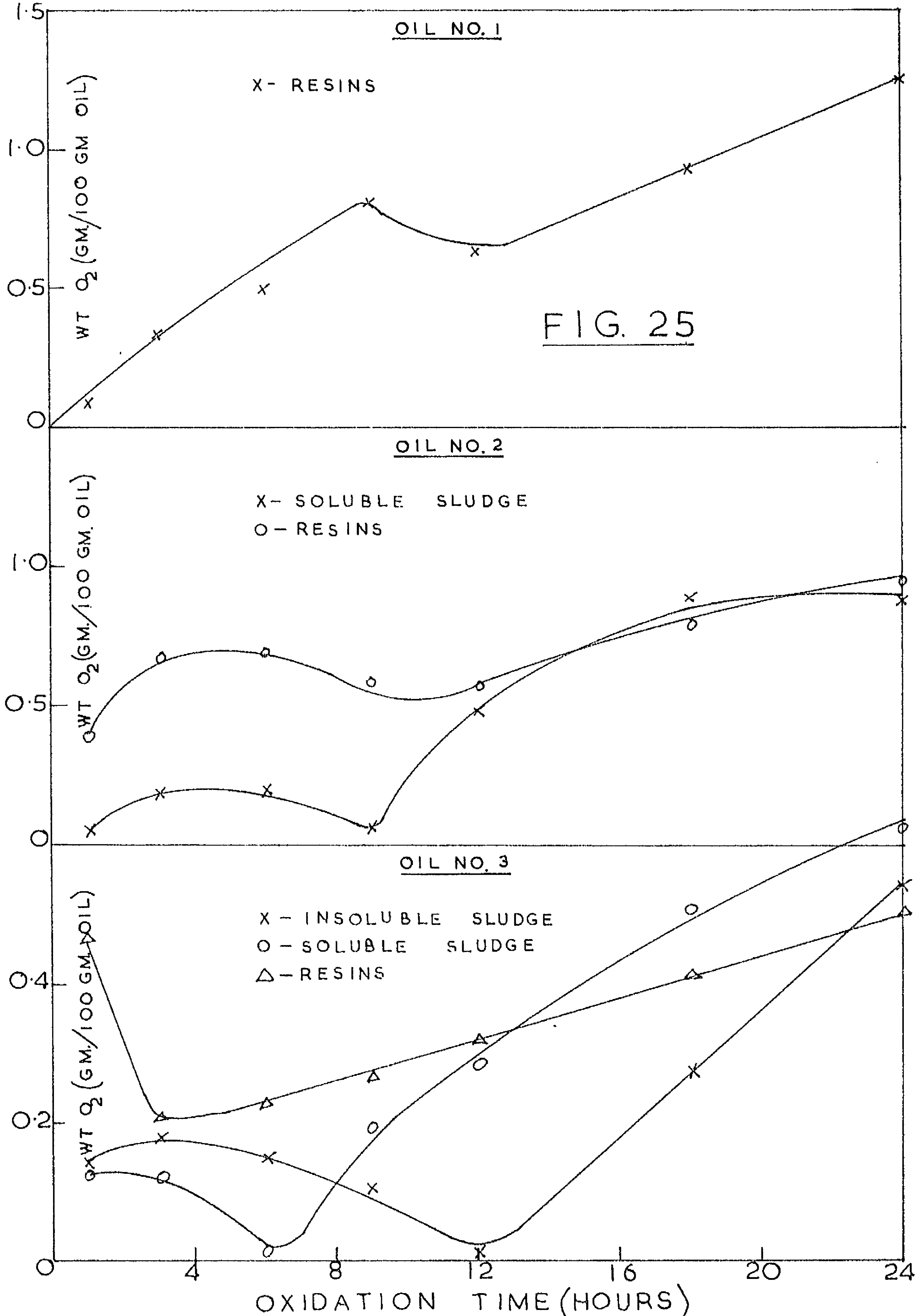


FIG. 25
OIL NO. 1
X- RESINS
WT O_2 (GM./100 GM OIL)
1·5
1·0
0·5
0
OIL NO. 2
X- SOLUBLE SLUDGE
O- RESINS
WT O_2 (GM./100 GM. OIL)
1·0
0·5
0
OIL NO. 3
X- INSOLUBLE SLUDGE
O- SOLUBLE SLUDGE
△- RESINS
WT O_2 (GM./100 GM. OIL)
0·4
0·2
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

present in the resins, then insoluble sludge and finally the least in the soluble sludge. After 24 hours oxidation the greatest weight of oxygen was present in the soluble sludge, followed by insoluble sludge and finally resins.

With Oil No.1 both the weight and percentage oxygen present tended to increase with increasing oxidation time showing that the absorption of oxygen outweighed losses due to cracking reactions. Since there could have been no losses of oxygen by further oxidation of the resins to form sludge, the oxygen content of the resins from this oil was much higher than those from Oils 2 and 3.

With Oil No.2 it was seen that after 9 hours oxidation the percentage oxygen in the resins reached an approximately constant value and at the same time the weight of the oxygen present in the sludges began to show a rapid increase indicating that dynamic equilibrium had been reached in the reaction hydrocarbons ---> resins ---> soluble sludge. It was also noted that although the weight of oxygen present in the soluble sludge was increasing, its percentage was decreasing fairly rapidly indicating that further polymerisation of the sludge itself was taking place. Again since no oxygen was being lost in the formation of insoluble sludge, the oxygen content of the soluble sludge was higher than that for Oil No.3.

With Oil No.3 the percentage oxygen in both the sludges and resins tended to a constant value after an initial increase followed by a decrease in their value indicating that equilibrium had been reached in the reaction: hydrocarbons ---> resins ---> soluble sludge ---> insoluble sludge. This was also borne out by the fact that the increase in weight of oxygen present in insoluble sludge and soluble sludge only occurred after the percentage oxygen in soluble and resins tended to a constant value. It was also noted that although after 24 hours oxidation there was a greater weight of oxygen present in soluble than insoluble sludge, the rate of increase of the latter was very much greater.

It was noted in every case that the amount of oxygen present in the resins initially decreased and later gradually increased, possibly due to the early predominance of cracking type reactions. Similar losses in the sludges can be explained by further polymerisation of the sludge itself with removal of oxygen as water. Again this type of reaction probably plays a less important part as oxidation proceeds and the sludge becomes more polymerised.

Carbon Residue

From Fig. 26 it can be seen that the carbon residue of the resins was quite small and tended to increase slightly on oxidation. Since these materials are relatively unpolymerised and contain up to 10% oxygen it is surprising that there is no obvious relation between the carbon residue of the resins and their oxygen content. It must be concluded that the oxygen compounds in the resins were vaporised under the conditions

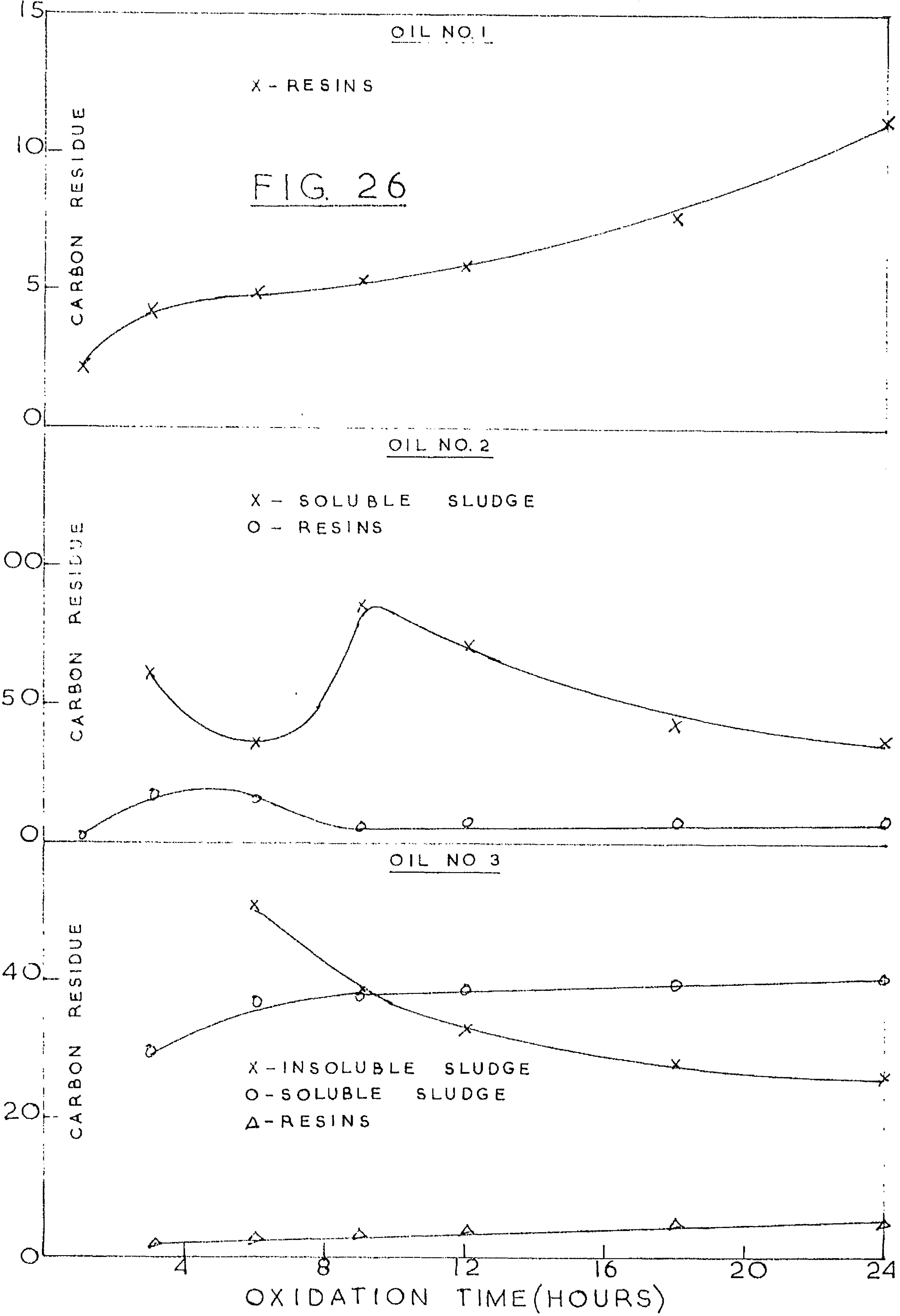
OIL NO. I
X - RESINS
CARBON RESIDUE
15
10
5
0
OIL NO. 2
X - SOLUBLE SLUDGE
O - RESINS
CARBON RESIDUE
00
50
0
OIL NO 3
CARBON RESIDUE
40
20
0
X - INSOLUBLE SLUDGE
O - SOLUBLE SLUDGE
Δ - RESINS
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 26

of the carbon residue test before the carbonisation process took place and could therefore play no part in it.

The values of the carbon residues of the soluble sludge from Oil No.2 varied inversely with the oxygen content of the oxidised oil although it showed no relationship with the oxygen content of the soluble sludge itself.

With Oil No.3 it was noted that the carbon residue values of the sludges showed a transition point in their rate of change at points corresponding to the change in oxygen content. With the insoluble sludge this was a slowing down in the rate of decrease, while with the soluble sludge it was a slowing down in the rate of increase.

With the insoluble sludge the initially high oxygen content gave rise to a large carbon residue, the value falling as the oxygen content fell then falling more slowly as the oxygen content increased. This points to the fact that initially the oxygen compounds were easily cracked or distilled off before they could play any part in the carbonisation. The falling in value with time was probably due to the more firm attachment of oxygen, possibly by ring linkages, which could then take part in the carbonisation. The falling in rate as the oxygen content increased was probably due to the formation of many ring polymers which increased the carbon/hydrogen ratio to such an extent that the increase in oxygen content had only a partial effect. At this stage it seems worthwhile to comment on the fact that the decrease in carbon residue with oxidation time and the increase in oxygen content rule out the possibility that the insoluble sludge contained any great percentage of elemental carbon as Nellensteyn[82] has suggested.

The opposite effect was noted with the soluble sludge, the carbon residue increasing with oxidation time as the oxygen fell and then increasing more slowly as the oxygen content started to increase. Thus the increase in oxygen content was not sufficient to overcome the increase of carbon residue of the polymerised sludge and the result was a net increase in carbon residue but at a lower rate.

Summarising, it can be said that the oxygen present in the resins was removed before it could affect the carbonisation, whereas the carbon residues of the sludges could be affected by the oxygen present, but that this was dependant upon the amount of oxygen, how it was attached and the degree of polymerisation of the sludges.

Acidity

From Fig.27 it can be seen that the resins from the more paraffinic type oils had a higher acid number. This was probably due to the known fact that paraffins on oxidation tend to produce a greater quantity of acids than any other hydrocarbon, allied to the fact that considerably less sludge was formed, and, hence there could have been no transfer of acidic material. This premise was borne out by the fact that where sludge was formed the acid numbers of the resins tended towards a constant value, whereas that of Oil No.1 kept on increasing with oxidation time.

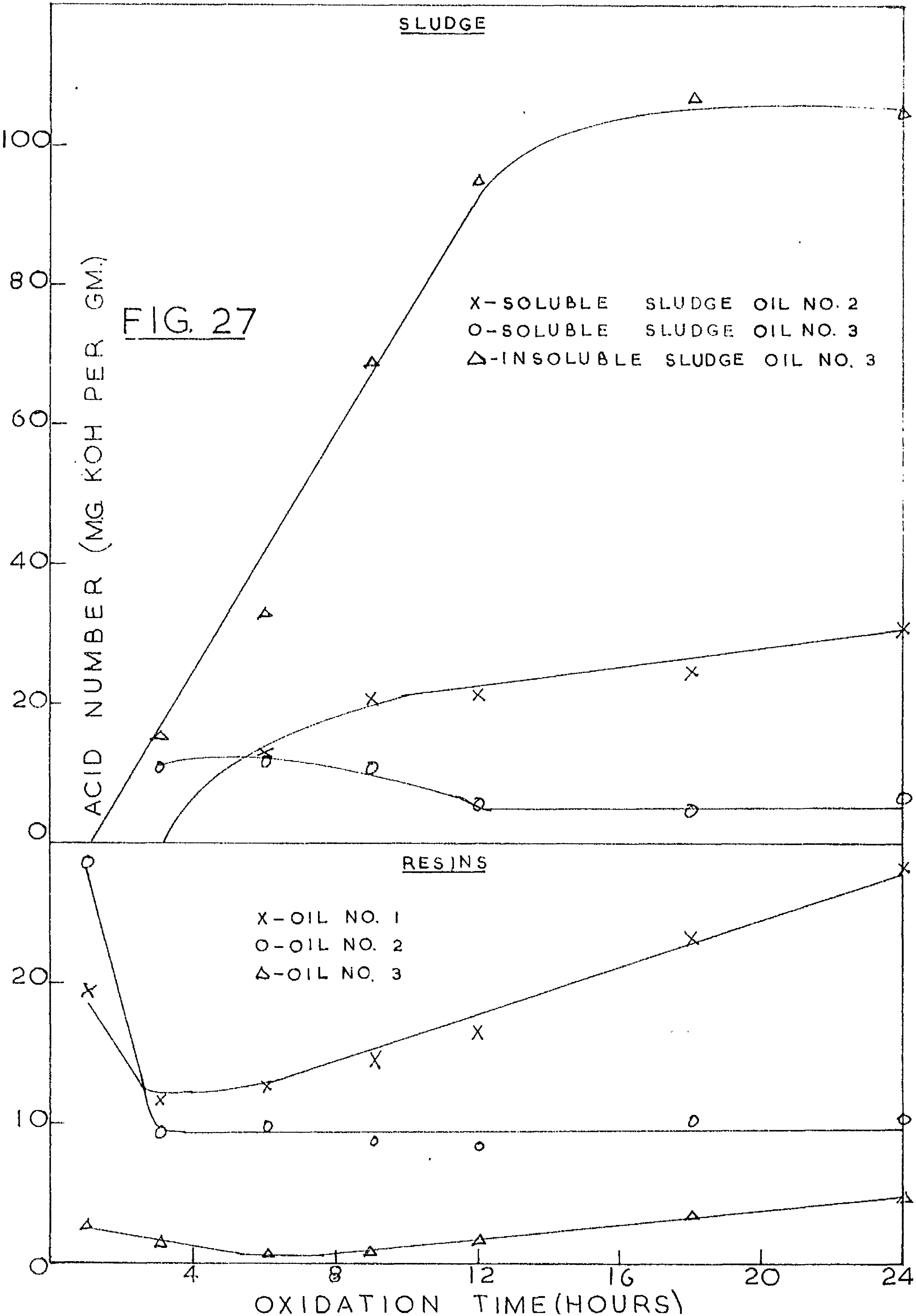


FIG. 27

SLUDGE
X-SOLUBLE SLUDGE OIL NO. 2
O-SOLUBLE SLUDGE OIL NO. 3
△-INSOLUBLE SLUDGE OIL NO. 3
RESINS
X-OIL NO. 1
O-OIL NO. 2
△-OIL NO. 3
ACID NUMBER (MG. KOH PER GM.)
100
80
60
40
20
0
20
10
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

A similar effect was seen in the acid numbers of the soluble sludges from Oils 2 and 3. With Oil No.3 which produced insoluble sludge, the acid number tended to decrease to a constant value, while that of Oil No.2, which formed no insoluble sludge under the conditions of oxidation, tended to increase with oxidation time.

The acid number of the insoluble sludge was far greater than those for sludges and resins, which had values of the same order for all three oils.

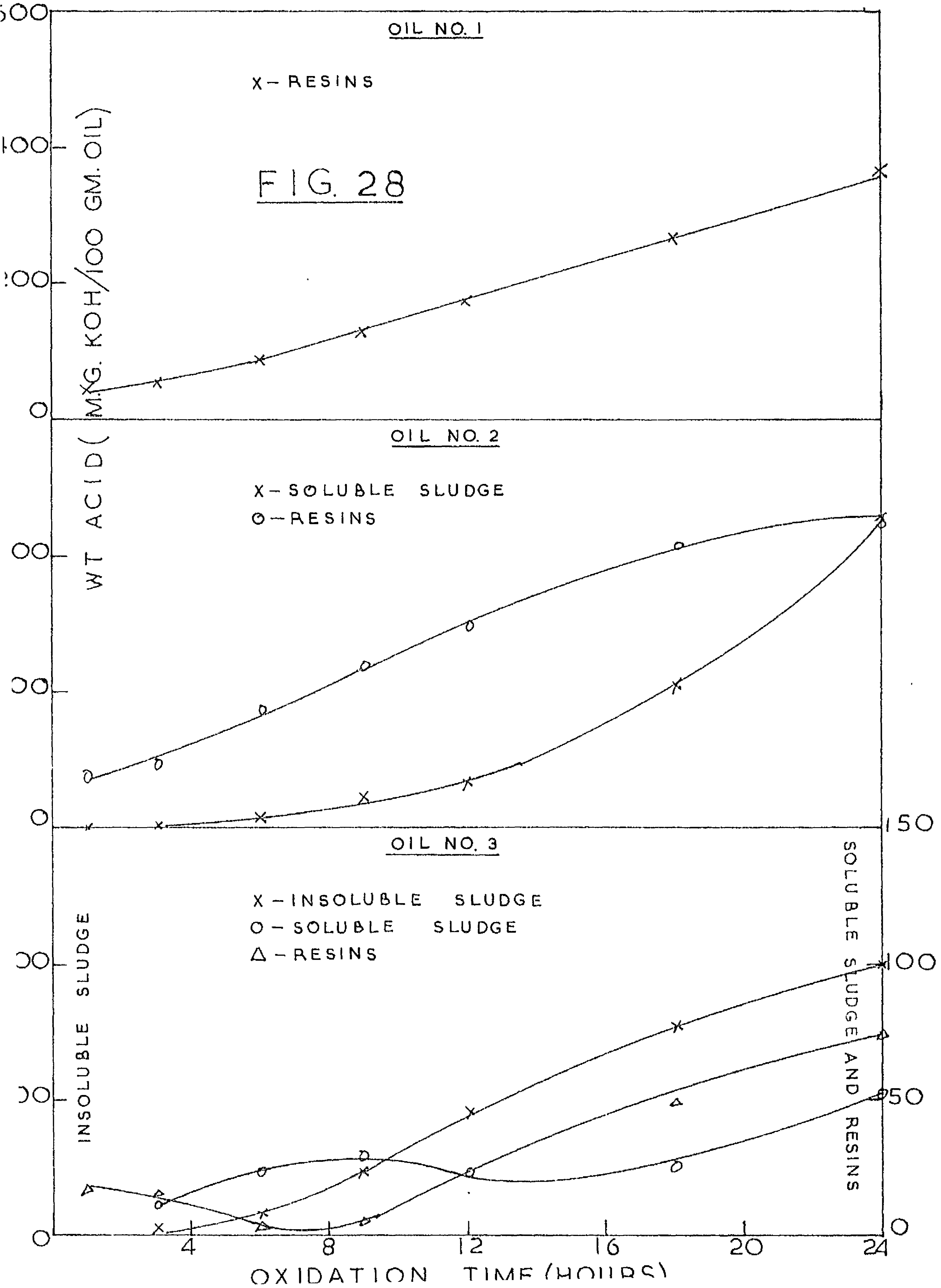
For Oil No.1 the weight of acid (in mg. KOH per 100 gm. of oil) in the resins increased linearly with oxidation time (Fig. 28) in much the same manner as the percentage increase. The weight present was much greater than in any other fraction with the exception of the insoluble sludge from Oil No.3.

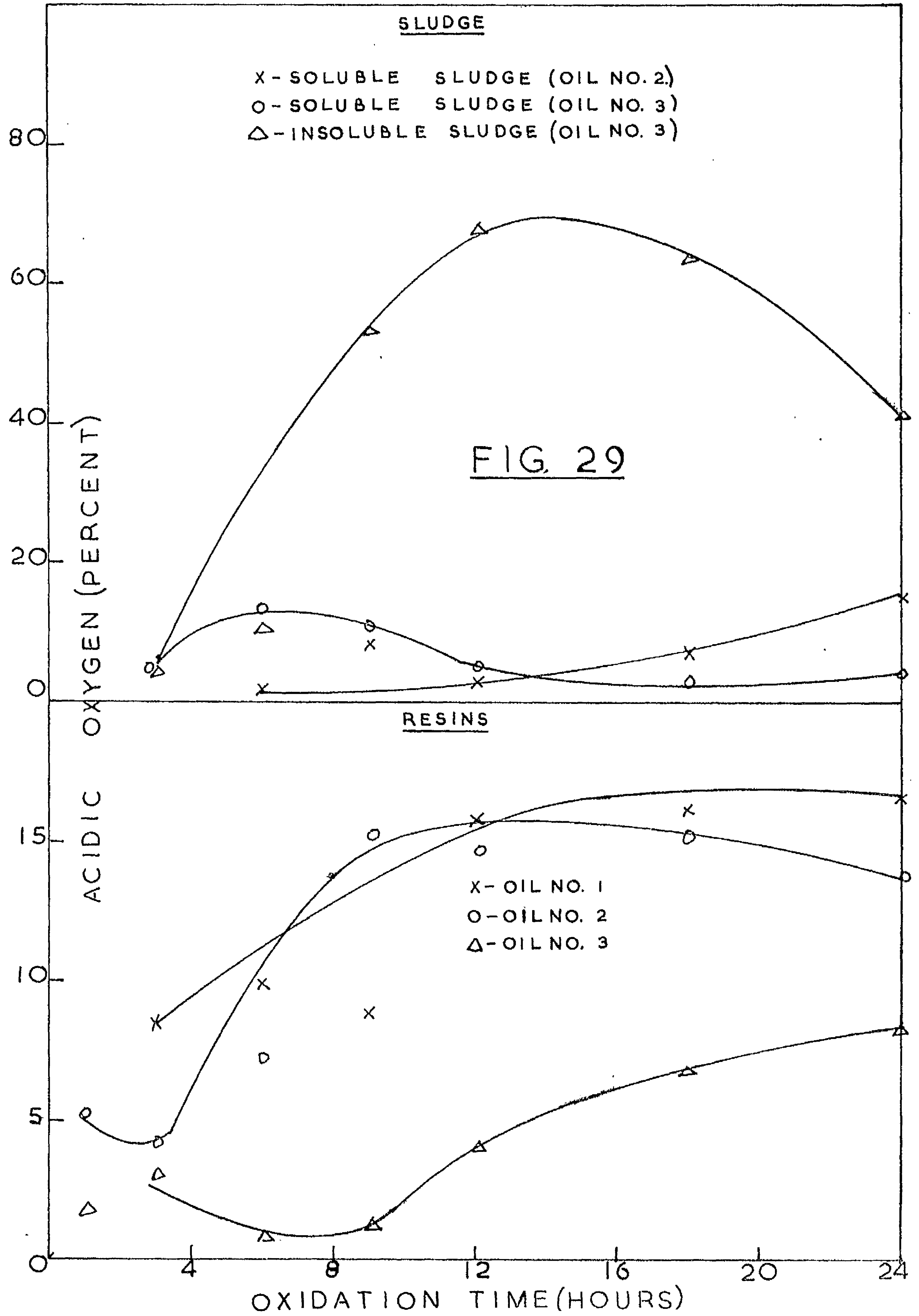
For Oils 2 and 3, the greater weight of acid was initially present in the resins. However, the rates of increase of the weights of acid were greater for the sludge than for the resins. With Oil No.2, equal weights of acid in sludge and resin were not produced until 24 hours oxidation, while for Oil No.3 this occurred after 12 hours and thereafter there was a greater weight of acid in the soluble sludge than in the resins.

When the oxygen present in acids (taken as -COOH as a first approximation) was taken as a percentage of the total oxygen present, it was evident (Fig. 29) that the acidic oxygen in the soluble sludges and resins was very much less than that of the insoluble sludge.

WEIGHT OF ACID IN SLUDGE AND RESIN

FIG. 28





SLUDGE
X - SOLUBLE SLUDGE (OIL NO. 2)
O - SOLUBLE SLUDGE (OIL NO. 3)
Δ - INSOLUBLE SLUDGE (OIL NO. 3)
RESINS
X - OIL NO. 1
O - OIL NO. 2
Δ - OIL NO. 3
ACIDIC OXYGEN (PERCENT)
80
60
40
20
0
15
10
5
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 29

In the past considerable thought has been given to the relationship between sludge and acidity developed on oxidation of lubricating oil fractions. It is known that over refined oils very quickly build up acids on oxidation, and that in the advanced stages of oxidation sludge forms frequently with a decrease in acidity. Marcusson[83] first suggested that acids were precursors of resins and sludges and Sachanen[73] advanced this view by claiming that the formation of sludge was due to the condensation of acids, probably with polycyclic naphthenes. This view is now no longer tenable since it is known that paraffinic type oils can produce very large amounts of acid, without the formation of sludge.

Haslam and Frohlich[84] suggested that the formation of aldehydes and ketones precedes that of sludge and Tast[85] has elaborated on this by making the hypothesis that sludge is produced by the condensation of aromatic hydroxyl compounds with carbonyl compounds, although no experimental evidence has so far been offered to support this viewpoint. If this theory is correct, however, then the formation of acids and sludge should be competitive as they would both be formed from identical compounds, namely carbonyl compounds.

Some evidence that this is indeed the case has been offered by Irving and Thompson[86] who oxidised transformer oils under conditions where the diffusion of oxygen was a rate controlling factor. They found that in all cases where the rate of acidity developed decreased, the rate of sludge formation increased and explained it on the assumption that the acidic components in the oil partially represented potential sludge since the sludge formed later had itself a high acidity. An important feature noted was that when oxygen was limited sludge formation predominated over acid formation.

Sachanen[75] has observed that the formation of hydroxy-acids, which are insoluble in petroleum oils, may be of importance in the production of sludges which are partially saponifiable. He has suggested that the acid constituents of the sludge are at least partially of the hydroxy variety.

It now seems unquestionable that there is some connection between acidity and sludge, but the nature of that connection is still open to doubt. In the present work it has been noted that the acidity of the insoluble sludge was very much higher than that of the soluble sludges and resins and that the acidic oxygen represented a greater percentage of the total than either that of the soluble sludge or resins. This being the case it seems likely that the acidity of the insoluble sludge is related in some way to its insolubility. Since the acidic groupings present are highly polar in nature, the polarity of the insoluble sludge must be considerably greater than that of the parent oil. It would then appear not unlikely that the soluble sludge on absorption of oxygen produced acids to such an extent that the polarity increased to such a value where the sludge was no longer soluble in the non-polar oil and precipitation resulted.

Density

If two similar compounds are homogeneously mixed and if d_1 and d_2 are their densities and W_1 and W_2 their respective weights then the average density of the mixture can be given by:

$$d_{av} = \frac{W_1 + W_2}{\frac{W_1}{d_1} + \frac{W_2}{d_2}}$$

Now if d_{av} is the density of the oil, resins and soluble sludge mixture and d_1 is the density of the oil and resin mixture, then d_2 the density of the sludge can be calculated from:

$$d_2 = \frac{d_{av} \cdot W_2 \cdot d_1}{(W_1 + W_2)d_2 - d_{av} \cdot W_1}$$

In a similar manner the density of the resins may be calculated.

From Fig. 30 it can be seen that after initial fluctuations in values the densities of the resins for all three oils tended to approach a constant value slightly above that of the original oil. This indicates that once equilibrium had been reached the resins produced are of a uniform nature. In this respect it was noted that the less sludge the oil formed then the longer the time required for the resins to tend towards a constant value of density. This was to be expected if resins were to be considered as an intermediate product in the formation of sludge.

A similar effect was noticed in the density of the sludges where it can be seen that the density of that from

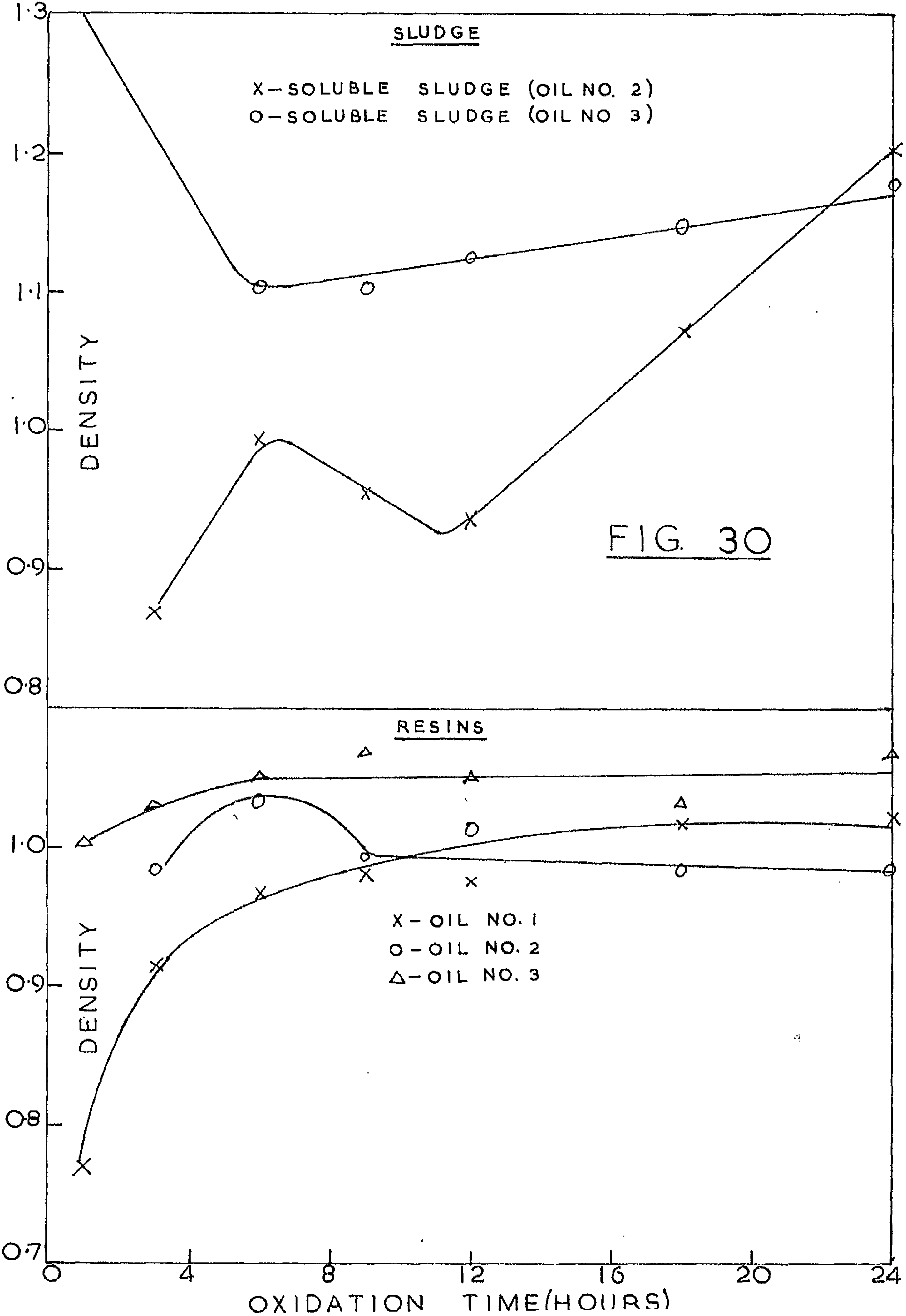

SLUDGE
X – SOLUBLE SLUDGE (OIL NO. 2)
O – SOLUBLE SLUDGE (OIL NO 3)
RESINS
X – OIL NO. 1
O – OIL NO. 2
Δ – OIL NO. 3
DENSITY
DENSITY
1·3
1·2
1·1
1·0
0·9
0·8
1·0
0·9
0·8
0·7
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 30

Oil No.2, which produced no insoluble sludge, after the initial fluctuations tended to increase far more rapidly than that from Oil No.3 whose denser material probably contributed to the formation of the insoluble sludge.

Molecular Weight

For a mixture of two similar compounds the molecular weight of the mixture can be expressed as:

$$M_{av} = x_1M_1 + x_2M_2$$

where x is the mole fraction.

As a first approximation, however, the value can be taken as:

$$M_{av} = x_1M_1 + x_2M_2$$

where x this time represents the weight fraction of the constituents.

If subscript 1 refers to the oil and resin mixture, and subscript 2 to the sludge,

then the molecular weight of the sludge can be given as:

$$M_2 = \frac{M_{av} - x_1M_1}{x_2}$$, where M_{av} is the molecular weight of the oil, sludge and resin mixture.

In a similar manner the molecular weight of the resins may be calculated.

From Fig. 31 it can be seen that the molecular weight of the resins from all three oils after initial fluctuations tended to a constant value. That of Oils 1 and 2 gave these values as just above those of the original oils which agrees

MOLECULAR WEIGHT OF SLUDGE AND RESIN

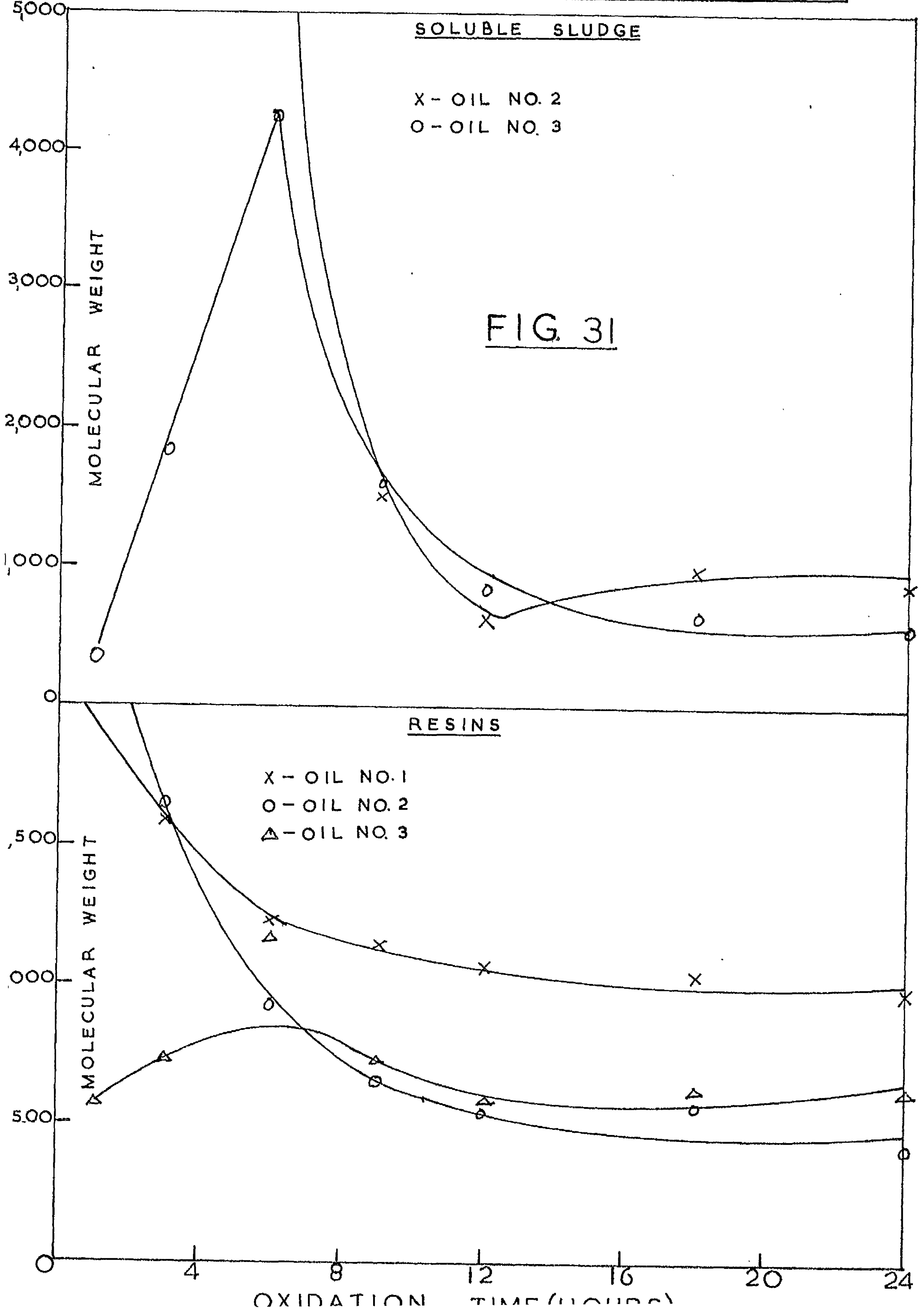


FIG. 31

with the observation of Sachanen and Vassilieff[87] that the molecular weight of resins in unoxidised oils was close to that of the fraction from which it was derived, exceeding it usually by 30 or 40. In this respect Naug[74] also found that the molecular weights of resins preformed and separated from lubricating oil distillates and those formed as a result of oxidation of the distillates had comparatively close values of molecular weight and elemental composition.

On the other hand the constant values approached by the resins from Oil No.3 corresponded to a dimer of the original oil. This is probably related to the high aromatic content of the oil, it being known that aromatics tend to polymerise to a much greater degree than any other hydrocarbon type.

The molecular weight of the soluble sludge from Oil No.3 rose initially then fell to values approaching that of its resins, while that for the soluble sludge from Oil No.2 was extremely high at first and then fell to values approaching that of a dimer.

Fenske et al.[49] using a cryoscopic method with naphthalene as solvent obtained values of around 1500 for both pentane and oil insoluble sludge. Sachanen[73] using an ebullioscopic method obtained values of up to 3000 for the molecular weights of the sludges. These values are comparable to those obtained in this work. However, other workers using a variety of methods obtained values which were widely different from those. Pfeiffer and Saal[88] using the Langmuirs method obtained values of from 5000 to 140,000. Swanson,[89] by a method involving diffusion and di-electric constant obtained similar values, while Katz and Beu[90] by means of an electron microscope obtained values of less than 65Å for the diameter of the sludge particles, corresponding to molecular weights of less than 50,000.

The fact that the molecular weight determinations were carried out on the sludge separated from the oxidised oil is of considerable importance. Variation in values by the different workers is likely to have been caused by different degrees of aggregation of the sludges on their precipitation.

Sachanen[73] has suggested that in solution sludges consist of high molecular weight material on to which is adsorbed resins so producing a micellar structure.

CHAPTER VIII

PROPERTIES AND CHEMICAL COMPOSITION OF OILS RECOVERED AFTER FULLERS EARTH TREATMENT

CHAPTER VIII

PROPERTIES AND CHEMICAL COMPOSITION OF OILS RECOVERED AFTER FULLERS EARTH TREATMENT

General Properties

The oil recovered after the treatment with Fullers Earth represented that portion of the oil which was not attacked in the course of oxidation. All samples recovered from the three oils were yellowish in colour. For Oil No.1 this did not vary very much from the colour of the original oil, but for Oils 2 and 3 the typical aromatic bloom that those oils had possessed before oxidation was lost.

The oxygen values of the recovered oils were slightly higher than those of the unoxidised oils, but this was found to be due to slight traces of water which had been entrained and emulsified in the oil during the oxidation process.

The carbon residues and viscosities all showed a tendency to decrease. Acidities for Oils 1 and 2 were zero as were those of the original oils, while that of Oil No.3 showed a slight increase. With Oil No.1 the density of the recovered portion was approximately the same as that of the original oil with slight variations as oxidation proceeded. Those of Oils 2 and 3 tended to decrease with the rate of decrease of Oil No.3 greater than that of Oil No.2.

For Oil No.1 the molecular weight decreased up to 1 hour and then increased to a constant value which was slightly below that of the original oil. Oil No.2 was similar with the constant value about that of the original oil, whereas the constant value approached by Oil No.3 was slightly higher than that of the original oil. This latter oil had also more fluctuations in the molecular weight of its recovered portion in the initial stages of oxidation than had the other two oils.

Thus it can be seen that the properties of the unoxidised part of the oils were similar to those of the original oils, with a tendency to decrease slightly in value as oxidation proceeds. This tendency was more pronounced with increasing aromaticity of the oils.

The above observations agree well with the work of Poell,[91] Noack,[92] Suide,[93] Marcusson[94] and Schindler[95] who found that the removal of resins from oxidised oils left the remaining oil in practically its original condition as far as its physical characteristics were concerned. Davis, Lincoln, Byrkit and Jones[76] came to the same conclusions after they removed resins stagewise from an oxidised oil and found that the neutralisation number, carbon residue, oxygen content and saponification number all approached the original oil characteristics.

From the results obtained it would appear that it is the heavier molecular weight, denser and more viscous material that bears the brunt of the oxidative attack on a lubricating oil fraction.

Viscosity Index

The standard method of expressing the variation of viscosity with temperature of an oil is the "viscosity index" which is based on an empirical scale. The standards are two series of lubricating oil fractions, the one obtained from a Pennsylvania crude being arbitrarily assigned a value of 100, and the other from a Gulf Coast crude a value of zero. The viscosity index of an oil of a given viscosity at 210°F is calculated from its viscosity at 100°F and the viscosity at 100°F. for each of the standards having a viscosity at 210°F. equal to that of the unknown. The viscosity index (V.I.) is then calculated from the following equation:

$$V.I. = \frac{L - U}{L - H} \cdot 100$$

where L, H and U are the viscosities at 100°F. of the zero V.I. standard, 100 V.I. standard and the sample respectively.

This method suffers from the disadvantages:

a) It is not exact.

b) It gives anomalous results at values higher than 100.

Cornelissen and Waterman[96] have developed a formula for expressing the variation of viscosity with temperature, which they claim obviates these disadvantages. This formula is:

$$\text{Log } V = (A/T^{x}) + B$$

where V = viscosity in cs.

T = absolute temperature in degrees Kelvin.

A, B and x are constants.

They have later shown[97] that the values for x are identical for similar compounds and that the log $\frac{V_{T_1}}{V_{T_2}}$ was a practical index for indicating the temperature dependence on viscosity. The authors claim that this is also an absolute index and have named it the "Fundamental Viscosity Temperature Index" (F.V.T.I.). For all recovered oils from the same original oil the values of x will be identical.

This above method was employed to determine how the viscosity/temperature relationship of the recovered oils varied. The two temperatures chosen were 20°C. and 50°C. as a simple matter of convenience. From Fig. 32 it can be seen that the F.V.T.I. of the recovered oils from Oil No.1 varied around that of the original oil in an irregular manner. On the other hand those of Oils 2 and 3 after a rapid initial decrease tended to decrease linearly with the rate of decrease greater for Oil No.3. Thus the more aromatic the oil the greater the tendency for the viscosity dependence upon temperature to become less as oxidation proceeds. This means in practice that the recovered oils have a better F.V.T.I. than the original oils, a point which could be of importance if it is intended that the oils should be used again after recovery.

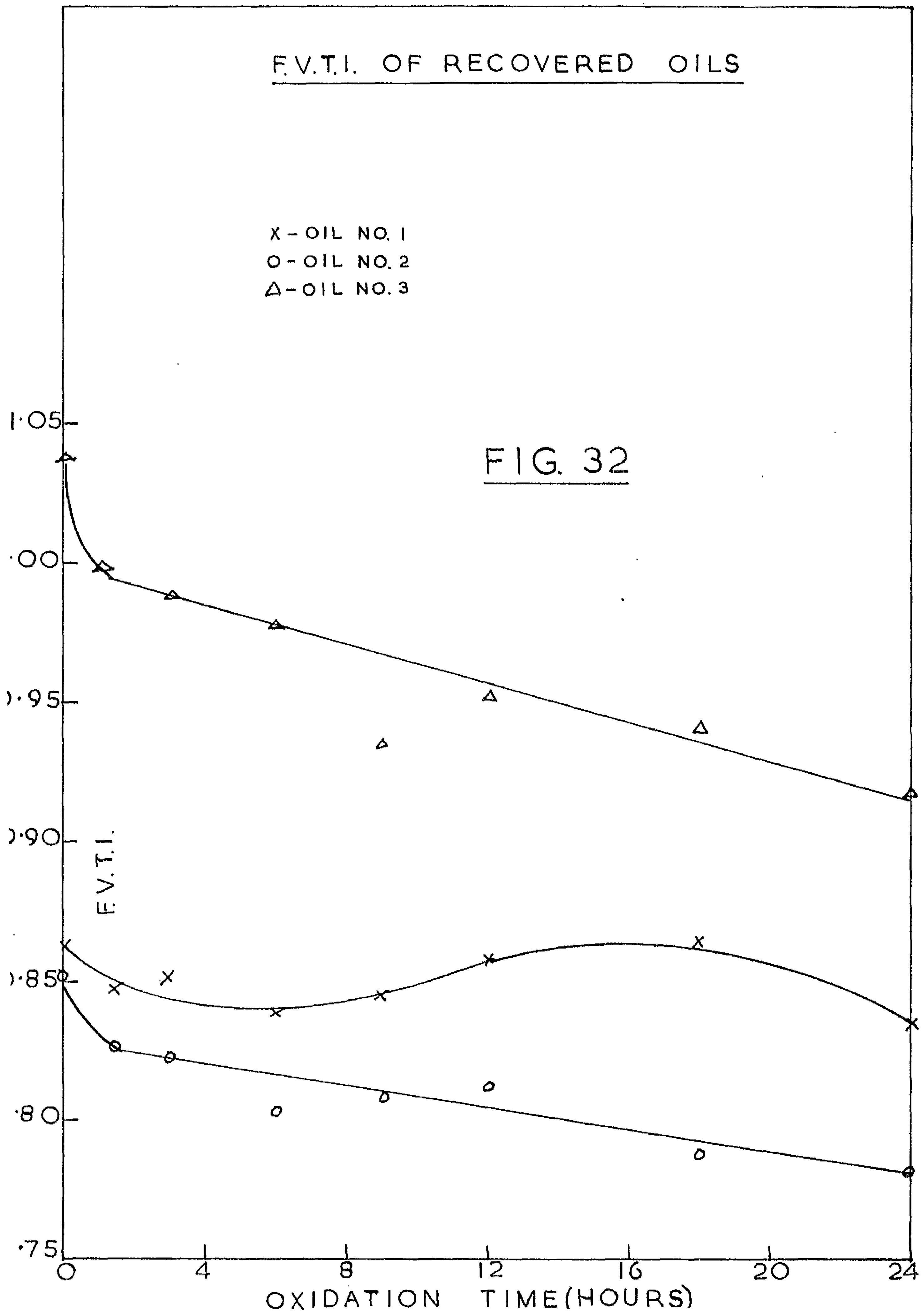

F.V.T.I. OF RECOVERED OILS
X - OIL NO. 1
O - OIL NO. 2
Δ - OIL NO. 3
1·05
·00
·95
·90
·85
·80
·75
F.V.T.I.
0
4
8
12
16
20
24
OXIDATION TIME (HOURS)

FIG. 32

Carbon Distribution

The carbon distribution of the recovered oils from Oil No.1 showed virtually no change with oxidation time. The changes in molecular weight of the recovered oils were therefore not associated with any particular hydrocarbon type. There must be in this oil, then, a molecular weight range of compounds of the same average composition and no specific type of compound was preferentially attacked.

With the recovered oils from Oil No.2 there was an initial increase in the percentages of C_R, C_N and C_A (Fig.33), and this was associated with the initial rapid decrease in molecular weight. This points to the fact that high molecular weight paraffinic compounds bore the brunt of the initial attack. After this initial increase in C_R, C_N and C_A, the values dropped to that of the original oil and then only slightly decreased for the remaining periods of the oxidation, again indicating that most of the oil consisted of compounds of the same average structure.

Oil No.3 showed much greater initial variations in average composition than Oil No.2 before it reached a constant value similar to that of the original oil. There was an initial drop in the carbon in ring structure associated with an increase in the molecular weight and then an increase in the percentage carbon in rings accompanied by a decrease in the molecular weight. This would appear to show an initial attack on low molecular weight aromatics as the percentage

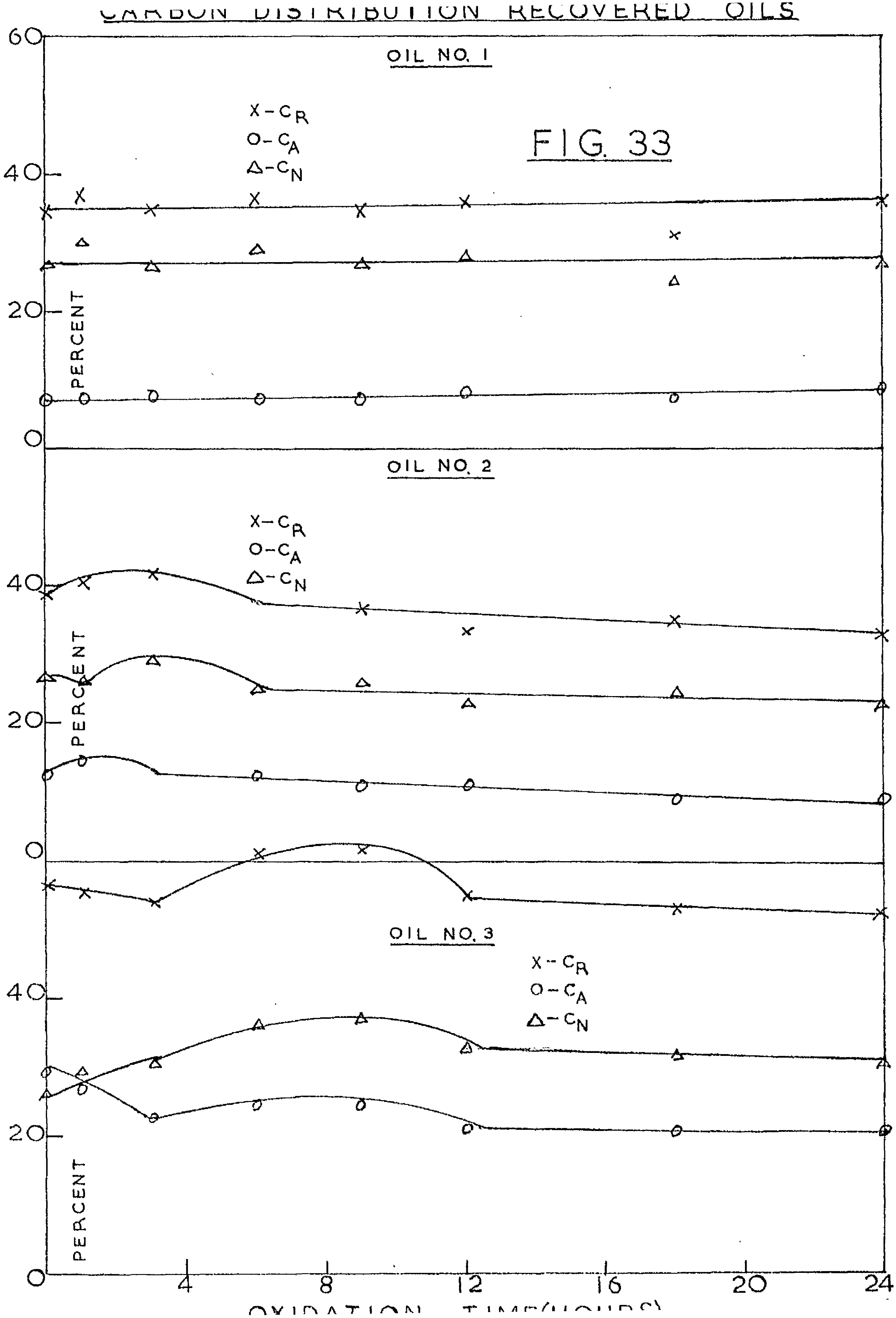

CARBON DISTRIBUTION RECOVERED OILS
OIL NO. 1
X – C_R
O – C_A
Δ – C_N
OIL NO. 2
X – C_R
O – C_A
Δ – C_N
OIL NO. 3
X – C_R
O – C_A
Δ – C_N
PERCENT
PERCENT
PERCENT
60
40
20
0
40
20
0
40
20
0
4
8
12
16
20
24
OXIDATION TIME(HOURS)

FIG. 33

C_A dropped at this stage while that of C_N showed a slight increase. This was followed by attack on high molecular weight paraffinic type compounds before a constant composition was reached. At the stage where oxidative attack on the paraffins was the predominant reaction it was noted that the percentage oxygen in the oil showed a decrease so it seems likely that the loss in paraffins was due to their undergoing cracking type reactions in which oxygen was also lost.

From a study of the above results it can be seen that the more aromatic the oil the longer the time required for the unoxidised part of the oil to reach a constant composition. This indicates that with the less refined oils the process of oxidation has the same effect on the oil as has the refining process, i.e. the compounds bearing the brunt of the oxidative attack in less refined oils are those compounds which would be removed by the refining process. These would appear to be initially aromatics and then high molecular weight paraffins. After removal of these extraneous compounds what may be termed the basic oil is left and this undergoes very little change in average structural composition, at least up to 24 hours oxidation, and under the given oxidation conditions.

CHAPTER IX

ACCELERATED OXIDATION AND OXIDATION OF A RECOVERED FRACTION OF THE NAPHTHENIC TYPE OIL (OIL No.3)

CHAPTER IX.

ACCELERATED OXIDATION AND OXIDATION OF A RECOVERED FRACTION OF THE NAPHTHENIC TYPE OIL (OIL No.3)

In previous chapters the deterioration of the oils and the properties of the recovered fractions with increasing oxidation time were studied. It was noted that the extent of oxidation and the composition of the recovered oils all approached constant values in the later stages of oxidation. It was, therefore, thought desirable to promote further oxidation and to see to what extent the previous tendencies were repeated and to determine the effect of the oxidation products on the oxidation process. To achieve the first of these aims it was necessary to obtain an accelerated oxidation test that would be as close as possible to the conditions laid down in the I.P. test. For the second it was necessary to remove the oxidation products after 24 hours oxidation under I.P. test conditions and then re-oxidise the recovered fractions under the same conditions for periods varying up to 24 hours.

Since Oil No.3 underwent the greatest oxidation, it was decided to carry out the experiments mentioned above on this oil. The apparatus and experimental procedure developed are described below.

1. AN ACCELERATED OXIDATION TEST

A survey of the various laboratory oxidation tests used was carried out, some of which were mentioned in Chapter IV. The test most closely approximating to the desired conditions was the "Indianna Stirring Oxidation Test", in which aeration of the oil is achieved by rapid stirring of the samples. This test was developed by Lamb, Loane and Gayner[64] in order to obtain an oxidation test that would give oxidation stability values comparable to those obtained in engine tests. The accelerated deterioration of the sample achieved was claimed by the authors to be due to a longer retention period of the volatile products catalysing the oxidation reactions.

It was therefore decided to combine the principles of this method with the conditions of the I.P. test as far as was practical, in order to achieve the required conditions. The test developed then consisted of bubbling air at the rate of 60 litres per hour through 160 ml. of sample by means of a hollow glass stirrer.

Details of Test

A view of the apparatus used, without the heating bath, is given in Fig. 34.

In order to obtain enough sample to carry out the required analysis it was necessary to scale up the apparatus from the I.P. test by increasing the quantity of oil oxidised from 40 ml. to 160 ml. The glass cell in which oxidation took

STIR OXIDATION APPARATUS

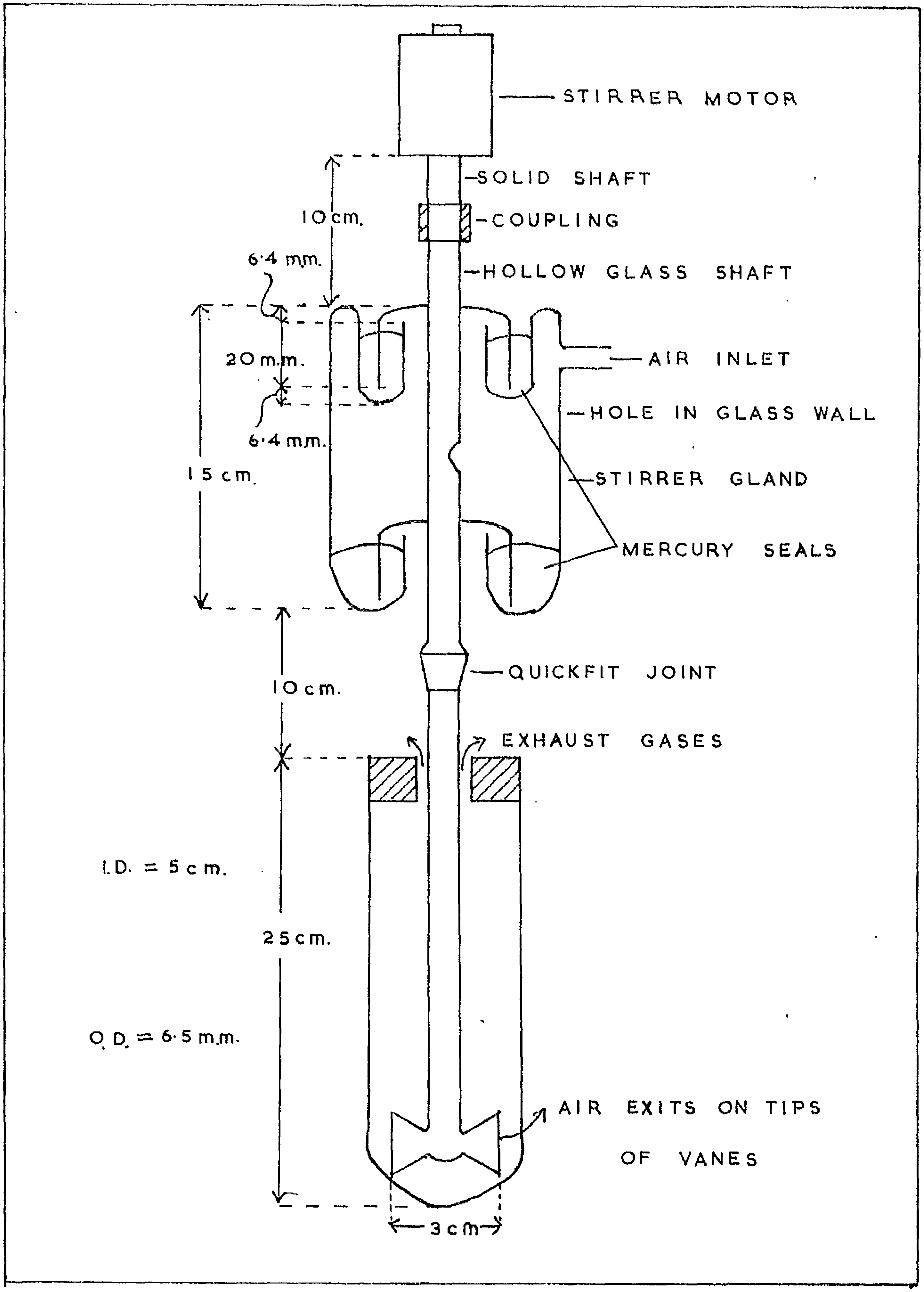


FIG. 34

place was 25 cm. in length and its internal diameter was 5 cm. being twice that of the cell in which the I.P. test was carried out. As a result the height of the oil in each cell was the same, being approximately 8 cm. The top of the cell was covered by means of a cork with a hole in the centre for the combined air inlet and stirrer shaft. This also served as an outlet for the volatile products of oxidation.

The combined air inlet and stirrer assembly consisted of an electric motor rotating the hollow glass tube which contained a stirrer gland. This gland was fitted with two mercury seals to allow air to be passed through the stirrer shaft and exit through the tips of the vanes at the end of the shaft, the latter extending to 4 mm. from the bottom of the cell. The lower section of the shaft was connected to the upper by means of a Quickfit joint just below the gland, enabling it to be disconnected for cleaning after an oxidation run. The height of the oil in the cell corresponded to a pressure of 0.231 inches of mercury. Thus in order that there should be no escape of air at the mercury seals, they were filled with mercury to a height of 0.50 inches.

The stirrer shaft was arbitrarily rotated at 500 r.p.m.

The heating bath in which the oil was immersed was 46 cm. high, 23 cm. in diameter, lagged with asbestos and heated by two 500 watt Bray heaters fitted externally to the bottom of the bath. The temperature was held at 200 ± 0.5°C. by means of a Sunvic control unit.

Experimental Details

Samples of Oil No.3 were oxidised under the conditions specified above and the sludge and resin values determined. Structural group analysis was also carried out on the fraction of the oil recovered after the Fullers Earth treatment. Oxidation was continued until the quantity of oxidised material began to approach a constant value, which occurred after approximately 30 hours oxidation.

2. RE-OXIDATION OF RECOVERED OIL

A number of samples of Oil No.3 were oxidised for 24 hours under the conditions of the I.P. test and mixed together to form a composite sample. This sample was then treated in portions of about 160 gm. with Fullers Earth and the unoxidised part of the oil recovered. This was repeated until enough sample had been recovered. The recovered oil was then oxidised as before for periods of up to 24 hours and the resulting oils analysed for sludge and resins. Structural group analysis was then performed on the oils recovered after the Fullers Earth treatment.

In the analysis of the results obtained, the periods of oxidation by this method were added on to those of the original oil so that the total period of oxidation of the oil under I.P. test conditions was 48 hours.

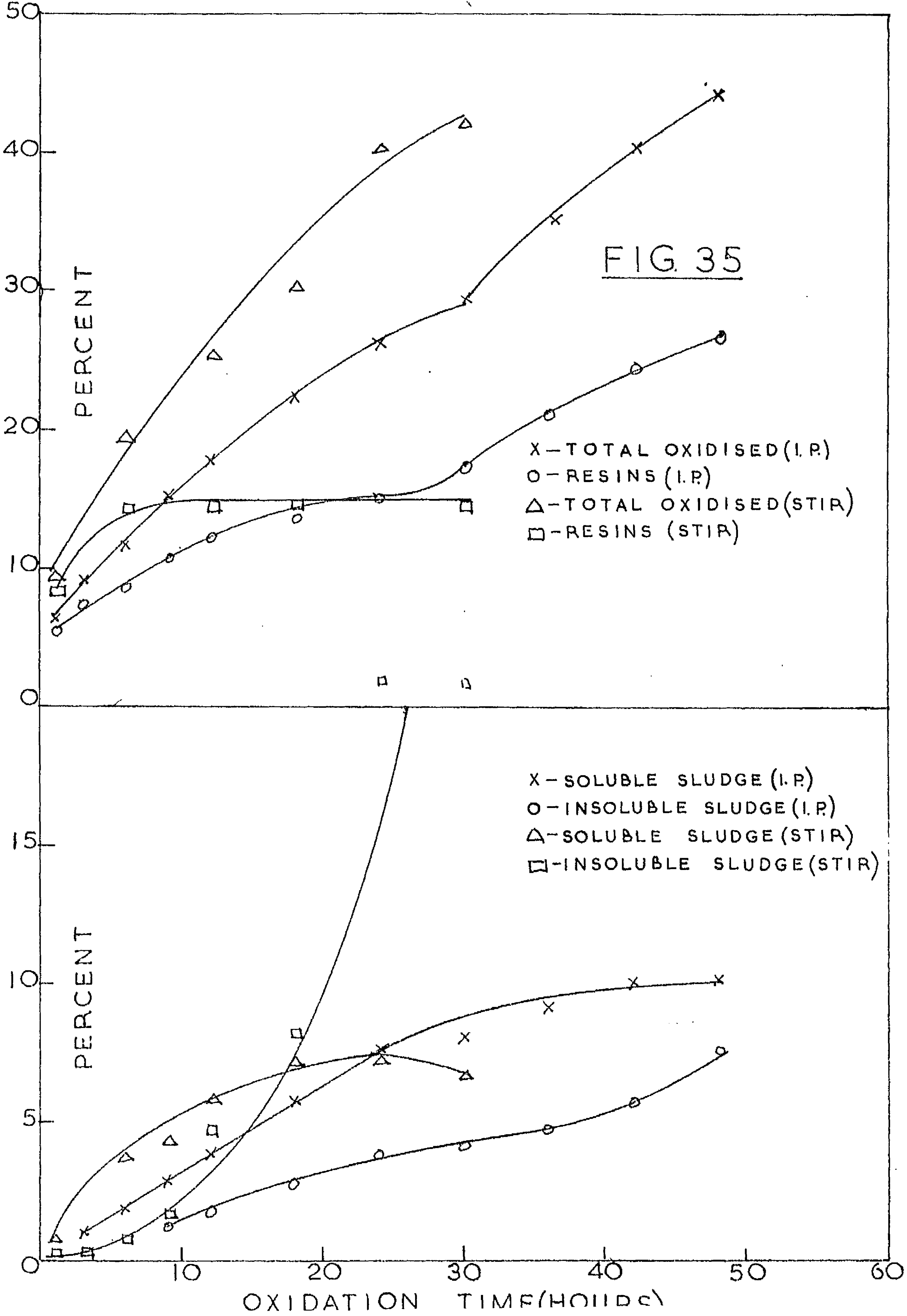
Extent of Oxidation

With the stirring method the quantity of oxidised material produced was greater than that obtained under the normal I.P. test conditions for similar periods of time (Fig.35). However, when the oxidation products were considered as resins, soluble sludge and insoluble sludge, it could be seen that the resins very quickly (6 hours) approached a constant value which was similar to that reached under the I.P. test conditions after 24 hours oxidation. A similar effect was noted with soluble sludge although the approach to a constant value did not take place until about 18 hours oxidation time. When the amount of insoluble sludge was considered, however, it was noted that this was much greater than that obtained under the I.P. test conditions and constituted a considerably greater percentage of the total oxidation products.

Thus, it appears obvious that under accelerated conditions the equilibrium between the reactions: hydrocarbons ---> resins ---> soluble sludge ---> insoluble sludge, was attained much more quickly and that the individual reactions were also much accelerated. As a result the approach to constant values in the amounts of resins and soluble sludge occurred sooner and insoluble sludge was then produced at a greater constant rate than that under normal unaccelerated I.P. test conditions.

After the removal of the oxidation products and the re-oxidation of the remaining oil it was noted that the general trends of the original oxidation were repeated with the resins tending to approach a constant value. However, instead of a linear increase of sludges it was found that the amount of

EXTENT OF OXIDATION



soluble sludge approached a constant value, while the insoluble sludge tended to show an autocatalytic type of increase. The total amount of oxidation products after a total oxidation period of 48 hours was similar to that after 30 hours oxidation by the stirring method, but the quantities produced in the second period of 24 hours were reduced from that of the original 24 hours.

The inhibiting effect of the oxidation products would not appear to be very great in this oil, the approach to constant values of the resins before removal of oxidised material being due to the establishment of equilibrium, rather than inhibition. The reduction in the amount of the oxidation products on re-oxidation was very likely due to the fact that the components of the oil which bear the brunt of the initial attack were already oxidised. After their oxidation, the oxidation of the oil as a whole was a steady uniform process. This would also account for the fact that on re-oxidation, equilibrium was attained in a shorter period of time.

Properties of the Recovered Oils

Some of the properties of the recovered oils are shown in Table 10, given below.

TABLE 10

Oxidation Time	n		d		M		$V_{20°C}$	
	I.P.	Stir	I.P.	Stir	I.P.	Stir	I.P.	Stir
0	1.5278	1.5278	0.9408	0.9408	326	326	1028	1028
1	1.5245	1.5212	0.9385	0.9360	344	380	846	874.2
6	1.5210	1.5170	0.9367	0.9294	304	384	793	819.2
12	1.5164	1.5140	0.9290	0.9237	346	391	696	788.2
18	1.5150	1.5110	0.9258	0.9185	350	371	650	765.8
24	1.5135	1.5090	0.9226	0.9170	352	382	606	765.8
30	1.5101	1.5054	0.9182	0.9131	393	402	620.7	743
36	1.5082	-	0.9138	-	406	-	611.1	-
42	1.5056	-	0.9131	-	424	-	627.5	-
48	1.5041	-	0.9093	-	434	-	628	-

It can be seen from the above table that the refractive indices and densities tended to fall with increasing oxidation time, with the rate of decrease being slightly greater under the stir test conditions. With the molecular weight and viscosities, however, it was seen that the discrepancies between the values obtained by the two methods was rather greater and this can be seen more clearly from Fig. 36.

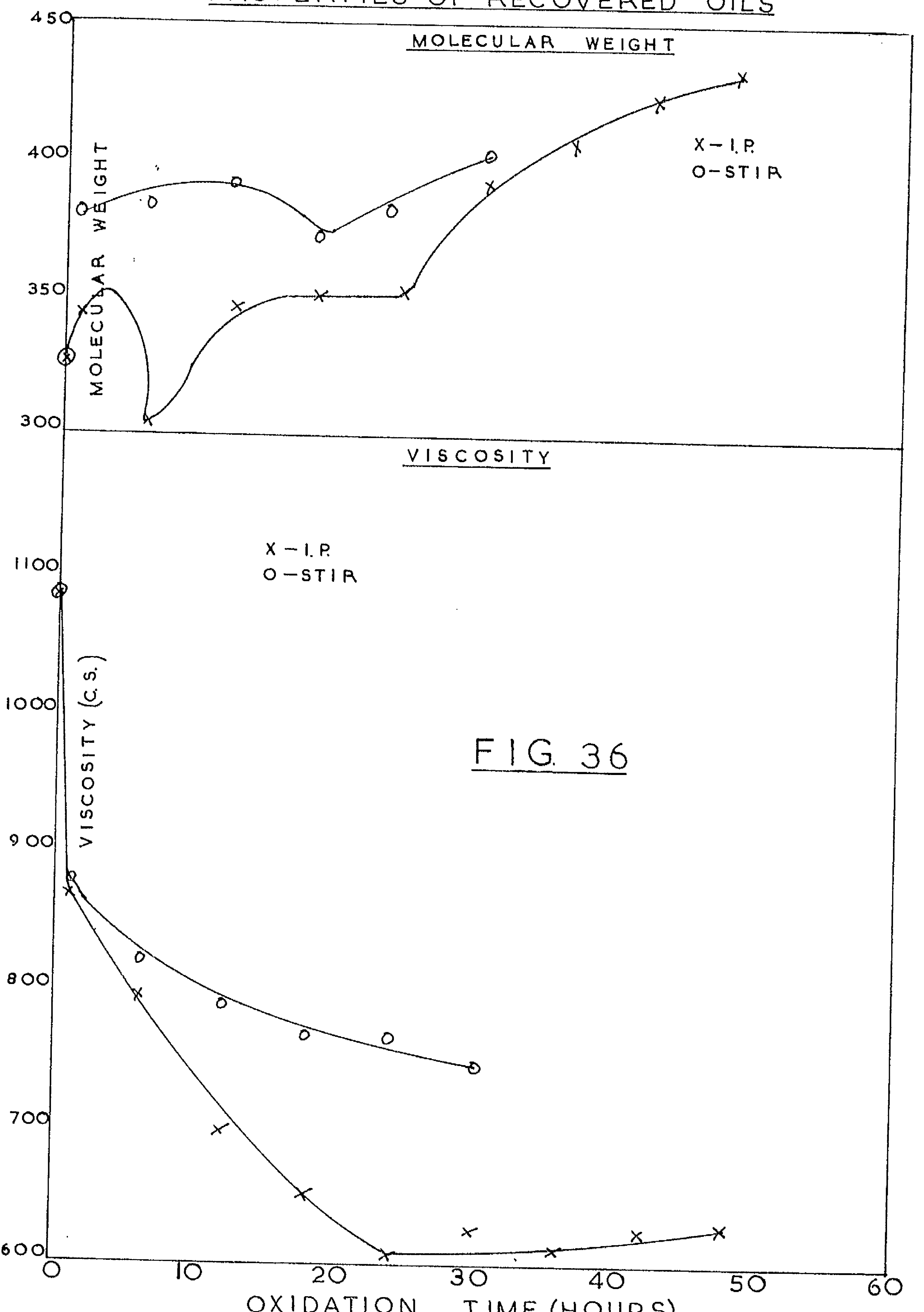

PROPERTIES OF RECOVERED OILS
MOLECULAR WEIGHT
MOLECULAR WEIGHT
450
400
350
300
X – I.P.
O – STIR
VISCOSITY
VISCOSITY (C.S.)
1100
1000
900
800
700
600
X – I.P.
O – STIR
0
10
20
30
40
50
60
OXIDATION TIME (HOURS)

FIG. 36

Under the stir test conditions the molecular weight of the recovered oils did not vary very much with oxidation time but on the whole tended to increase in value. The viscosities on the other hand tended to decrease, the rate after an initial high value falling with increasing oxidation time. This seems to indicate that oxidative attack was spread over the whole molecular weight and viscosity range of the oil, with the lower molecular weight and more viscous compounds being oxidised at a slightly greater rate than the others.

Under the I.P. test conditions the molecular weight of the recovered oils, after initial fluctuations, discussed earlier in Chapter VI, tended to approach a constant value higher than that of the original oil but lower than the values obtained under the stir test conditions. The viscosities of the recovered oils were considerably lower than the values obtained under the stir test conditions.

After removal of the oxidised material and re-oxidation the molecular weight of the recovered oils rose very sharply, while the viscosity also tended to increase but at a much slower rate. Thus, the products of oxidation while not inhibiting the extent of oxidation seem to have an effect on the molecular weight and viscosity of the compounds oxidised. Thus, before removal of the oxidised material an average molecular weight and high viscosity type compound was being oxidised while after their removal a low molecular weight and low viscosity type of compound was being preferentially attacked.

Carbon Distribution of Recovered Oils

On removal of the oxidised material and re-oxidation, the trends in carbon distribution of the recovered oils were continued but at a slightly greater rate. Thus, ring structures and particularly aromatics were still being preferentially attacked to a slight degree (Fig. 37).

Under the stir test condition, however, the carbon in ring structures fell then rose in the later stages of oxidation, the carbon in aromatics showed a slight decrease, while that in naphthenes first of all decreased slightly then rapidly increased. Thus, initially the aromatics bore the brunt of the attack, with the paraffins playing an increasingly important part as oxidation proceeded.

From analysis of the above results it would appear that with the I.P. test oxidative attack tended to concentrate more on the aromatics than on any other type of molecule. In the oil, of course, these aromatics will be associated with other hydrocarbon types which would also be removed as oxidation products even though they might not have undergone direct oxidation. This being the case, it might well be that the aromatics were attacked to a far greater degree than was apparent on examination of the deresined oils. The oxidation products did not affect the structural types attacked but did appear to have some effect on the molecular weight and viscosity of the compounds oxidised.

With the stir test, where the oxidation was catalysed by the volatile product of oxidation, attack was more widely

CARBON DISTRIBUTION OF RECOVERED OILS

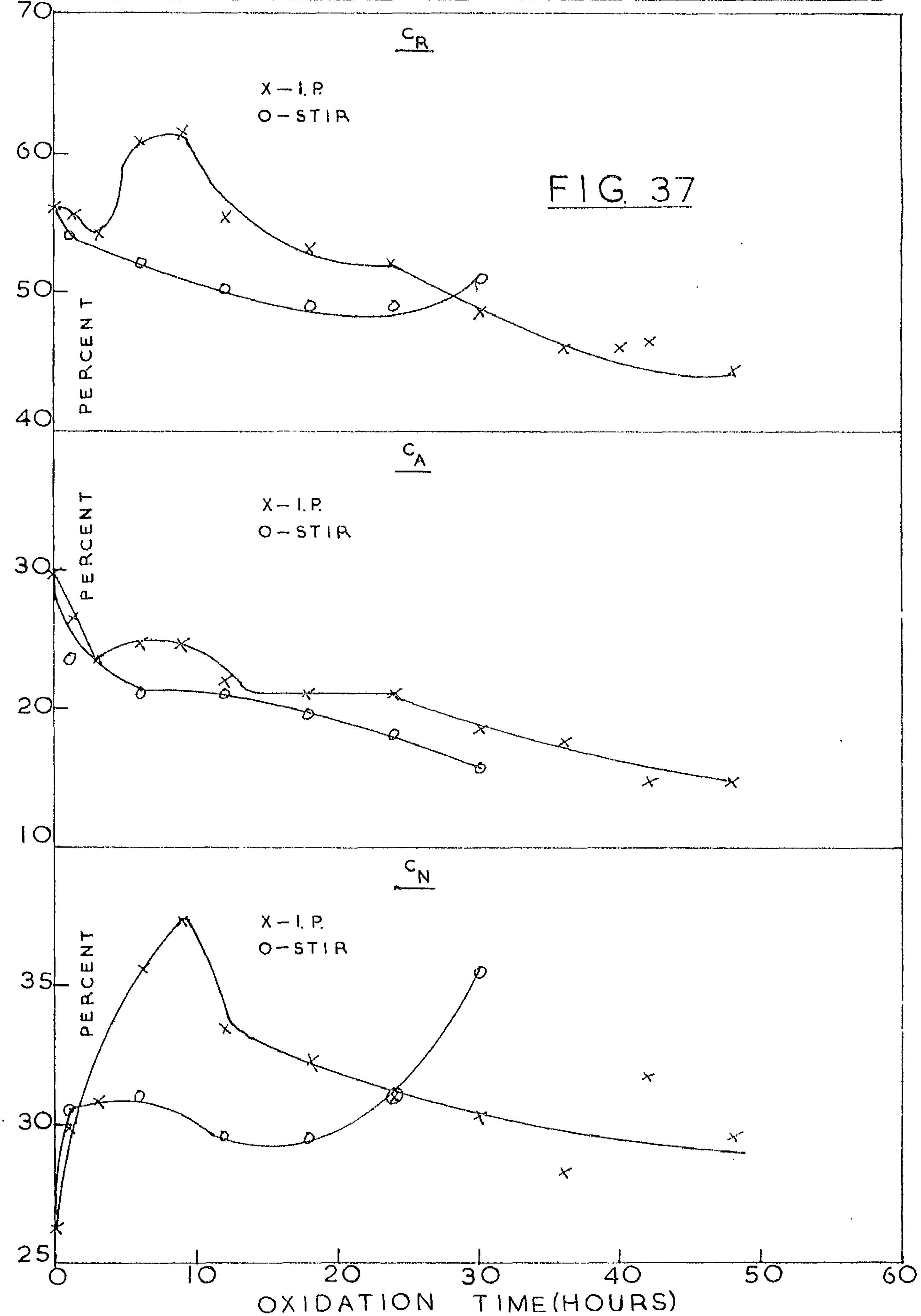


FIG. 37

spread over the various structural types of hydrocarbon. This was probably due to the catalytic effect reducing the activation energies of the compounds not previously oxidised, to such an extent that they were then capable of being oxidised and this resulted in oxidation taking place over a smaller range of molecular weight and viscosity.

CHAPTER X

DISCUSSION

CHAPTER X

DISCUSSION

Waterman, Leenderste and Palm[98] have reported that the total sludge produced on oxidation of a lubricant increased with the percentage aromatics in the oil. Hibbard,[99] Dooser and Fenske[56] have also reported similar effects with lubricating oil fractions oxidised at temperature lower than 200°C. These effects were also noted in more recent work by Gibson[77] who found that absorption of oxygen passed through a minimum at around 10% C_A, but that the amount of sludge formed was a function of the aromatic content of the oil. In the present work it has been found that the total amount of sludge produced was proportional to the aromatic content, but that this was not necessarily the case with the total amount of oxidation products. For instance, Oil No.2, which is of intermediate aromatic content, produced more resins than the other oils and after 24 hours oxidation, more total oxidation products present in the oxidised oils.

In this respect it should be noted that high absorption of oxygen itself need not be a criterion of low oxidation stability. What is more important is the nature of the oxidised compounds formed and their effect on the properties of the lubricant. Thus the formation of total resins is probably due to the presence of paraffins and naphthenes, with the sludge being formed from the aromatics.

Hicks-Bruun et al.[59] have shown that highly refined oils absorb considerably more oxygen than less refined oils. Since highly refined oils produce the smallest amount of retained oxidation products, the bulk of the oxidation process is probably concerned with reactions in which volatile products are formed. As the aromatic content of the oil increases there is a greater tendency for polymerisation reactions to take place, producing sludge which is retained in the oil. With the intermediate aromatic oil this resulted in the formation of only soluble sludge of comparable amounts produced by the higher aromatic oil, which over and above this also produced considerable quantities of insoluble sludge. Thus there is the tendency for highly refined oils to produce resins and volatile oxidation products and for the less refined oils to produce resins and sludge.

The amount of oxygen retained by all three oxidised oils was of comparable value, with a slight tendency for there to be more in the higher aromatic oils, probably due to the greater degree of oxidation.

Carbon residues of the oxidised oils increased with their aromatic content, and this has been shown to be due to the increased contribution to the total increase, from the more heavily oxidised material. The oxygen present in the oil has been shown to play a less important part in determining the carbon residue, as the aromaticity of the oils increased.

The viscosity, on the whole, tended to increase at a greater rate with increasing aromaticity. In the later stages of oxidation, however, this was found to be not necessarily the case, as the rate of increase of viscosity of Oil No.2 then showed the highest value. This was probably due to the fact that this oil produced only soluble sludge while Oil No.3 also produced insoluble sludge. This then resulted in the rate of increase of viscosity of the filtered oil of the latter not being so great due to the loss of some of the high viscosit soluble sludge as insoluble sludge. It has been found that the contribution of the sludge to the viscosity tended to increase with oxidation time and was directly proportional to the amount of sludge. Removal of sludge, on the whole, decreased the viscosity to values similar to that before oxidation.

The total acidity of the oxidised oils increased linearly with oxidation time with the rate greater with increasing aromaticity, while the acidity of the desludged oils was a function of the paraffinic content of the original oil. Therefore it would appear that there were two types of acid formation: that associated with the resins (i.e. paraffinic content of the oil) and that associated with the sludge (i.e. aromatic content of the oil). The former type of acidity was likely to be carboxyl formation while the latter was more likely to be hydroxyl formation (i.e. Phenols etc.).

The increase of density on oxidation was directly proportional to the aromatic content of the original oils. A similar effect to that with viscosity was noted when the sludge was removed, in that the density decreased to values similar to those of the oils before oxidation.

There were no general tendencies in the molecular weight of the oxidised oils that could be directly related to the aromatic or paraffinic content of the unoxidised oils.

The amount of oxygen present in the sludges and resins was found, on the whole, to increase with oxidation time. Davis, Lincoln, Byrkit and Jones[76] also came to the same conclusion on the ultimate analysis of the resin fraction produced on oxidation of lubricating oil fractions. The sludge and resin from the more aromatic oils had slightly less oxygen present in them than those from the paraffinic oil. This was probably associated with the fact that the former tended to polymerise to a greater degree with resulting loss of oxygen in water of condensation.

The carbon residues of the resins from all three oils were found to be similar and much less than those of the sludges. The values of carbon residue of the soluble sludge from Oil No.2 tended on the whole to be greater than those from Oil No.3, but the constant values which were approached were similar for both. The carbon residues of the insoluble sludge from Oil No.3 were rather less than those of the soluble sludges, indicating that their degree of polymerisation was of the same order.

The acidity of the resins tended to increase with the paraffinic content of the original oil as did that of the soluble sludge. The acidity of the insoluble sludge was considerably greater and increased in the earlier stages of oxidation at a much greater rate, to approach a constant value.

Densities of the resins varied very little with oxidation time once equilibrium had been reached and were only slightly above that of the original oils. It was also found that the less sludge the oil formed, then the longer the time required for equilibrium to be reached as far as the densities were concerned. The density of the soluble sludge from Oil No.2 increased fairly rapidly with oxidation time, while that of Oil No.3 showed only a slight tendency to increase.

The molecular weight of the resins from Oils 1 and 2 was just above that of the original oils, while that from Oil No.3 approached that of a dimer. This was thought to be due to the tendency of aromatics to polymerise on oxidation to a greater degree than other hydrocarbons. After initial high values the molecular weights of the soluble sludges from Oils 2 and 3 tended to decrease towards that of the resins. This is believed to be due to the fact that on increasing oxidation there is an adsorption of resins on to the surface of the very high molecular weight sludge and these resins are separated with the sludge in the precipitation process.

Sachanen[73] maintains that there is a close relationship between sludge, resins and high molecular weight polycyclic hydrocarbons, the ultimate analysis of which, he found, to be very close to each other. As a result the chemical structures of sludges and resins should be more or less similar, the principal differences lying in their physical and physico-chemical properties. He also claims that, owing to the high specific gravity and refractive index of the resins present in unoxidised oils, that the number of paraffinic side chains should be small. In this respect it should perhaps be again mentioned that Haus[74] found that resins preformed and separated from lubricating oil distillates and those formed as a result of oxidation had comparatively close values of molecular weight and elemental composition.

In the present work it has been found that the properties of the resins, on the whole, were not very much different from those of the original oils, but tended to be slightly higher as regards acidity, density and carbon residue. It would appear that the soluble sludge was more oxidised and polymerised thus causing them to have higher values of density, viscosity, carbon residue, acidity, etc. On their removal from the oil it was generally found that the properties of the original oils were approached. Removal of the resins caused reductions in values from those of the original oils, indicating that on the whole the heavier compounds present in the unoxidised oil were being preferentially oxidised. With regard to Sachanen's observations[75] on the nature of the resins present in unoxidised oils, and the properties of aromatic hydrocarbons it would appear not improbable that these compounds would be of an aromatic nature. This is borne out on examination of the carbon distribution of the recovered oils when it was seen that, on the whole, there was a tendency for aromatic hydrocarbons to be preferentially oxidised. That this effect was not greater was probably due to the fact that these aromatic hydrocarbons were probably associated with other hydrocarbon types in the original oil. These other types were then also removed by the Fullers Earth treatment even though they had not undergone any direct oxidative attack.

It was not possible to determine the nature of the insoluble sludge from Oil No.3 except in a limited number of cases, but where it was possible, it appeared that there was no great fundamental difference in the nature of soluble and insoluble sludge.

There is a considerable amount of evidence in the literature[53,74,76,100] indicating that the deterioration of an oil follows the pattern of: hydrocarbons ---> resins ---> oil soluble sludge ---> oil insoluble sludge.
This mode of oxidation was substantiated by this present investigation and a résumé of the evidence obtained is given below.

On oxidation the rate of formation of resins produced by all three oils decreased after about 12 hours oxidation time. With Oil No.1, which formed no sludge, this reduction in rate was probably due to equilibrium being approached in rates of resin formation and formation of volatile oxidation products from the resins. As the aromatic content of the oils increased this type of reaction became of less importance and the decrease in rate of resin formation was probably due more to the fact that equilibrium was being reached in the rates of formation of resins and soluble sludge from the resins. This was borne out by the fact that in Oil No.2, the rate of formation of soluble sludge showed an increase at a period corresponding to the rate of decrease of resin formation. Oil No.2, which produced no insoluble sludge, showed an autocatalytic type of increase of soluble sludge formation, while that of Oil No.3 was linear indicating that where no insoluble sludge was formed the rate of increase of soluble sludge formation increased with oxidation time. Up to this stage of the oxidation (24 hours) the insoluble sludge from Oil No.3 increased linearly.

Under accelerated conditions it was found that the resins approached a constant value similar to that obtained under I.P. test conditions, but in a much shorter period of time. However, the rate of formation of soluble sludge was linear until the amount produced had reached that produced under the I.P. test conditions, when the rate fell to zero. At about this stage the rate of formation of insoluble sludge showed a rapid increase. Thus under accelerated conditions it would appear that equilibrium had been reached in the rates of formation of resins, soluble sludge and insoluble sludge. Under the I.P. test conditions the rates of oxidation were too low for these effects to become apparent in the oxidation times employed.

On oxidation, under I.P. test conditions, of the recovered oils equilibrium was reached in the rates of formation of resins, soluble sludge and insoluble sludge after about 18 hours. The fact that equilibrium was attained in the recovered oils after a much shorter period of oxidation than the original oil is probably related to the fact that this oil has possibly a fair spread of hydrocarbon types in its make up. Thus on oxidation of the original oil soluble sludge was produced at a rate greater than that of the insoluble sludge and showed no decrease in rate of formation until easily oxidised compounds were first of all oxidised. Thereafter the rate of formation of insoluble sludge approached that of the soluble sludge and this resulted in an apparent increase in rate of formation of the latter, as equilibrium was reached. Also on removal of those easily oxidised compounds the rate of formation of total oxidation products showed a slight decrease.

The above hypothesis was also borne out on examination of the change in properties of resins and sludges from the three oils with oxidation time. For example, from consideration of the percentage weights and total weights of oxygen present in the resins and sludges, it would appear that there was a transfer of oxidised material from the resins to the soluble sludge and from the soluble sludge to the insoluble sludge. Where there was no insoluble sludge formed, there was a build up of oxidised material in the soluble sludge, but in the case where no soluble sludge was formed this was counterbalanced by the loss of oxidised material as the volatile product of oxidation.

With Oil No.1 no sludge was formed and as a result the acidity of the resins increased with oxidation time. With Oil No.2 which formed soluble sludge, the acidity of the resins approached a constant value, but that of the soluble sludge increased with oxidation time. With Oil No.3, which produced both soluble and insoluble sludge along with resins, the acidities of the resins and the soluble sludge approached constant values, while that of the insoluble sludge kept on increasing with oxidation time. It also appeared as though there was a transfer of acidic material from the resins to the soluble sludge and from the soluble sludge to the insoluble sludge as the weights of acid present in soluble sludge from Oil No.2 increased at a greater rate than that of resins, while a similar effect was noted with insoluble and soluble sludge from Oil No.3.

It was also found that the densities of the resins from all three oils tended to approach a constant value on oxidation. The time required, however, for this to occur was longer as the amount of sludge formed decreased. This is understandable if one assumes that there is a transfer of denser material from resins to soluble sludge. A similar effect was also noted for the densities of the soluble sludge from Oils 2 and 3. The former produced no insoluble sludge and the density of the soluble sludge increased at a much greater rate than that of Oil No.3, whose denser material probably contributed to insoluble sludge formation.

A considerable amount of evidence has,therefore, been obtained in this work, indicating that there is an equilibrium in rates of formation of resins and soluble sludge and soluble sludge and insoluble sludge. There has also been found no fundamental difference between the resins and the sludges, and this agrees well with work that has been done in the past. This then gives rise to the question as to what is the essential difference between the resins and sludges that causes precipitation of the latter, either on the addition of hydrocarbon solvents or simply on oxidation.

It would appear that on oxidation of a lubricating oil fraction, the hydrocarbons present in the oil are lightly oxidised to produce resins. Part of these resins then undergoes further oxidative polymerisation, possibly by the condensation of aromatic hydroxyl compounds and carbonyl compounds, which would account for the fact that the acidity of the resins approached a constant value when sludge was formed. The high molecular weight compounds so formed are then capable of adsorbing on to their surface considerable quantities of resins, and so reducing their average molecular weight to that of the resins.

The peptising effect of these resins on the sludge is of great importance. Faust[101] has pointed out that residual oils at high temperatures produced sludges which were peptised by resinous constituents and converted the oils into asphaltic systems. On the other hand sludges formed in distillate oils low in resins were segregated into heterogeneous particles which did not substantially affect the viscosity and microstructure of the oil. Sachanen[73] has also observed that sludges are dispersed colloidally in petroleum products due to the peptisation by adsorbed resins and heavy polycyclic hydrocarbons whereas resins form true solutions in the oxidised oil.

Sludges are lyophilic with respect to aromatics and lyophobic with respect to paraffins. Consequently the sludges are colloidally dispersed in aromatic products, such as the lubricating oil fraction from which they are derived, but in an excess of petroleum ether and similar paraffinic hydrocarbons they are coagulated and precipitated. It is this latter fact that is used in the determination of the amount of soluble sludge produced on oxidation. The resins which are readily adsorbed by the sludges act as protective layers and isolate the colloidal particles from the coagulative action of the lyophobic constituents of the oil. If the proportion of peptising constituents in a petroleum oil is insufficient, then the sludges form a suspension.

It would appear likely that on further absorption of oxygen and adsorption of resins, the nature of the soluble sludge is altered to such a degree that it was no longer soluble in the oxidised oil. It has been suggested in Chapter VII that, owing to the high acidity of the insoluble sludge and consequently its comparatively high polarity, this could be a cause of the precipitation. Since oils forming sludge and in particular insoluble sludge are high in aromatics, known to produce hydroxy acids on oxidation, and in view of Sachanen's[73] observation that these compounds are insoluble in petroleum oils, it appears likely that this could be the case. This effect is probably allied to the fact that on oxidation the amount of peptising constituents in the oil are increased, causing increased aggregation of the soluble sludge. If this insoluble sludge is associated with a greater amount of resins than the soluble sludge, this would account for the fact that its carbon residue were on the whole lower than those of the soluble sludge.

As the aromatic content of the oils increased it was found that, the amount of total sludge produced increased. This can be explained on the basis of Taat's[85] hypothesis that sludge is produced from the condensation of aromatic hydroxyl compounds and carbonyl compounds. With low aromatic oils these aromatic hydroxyl compounds would not be produced in sufficient amounts to give rise to any appreciable quantity of sludge. As the aromatic content of the oils increases the quantity of hydroxyl compounds produced would also increase and give rise to an increasing amount of sludge. Again as the aromatic content increases further the amount of aromatic hydroxyl compounds would become greater than the amount of carbonyl compounds available for reaction and this would then result in an excess of them being present in the soluble sludge. As a result of the build up of these compounds the soluble sludge would then become insoluble and precipitation as insoluble sludge would occur.

The similarity of the process of formation of resins and sludge in all three oils was substantiated by the similarity in properties of the resins and sludge from all three oils. This was particularly noticeable in regard to the contribution to viscosity increase per gramme of oxidised material, when it was found that the contribution of the resins was approximately constant with oxidation time and was similar for all three oils. The same effect was noted with the soluble sludge, although this was more liable to variation. It was also found that the carbon residues approached constant values which were similar for soluble sludge from Oils 2 and 3.

Further work of interest would be the oxidation, recovery and re-oxidation of a high aromatic oil for several periods of up to 24 hours, until complete breakdown of the oil is achieved. Analysis of sludges, resins and the carbon distribution of the recovered oils should throw some interesting light on the process of oxidation of the oil, the effect of the oxidation products on the oxidation rate and the chemical make up of the oil.

Of interest, also, would be the addition of certain model compounds to the oil before oxidation, to determine their effect on the formation of sludge. Such compounds would be those known to produce phenols, carbonyl compounds, and hydroxy acids on oxidation.

CHAPTER XI

METHODS OF ANALYSIS.

CHAPTER XI

METHODS OF ANALYSIS

REFRACTIVE INDEX

Measurement of refractive indices was made by an Abbe Refractometer, regularly checked with distilled water. All determinations were carried out at 20°C, ± 0.01°C, the instrument giving readings for the sodium D-line. Temperature control was achieved by pumping water from a thermostatically controlled bath, through the instrument.

DENSITY

Densities were measured using a simple U-tube pycnometer, the capacity of which was about 2 ml.

The pycnometer used was a modification of the Cup-type pycnometer recommended by van Ness and van Westen for the n-d-M method,[28] and described by Lipkin et al.[102] The essential difference was that the removable cups on each limb (for expansion or filling purposes) were omitted. In the present work filling and weighing the pycnometer was generally carried out at just under the measuring temperature of 20°C, and the ground glass top surfaces could easily cope with any droplets of oil forced out by the expansion.

No correction for buoyancy was applied to any weighing during calibration or density determination, but an apparent volume was calculated and used to obtain the apparent density.

This differed from the actual density by not more than three figures in the fourth decimal place. For greater accuracy application of an equation to give the true density in vacuo could be applied if required. This method was that recommended by Lipkin et al.[102]

The apparent volume of the pycnometer was found using fresh distilled water.

The clean, dry pycnometer was washed on the outside with acetone and weighed to the nearest 0.1 mg. It was then filled, by means of suction, with distilled water and suspended for 20 minutes in a water bath maintained at 20°C ± 0.01°C. Excess water was carefully removed from the top of the limbs by absorbent paper. The pycnometer was then removed from the bath, cleaned and dried on the outside and washed with acetone before weighing. The apparent volume was found by dividing the weight of water in air by the density of water at 20°C (0.99823 gm./ml.).

Oil densities were determined in a similar fashion. Apparent density was calculated by dividing the weight of oil in air by the apparent volume of the pycnometer. Addition of a correction factor C to the apparent density gave the true density in vacuo.

According/

According to Lipkin,[102]

$$C = 0.0012(1 - d_A)$$

where,

C = correction factor,

d_A = apparent density.

MOLECULAR WEIGHT

For the determination of molecular weights for use in the n-d-M analysis van Ness and van Westen[28] have recommended the ebullioscopic method as being more reliable than the cryoscopic one. Under ideal conditions the molecular weight of a solute in any chosen solvent is related to the rise in boiling point by the following equation:

$$M = \frac{K.W}{T}$$

where,

M = molecular weight of solute.

W = weight of solute.

T = elevation of boiling point.

K = constant whose value depends on the apparatus, nature and amount of solvent.

In practice, however, ideal conditions are only achieved at infinite dilution and as a result calculated molecular weights can vary with the concentration of the solute. Consequently the molecular weight at infinite dilution is normally calculated by plotting apparent molecular weight against concentration and extrapolating to zero concentration.

The apparatus normally used for the determination is an ebullioscope, consisting of a Cottrell vapour lift pump, provided with means of heating, solute addition and direct measurement of the boiling point of the solution by means of a Beckmann thermometer.

With this method, however, the time required for initial warm up and stabilisation of the Beckmann thermometer is rather long and for this reason Davies, Phillpotts and Swanson[103] studied ways and means to speed up the ebullioscopic method. Their efforts culminated in a method in which the Beckmann thermometer is replaced by a thermistor sensing element of low thermal capacity, and changes in resistance measured on a sensitive Wheatstone bridge. The apparatus used in this case was manufactured by Gallencamp and Co. and embodies the same basic principles although the experimental set up is rather different having been modified and made more compact.

The apparatus consists of an electrically heated block, fitted with a draught shield, used for heating a modified Cottrell pump. The ebulliometer vessel has provision for a thermistorised rapid response sensing element and a cold finger condenser. A Wheatstone bridge with a built in galvanometer and internal batteries is used for detecting resistance changes.

Initially the apparatus was used in its original form with the following method of operation:

The ebulliometer vessel was washed with benzene and then dried in a drying chamber. 10 ml. of benzene measured at 20°C. were pipetted into the flask and the apparatus assembled. The control dial on the heating block was set at a predetermined value and the condenser water turned on to an approximately known and steady rate. After equilibrium was reached the Wheatstone bridge was balanced and the resistance of the boiling solvent noted. Solute was then added by removing the cold finger condenser and adding solids as weighed pellets and liquids from a weighed pipette. The cold finger condenser was then replaced and after stabilisation the new resistance noted. This procedure of solute addition was repeated several times and the constants at each concentration calculated from the following equation:

$$K = \frac{R.M}{W}$$

where, K = constant depending upon the apparatus, nature and quantity of solvent.

W = weight of solute added.

M = molecular weight of solute added.

R = resistance change dependant upon the molecular weight and quantity of solute.

Now when the cold finger condenser is raised for the addition of solute, the benzene vapour in the vessel rises and condenses on the receiving arm of the condenser. When the condenser is replaced some of this solvent remains in the arm and this "hold up" reduces the effective amount of solvent in the vessel and thus alters the actual concentration of solute. This "hold up" is not constant and varies from addition to addition with the result that the normal concentration/constant or molecular weight effect is not met with but a spread of results is obtained which must be averaged to obtain the best result. Thus when determining molecular weights an average constant and an average molecular weight have to be calculated, both of which according to Mair[104] entail possible sources of error.

To overcome this defect it is obviously desirable to produce a constant "hold up" and this was achieved by dispensing with the cold finger condenser and replacing it by permanently fixing a Leibig type condenser to the ebulliometer vessel. The top of the condenser was fitted with a "Quickfit" socket and an extended "Quickfit" cone and socket made into a bottle used for the weighing and addition of the liquid solute (Fig. 38). The results obtained by this means showed a greater consistency and the values of constants and molecular weights enabled to be extrapolated to infinite dilution. Figures 39 and 40 show the comparative results obtained by the different methods. It can be seen that the

MODIFIED EBULLIOSCOPE

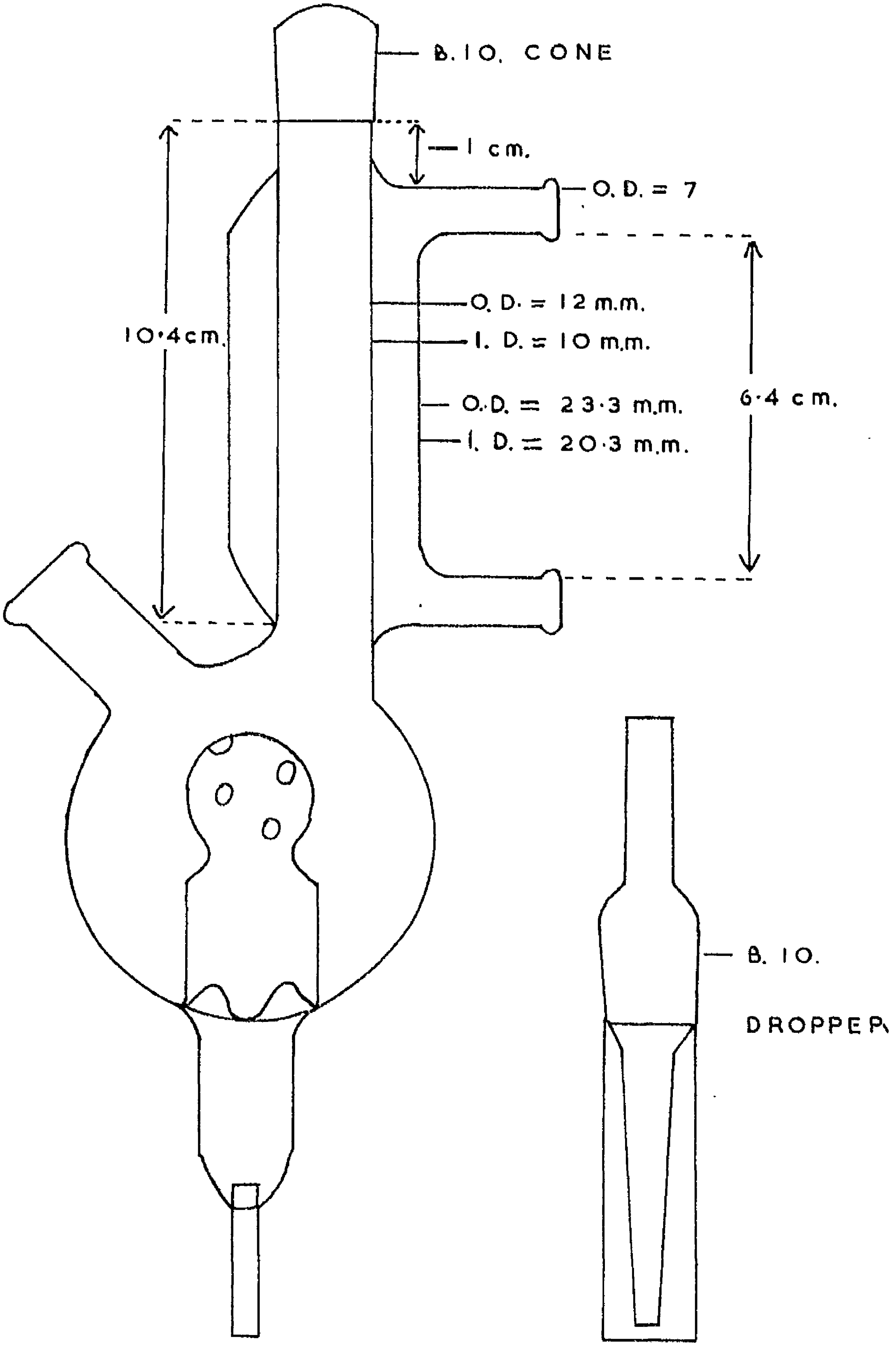
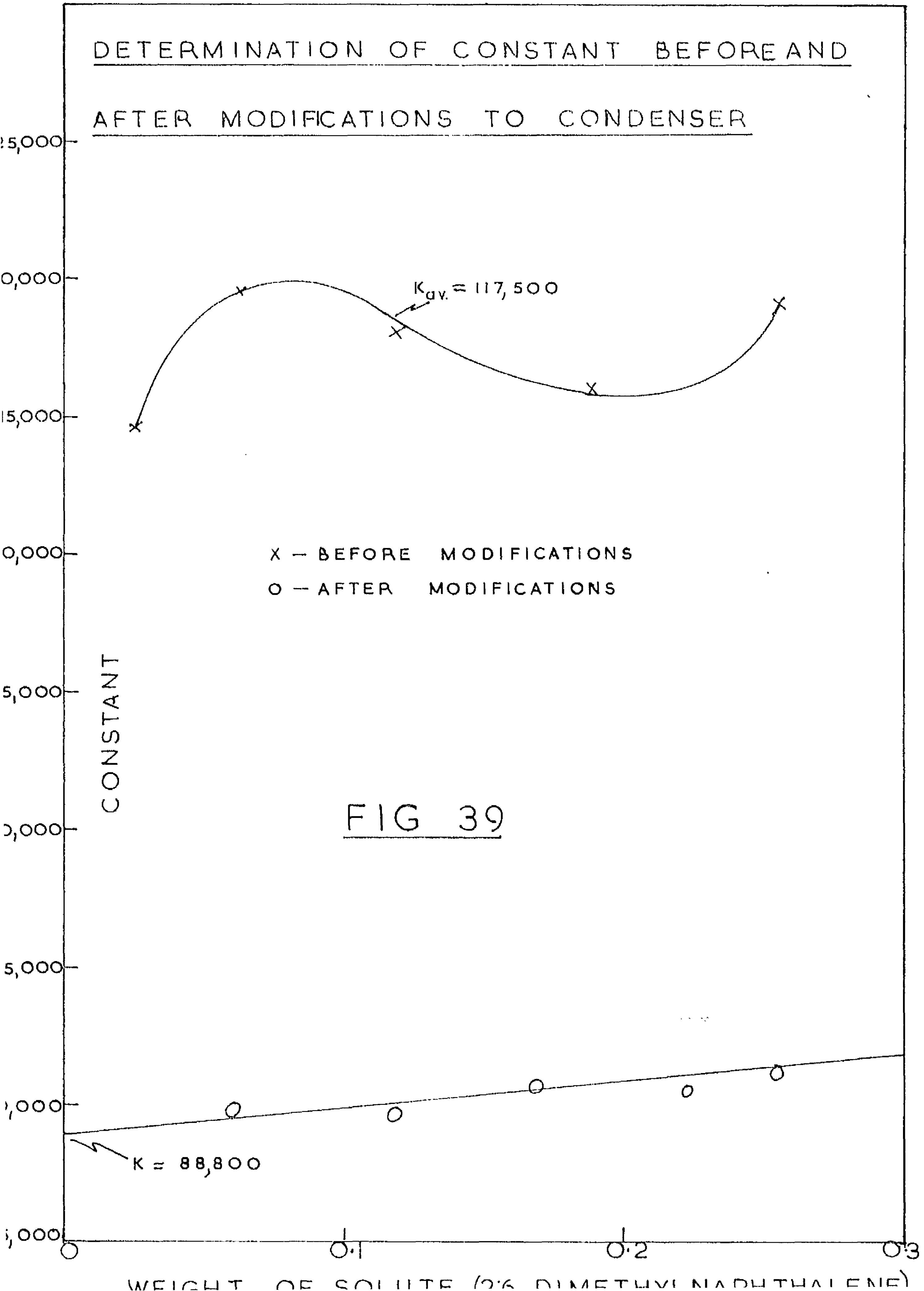
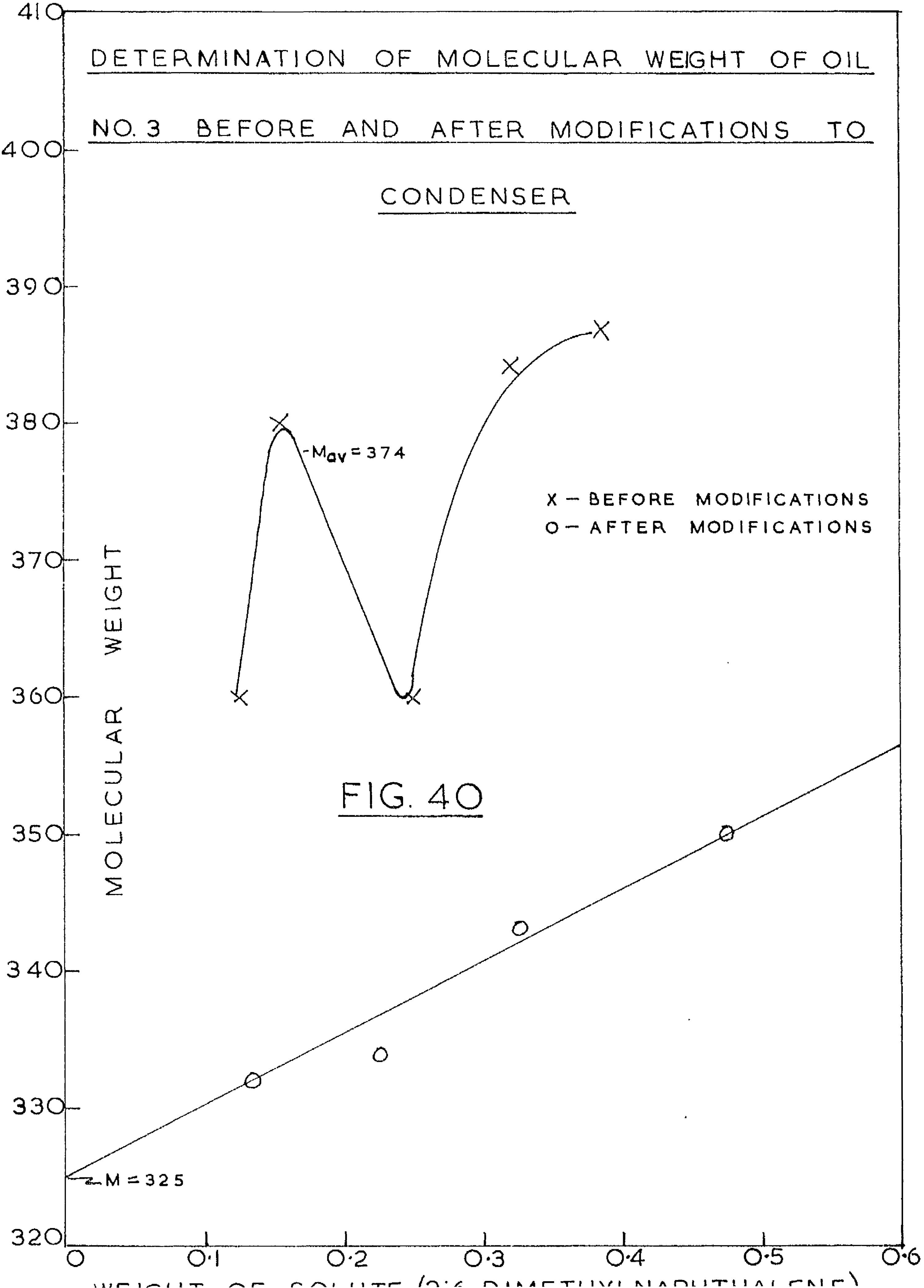


FIG. 38



DETERMINATION OF CONSTANT BEFORE AND AFTER MODIFICATIONS TO CONDENSER

FIG 39



DETERMINATION OF MOLECULAR WEIGHT OF OIL NO. 3 BEFORE AND AFTER MODIFICATIONS TO CONDENSER

FIG. 40

values after modifications are much lower indicating the extent of error when values cannot be extrapolated to infinite dilution.

van Ness and van Weston[28] give a formula for the correction of ebullioscopic constant for different atmospheric pressures. To determine if a comparable formula could be calculated for this type of apparatus, experiments were carried out at different states of atmospheric pressure using tetralin, 2:6 dimethylnaphthalene and acenanaphthene as solute. For the same atmospheric pressure these three materials gave close agreement for the value of the constant, but results over a range of atmospheric pressure showed no relationship between constant and atmospheric pressure, in fact the same pressure being obtained after a period of two to three days gave a different constant. However, if at each atmospheric pressure a constant and molecular weight determination was carried out close agreement was always obtained. For this reason, when carrying out a determination of molecular weight on an unknown an experimental constant was determined immediately before and this value used. By this means the molecular weights of several oils was carried out at different atmospheric pressures and the mean molecular weights determined. The results obtained are shown below in Table 11.

TABLE 11

Oil	Mean Molecular Weight	Mean Deviation
Pool	327	0.7%
Naphthenic	326	0.3%
Kuwait	471	1.1%
Venezuelan	498	1.0%

Results obtained by this method were compared with those obtained by the conventional ebulliometer and are shown below in Table 12.

TABLE 12

Oil	Thermistor Method	Beckmann Method
Pool	327	328
Naphthenic	326	410
Kuwait	471	538
Venezuelan	498	476

The formula for calculating molecular weight is:

$$M = \frac{K.W}{R}$$

and it can be seen that the larger the molecular weight the smaller is R for a given concentration of solute. Results obtained by the thermistor method are lower than those obtained using a Beckmann and this indicates a greater accuracy of the former method due to its ability to detect more accurately small changes in temperature.

OXYGEN CONTENT

The method used to determine the oxygen content of the oils was based on that described by Unterzaucher,[105] which determines the oxygen content of a compound directly and replaces the proximate analysis method which is subject to many sources of error. Owing to the complexity of the oxidised material present in an oxidised lubricating oil, certain details of procedure had to be modified before reliable and consistent results were obtained. In order to understand better the significance of these modifications a brief résumé of the Unterzaucher method is now given.

The substance to be examined is decomposed in a 10ml./minute stream of nitrogen and the resulting mixture of gases is passed over carbon at a constant temperature of 1120°C, whereby the available oxygen is converted into carbon monoxide. After removal of interfering gases by solid alkali the carbon monoxide is caused to react with iodine pentoxide at 120 - 140°C, carbon dioxide and iodine being formed. The iodine is absorbed in dilute sodium hydroxide solution and can be determined directly. The conversion factor is, however, increased six times by oxidising the iodine to iodic acid by means of bromine. The excess bromine is destroyed by formic acid and the iodic acid caused to react with potassium iodide. The liberated iodine is then determined by sodium thiosulphate solution.

It is finally found that:

1 mg. of $O_2 \equiv$ 7.5 ml. of 0.02N $Na_2S_2O_3$

All reagents used can be obtained commercially pure, except the iodine pentoxide. Unterzaucher purified this by crystallisation from strong nitric acid and then drying at 160 - 180°C in vacuo which also removed any free iodine present

MODIFICATIONS

Details of the apparatus used were similar to Unterzaucher's with the exception of the flow measurement. The bubble counter was replaced by a rotameter controlled by a needle valve to give more accurate control and the bubble counter placed at the end was used to check for gas leaks.

1. Reagents

The method used by Unterzaucher[105] for the purificatio of commercial iodine pentoxide was found unsatisfactory, the method of drying invariably producing free iodine even after repeated crystallisation.

The method of purification adopted, was repeated crystallisation in 60% nitric acid followed by washing with 65% acid. The iodine pentoxide was then filtered through a sintered glass crucible. After filtration, the crystals were washed with carbon tetrachloride to remove free iodine and again filtered. Drying was achieved by placing a sintered glass crucible containing anhydrone over the crucible containing the crystals and leaving under vacuum for several hours. Final drying was achieved by placing the crystals in the apparatus and running until a constant blank value of about 0.25 ml. of 0.02N $Na_2S_2O_3$ was obtained.

2. Procedure

The procedure described by Unterzaucher[105] was used for oxygen determinations on simple organic compounds such as benzoic acid and was found to be perfectly satisfactory. However, when it was used for oxidised oil samples inconsistent results were obtained which were suspected to be low since no appreciable difference was obtained in oxygen content for unoxidised and heavily oxidised oils. This was thought to be due to the complexity of the oxidised material preventing complete cracking, and modifications in the procedure were based on this premise.

a) Decomposition

With substances like benzoic acid a medium bunsen flame was all that was required to achieve cracking. However, examination of the platinum boat after an oil had been subjected to the same treatment revealed traces of oil still remaining. In order to remove this and ensure complete vaporisation a very strong bunsen flame was required for a slightly longer period of time.

b) Conversion to Carbon Monoxide

With increased heating, results improved slightly but were still not considered consistent enough. This was thought to be due to incomplete conversion in the carbon furnace at 1120°C. The temperature was therefore increased to 1140°C and the amount of carbon increased by addition of more to the end of the tube nearest the sample. This meant that carbon projected out of the furnace and at first even lower values of oxygen content were obtained. This was found to be due to the oil vapours condensing in the centre of the extra carbon and very strong heating was necessary to remove it completely. Results still showed no real increase in consistency and it was decided to reduce the nitrogen flow rate in order to increase the retention time in the carbon. Various flow rates were tried and the results shown in Fig. 41.

EFFECT OF NITROGEN FLOW RATE ON THE PERCENTAGE OXYGEN FOUND BY ANALYSIS

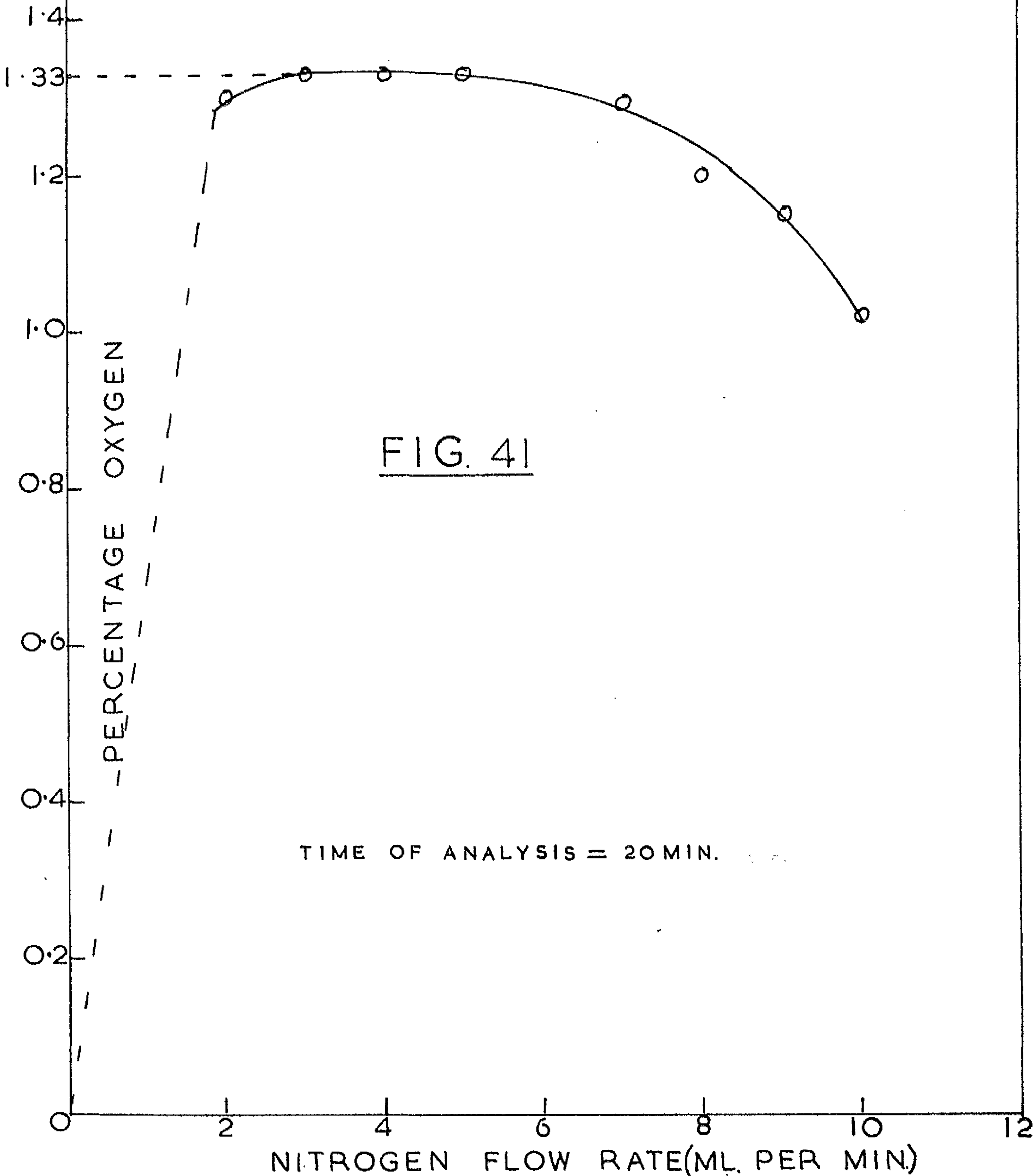


FIG. 41

TIME OF ANALYSIS = 20 MIN.

Results showed a marked improvement but it was thought that since the flow rate had been reduced the time of analysis should be increased in order to ensure complete removal of carbon monoxide and iodine from the system. The effect of increasing the time is shown in Fig. 42. Results showed a slight increase from 20 minutes (as recommended by Unterzaucher) to 30 minutes, and this time was chosen as the optimum.

Tests carried out using a flow rate of 4 ml./minute and a time of 30 minutes were then carried out repeatedly and a great degree of consistency obtained.

Occasional anomalous results were obtained, some high and some low. This was found to be due to the position of the sodium hydroxide tube. If this sloped towards the iodine pentoxide reaction tube then caustic soda ran back producing a high value. When the absorption tube sloped towards the bubbler the caustic ran out of the tube and absorption of liberated iodine was incomplete giving a low value. Great care was therefore taken to ensure that the absorption tube was always horizontal and no further trouble was encountered.

VISCOSITY

Kinematic viscosities were measured by miniature suspended level viscometers in a thermostatically controlled bath, by the procedure of I.P. 71 - "Viscosity-Kinematic in C.G.S. Units". The viscometers were calibrated according to British Standard Specification, B.S.188.

EFFECT OF TIME OF ANALYSIS ON THE PERCENTAGE OXYGEN FOUND BY ANALYSIS

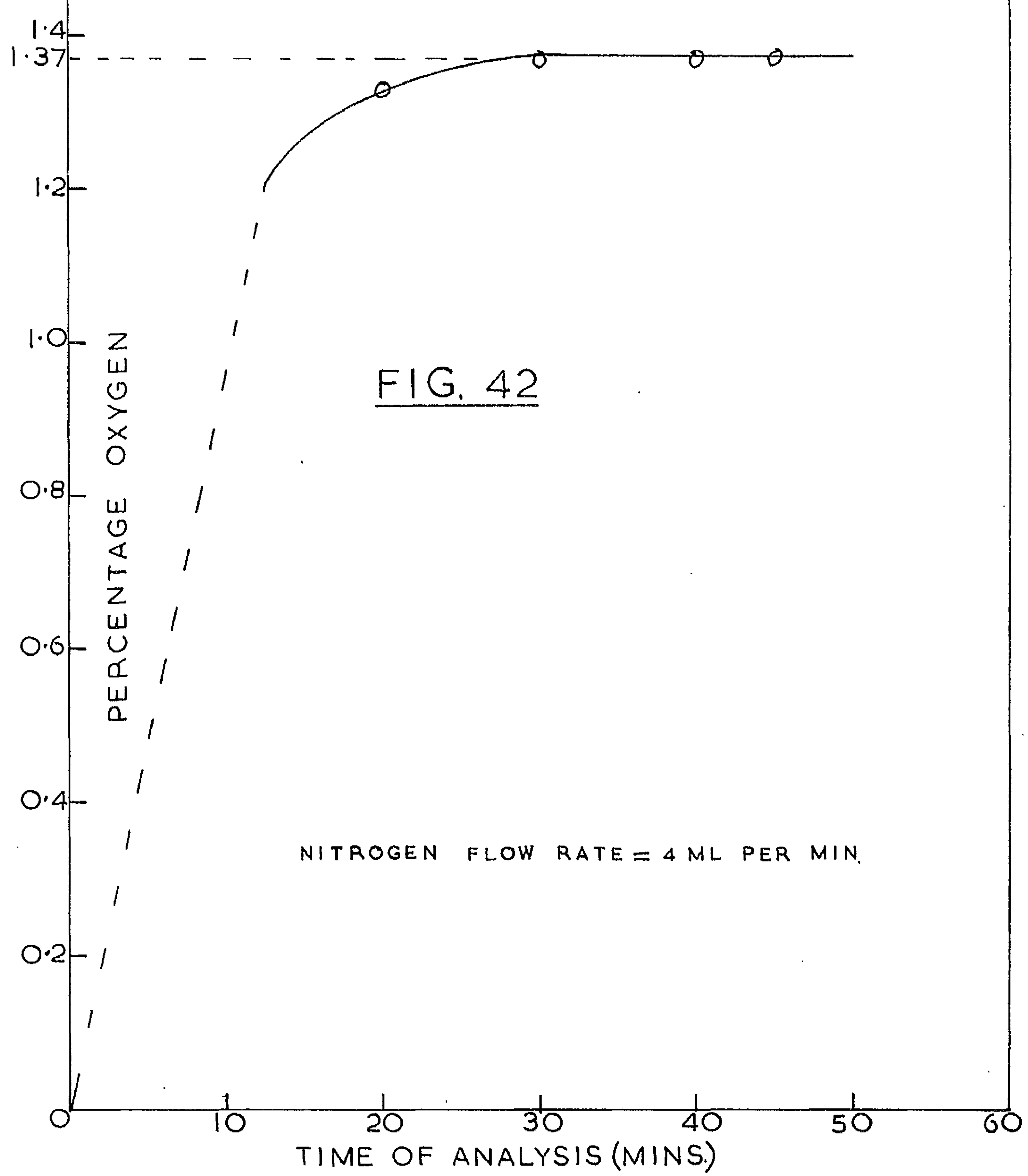


FIG. 42

RAMSBOTTOM CARBON RESIDUE

Determination of the Ramsbottom carbon residue was carried out according to I.P.14. This test measures the carbon residue remaining in a pyrex glass or silica bulb of specified dimensions, after vaporisation of 1 - 4 gm. of the oil at 550°C. The apparatus specially constructed to take two bulbs is shown in Fig. 43.

ACIDITY

The acidities of the oils were determined by a modification of the standard potentiometric method (A.S.T.M. D664). This method employs as solvent a 50:50 mixture of iso-propanol and benzene, but for the purposes of this work a 50:50 mixture of n-butanol and toluene was used as this was found to be a better solvent for the oxidised oils.

RAMSBOTTOM APPARATUS

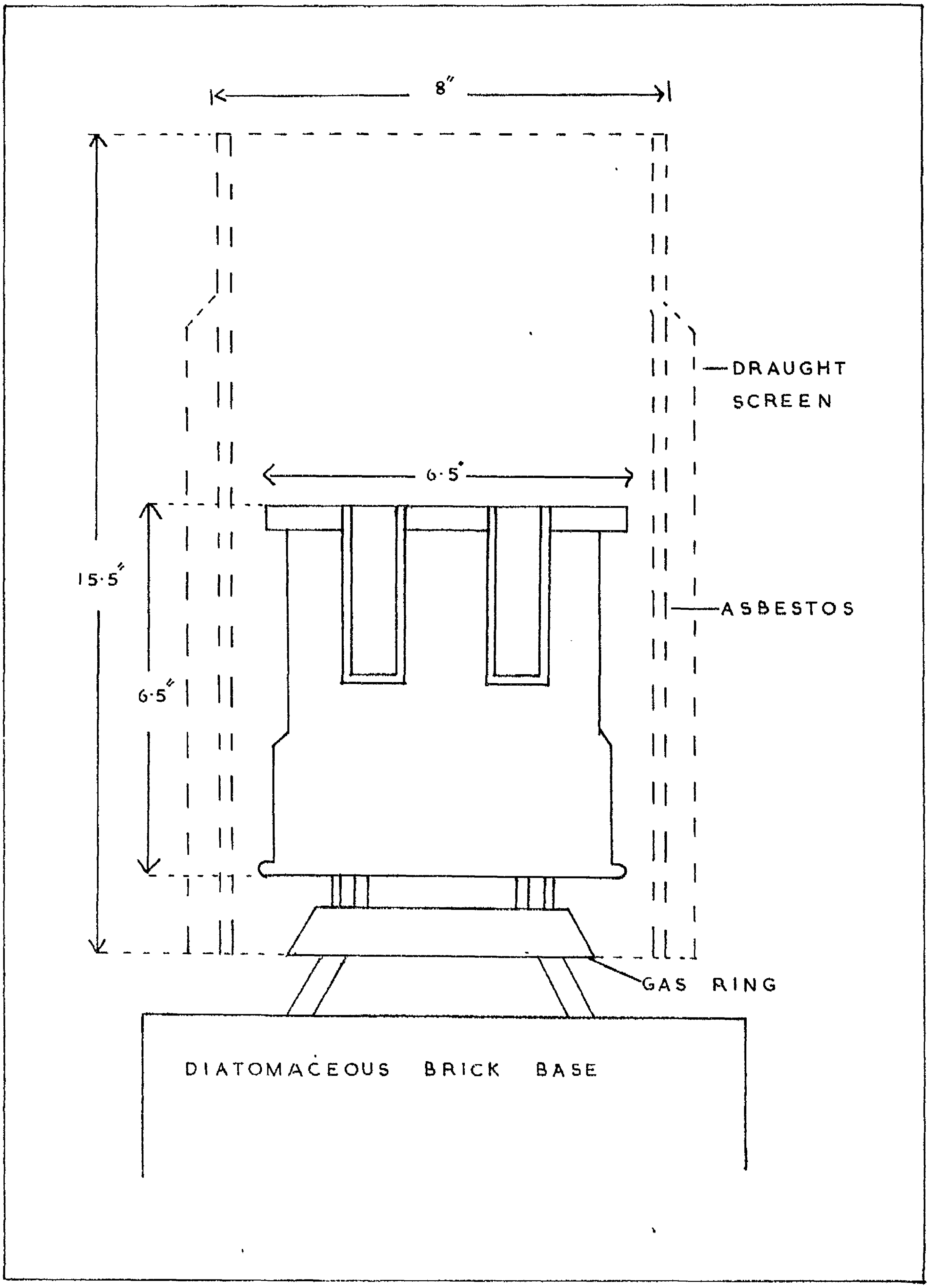


FIG. 43

BIBLIOGRAPHY

Bibliography

1. Sachanen, A.N. and Virobianz, R.A., Erdoel und Teer, 2, 170, (1933).

2. Fenske, M.R., Carnahan, F.L., Breston, J.N., Caser, A.H., Rescorla, A.R., Ind. Eng. Chem., 34, 638, (1942).

3. Von Fuchs, G.H., and Anderson, A.P., Ibid., 29, 319, (1937

4. Carnahan, F.L., Oil Gas J. (June 30, 1938).

5. Rossini, F.D., A.P.I. Proc. (November 1938).

6. Leslie, R.T., and Heuer, W.W., J. Research Bureau Standards, 21, 515, (1938).

7. Mair, B.J., Willingham, C.H., and Streiff, A.J., Ibid., 21, 536, (1938); 21, 565, (1938); 21, 581, (1938).

8. Bielenberg, W., Z. phys. Chem., 149, 42, (1930): 154, 364, (1931).

9. Vlugter, J.C., Waterman, H.I., and van Westen, H.A., J. Inst. Petrol. Tech., 18, 735, (1932).

10. Mueller, J., and Neyman-Pilat, E., Ibid., 23, 669, (1937).

11. Hood, A., Clerc, R.J., and O'Neal, M.J., J. Inst. Pet., 45, 168, (1959).

12. Robinson, E.A., Refiner, (March 1942).

13. Coats, C.E., and Best, A., J. Am. Chem. Soc., 27, 317, (1905).

14. Mabery, C.F., Am. Chem. J., 28, 165, (1902).

15. Mabery, C.F., Ibid., 33, 261, (1905).

16. Mabery, C.F., Ind. Eng. Chem., 15, 1233, (1923): 18, 814, (1926).

17. Mabery, C.F., and Buck, D.M., J. Am. Chem. Soc., 22, 553, (1900).

18. Mabery, C.F., and Mathews, J.H., Ibid., 30, 992, (1908).

19. Bestougeff, M.A., Erdoel und Teer, 7, 159, (1931).

20. Kurtz, S.S., and Lipkin, M.R., Ind. Eng. Chem., 33, 779, (1941).

21. Lipkin, M.R., and Kurtz, S.S., Detroit Meeting Am. Chem. Soc., 1940.

22. Grosse, A.V., Refiner, (April, 1939).

23. Mikeska, L.A., Ind. Eng. Chem., 28, 970, (1936).

24. Cosby, J.N., and Sutherland, L.H., A.P.I. Proc., November, 1941.

25. Kramer, G., and Spilker, A., Ber., 24, 2785, (1891).

26. Spilker, A., Petr. Z., 23, 448, (1927).

27. Mikeska, L.A., Smith, C.F., and Lieber, E., J. Organ. Chem., 2, 499, (1938).

28. Van Ness, K., and van Westen, H.A., "Aspects of the Constitution of Mineral Oils", Amsterdam: Elsevier Publishing Co. Inc. 1951.

29. Vlugter, J.C., Waterman, H.I., and van Westen, H.A., J. Inst. Petrol. Tech., 21, 661, (1935): 25, 678, (1939)

30. Bone, W.A., and Townend, D.T.A. "Flame and Combustion in Gases", London: Longmans Green and Co. 1927.

31. George, P., Rideal, E.K., and Robertson, A., Proc. Roy. Soc., 185, 288, (1946).

32. Bach, R., C.R. Acad. Sci. Paris. 124, 951, (1897).

33. Engler, C., and Wild, W., Ber., 30, 1669, (1897).

34. Callender, H.L., Engineering, 123, 147, (1927).

35. Ubbelohde, A.R., Proc. Roy. Soc., A152, 354, (1935).

36. Farmer, E.H., and Sandrelingham, A., J. Chem. Soc., 121, (1942).

37. Chavanne, G., and Bode, E., J. Am. Chem. Soc., 52, 1609, (1930).
Chavanne, G., Tock, H.N., and Roduta, F.L., Bull. Soc. Chim. Belg., 41, 630, (1932).

38. Stevens, H.N., J. Am. Chem. Soc., 48, 1824, 2920, (1926): 50, 2523, (1928).
Stevens, H.N., and Roduta, F.L., Ibid., 57, 2380, (1935).

39. George P., Rideal, E.K., and Robertson, A., Nature, 149, 601, (1942).

40. Larsen, R.G., and co-workers, Shell Development Co., Unpublished work.

41. Balsbaugh, J.C., and Oncoley, J.C., Ind. Eng. Chem., 31, 318, (1939).

42. Dornte, R.W., Ibid., 28, 26, (1936).

43. Denison, G.H., Ibid., 36, 477, (1944).

44. George, P., and Walsh. Faraday Society Discussion "Oxidation".

45. Twigg, G.H., Chem. Eng. Sci., Special Suppl., 5 - 16.

46. Dupont, P., and Chavanne, G., Bull. Soc. Chim. Belg., 42, 537, (1933).

47. Burwell, A.W., "Science of Petroleum", Vol. II, pp. 1028-32, London, Oxford University Press, 1938.

48. Fenske, M.R., Stevenson, C.E., Lawson, N.D., Herbolsheimer, G., and Koch, E.F., Ind. Eng. Chem., 33, 516, (1941).

49. Fenske, M.R., Stevenson, C.E., Rush, R.A., Lawson, N.D., Cannon, M.R., and Koch, E.F., Ibid., Anal. Ed., 13, 51, (1941).

50. Hoffman, J., and Boord, C.E., J. Am. Chem. Soc., 78, 4973, (1956).

51. Zuidema, H.H., "The Performance of Lubricating Oils", Reinhold Publishing Corporation, New York, 1952.

52. Larsen, R.G., Thorpe, R.E., and Armfield, F.A., Ind. Eng. Chem., 34, 183, (1942).

53. von Fuchs, G.H., and Diamond, H., Ibid., 34, 927, (1942).

54. Chernozhukov, N.I., and Krein, S.E., J. App. Chem. (U.S.S.R.) 10, 1435, (1937): Chem. Abstracts, 32, 1664, (1938).

55. Hock, H., and Lang, S., Ber., 75B, 300, 1051, (1942).

56. Booser, E.R., and Fenske, M.R., Ind. Eng. Chem., 44, 1850, (1952).

57. Dornte, R.W., and Ferguson, C.V., Ibid., 28, 863, (1936).

58. Dornte, R.W., Ferguson, C.V., and Haskins, C.P., Ibid., 28, 1342, (1936).

59. Hicks-Bruun, M.M., Ritz, B.L., Ledley, R.E., and Bruun, J.H., Ibid., 36, 562, (1944).

60. Clark, F.M., Ibid., 31, 327, (1939).

61. "Standard Methods for Testing Petroleum and its Products" London: Institute of Petroleum.

62. Dornte, R.W., Ind. Eng. Chem., 28, 26, (1936).

63. Rogers, T.H., and Shoemaker, B.H., Ibid. Anal. Ed., 6, 49, (1934).

64. Lamb, G.G., Loane, C.M., and Gaynor, J.W., Ibid., 13, 317, (1941).

65. Sligh, T.S., Proc. A.S.T.M., 21, 964, (1924).

66. C.R.C. Handbook, 1946.

67. Larsen, R.G., Armfield, F.A., and Whitney, G.M., Trans. Soc. Automot. Engrs., New York, 51, 316, (1943).

68. Larsen, R.G., and Armfield, F.A., Ind. Eng. Chem., 35, 581, (1943).

69. Brook, J.H.T., Matthews, J.B., and Taylor, R.P., J. Inst. Pet., 39, 454, (1953).

70. Garner, F.H., Kelly, C.I., and Taylor, J.L., Proc. of World Petrol. Congress, London, 2, 448, (1933).

71. Levin, H., and Towne, C.C., Ind. Eng. Chem. Anal. Ed., 11, 181, (1939).

72. Hall, F.W., Levin, H., and McMillan, W.A., Ibid., 11, 183, (1939).

73. Sachanen, A.N., "The Chemical Constituents of Petroleum", Reinhold Publishing Corporation, New York, 1945.

74. Haus, E., Oel and Kohle, 14, 299, 321, (1938).

75. Matthews, J.B., Thornton Research Centre, Shell Petroleum Co.Ltd., Private Communication.

76. Davis, L.L., Lincoln, B.H., Byrkit, G.D., and Jones, W.A., Ind. Eng. Chem., 33, 339, (1941).

77. Gibson, H., Ph.D. Thesis, Glasgow, 1960.

78. Smith, N.A.C., R.I. 2806, Bureau of Mines, Washington D.C., 1927.

79. Vassilieff, N.A., See Sachanen, "Crude Oils and Oil Products", page 279, Moscow, 1931.

80. Burwell, A.W., Ind. Eng. Chem., 26, 204, (1934).

81. Larsen, R.G., New York Meet. Am. Chem. Soc., Sept. 1944.

82. Nellensteyn, F.J., 11 Petroleum Congress, London, 1933.

83. Marcusson, J., Z. angew. Chem., 29, 345, (1916).

84. Haslam, R.T., and Frohlich, P.K., Ind. Eng. Chem., 19, 292, (1927).

85. Taat, W.J., Ph.D. Thesis, Delft: 1956.

86. Irving, R., and Thompson, C.N., J. Inst. Pet., 37, 67, (1951).

87. Sachanen, A.N., and Vassilieff, N.A., Z. Petr., 27, 1618, (1927).

88. Pfeiffer, J.P., and Saal, P.N.J., J. Phys. Chem., 44, 138, (1940).

89. Swanson, J.M., Ibid., 46, 141, (1942).

90. Katz, D.L., and Beu, K.E., Ind. Eng. Chem., 37, 1954, (1945).

91. Poell, H., Erdoel und Teer, 7, 350, 366, (1931).

92. Noack, K., Oel Koehle Erdoel Teer, 13, 959, (1937).

93. Suide, H., Ibid, 13, 201, 225, (1937).

94. Marcusson, J., Burchartz, H., and Wilke, P., "Die Naturlichen und Kunstlichen Asphalte", 2nd ed. rev., Leipzig, Wilhelm Engelman, 1931.

95. Schindler, H., and Bondi, A., Z. Petr., 34, No. 10, Motorenbetreib und Maschinen-Schmierung, 11, No. 3, 2-6, 1938.

96. Cornelissen, J., and Waterman, H.I., Chem. Eng. Sci., 4, 238, (1955).

97. Cornelissen, J., and Waterman, H.I., J. Inst. Pet., 42, 62, (1956).

98. Waterman, H.I., Leenderste, J.J., and Palm, E.C.H., Ibid, 23, 483, (1937).

99. Hibbard, R.R., Ind. Eng. Chem., 41, 197, (1947).

100. Gruse, W.A., and Livingstone, C.J., J. Inst. Pet., 26, 413, (1940).

101. Faust, J., Oil and Gas J., (Jan. 20, 1944).

102. Lipkin, M.R., Mills, I.W., Martin, C.C., and Harvey, W.T. Anal. Chem., 21, 504, (1949).

103. Davies, A.J., Phillpotts, A.E., and Swanson, B.W., Proc. Fourth World Petrol. Congr., 5, 351, (1955).

104. Mair, B.J., Nat. Bur. Standards, 14, 345, (1935).

105. Unterzaucher, J., The Analyst, 77, 584, (1952).