THE OXIDATION OF MINERAL LUBRICATING OIL

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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May 1960

ACKNOWLEDGEMENT

The author is indebted to Professor P. D. Ritchie of the Department of Chemical Technology, The Royal College of Science and Technology, Glasgow, for providing the opportunity and necessary facilities for this work, and to Dr. William Gibb for initiating and supervising the investigation.

Acknowledgement is also made to Mr. A. Clunie and Staff of the Departmental Workshop for assistance in the fabrication of apparatus.

May, 1960.

PUBLICATION

Part of the work presented in Chapter VII of this thesis has already been published in the following paper:

'Determination of Acidity in Dark Lubricating Oils' - Gibb, W., and Gibson, H., Petroleum, Lond., 22 (7), 257, (1959).

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CHAPTER I

Lubricating Oil Oxidation Tests.

Purpose of Research.

CHAPTER I

INTRODUCTION

I.1. Lubricating oils for most applications today are generally prepared from petroleum products, and, although many different specifications have to be met, one common essential is that they should suffer a minimum of deterioration during service.

The life of an oil in an internal combustion engine can be limited by contamination due to extraneous material such as dust, water, products of incomplete combustion of the fuel, iron oxide resulting from wear of the engine and lead oxide or salts resulting from the combustion of leaded gasoline. Such contamination naturally changes the lubricating characteristics of the oil but can be outweighed in effect by changes which result from oxidative modification of the oil molecules themselves.

Conditions in an engine are unfortunately those which will promote lubricating oil oxidation, viz. splashing of hot oil and subsequent intimate contact of thin films of this oil with air. This type of deterioration is characterised by viscosity increase, acid and sludge formation, and produces in an engine,bearing corrosion, lacquer formation, piston ring sticking, blockage of oil channels, etc. With advancement of engine design the conditions which oils have to withstand are becoming more severe.

I.2. Lubricating Oil Oxidation Tests.

Over the years a number of test methods have been introduced for the purpose of estimating the probable behaviour of lubricating oils under conditions of oxidation. Small scale laboratory tests give useful information but are limited in their scope. Engine tests which simulate service conditions are of more practical value but provide very little fundamental information.

Oxidation stability of lubricating oils is normally examined by bringing the hot oil into contact with air or oxygen, generally by bubbling the gas through the oil.

Many variations of this method have been used but only one has been adopted for standard use in this country. This is the Institute of Petroleum test for lubricating oils - I P 48[1], which was originally the British Air Ministry test for aviation engine oils. Garner and co-workers[2] examined the test from the point of view of reproducibility of results and the effect of variations in the specified conditions.

In this test air at 15 litres / hour is bubbled through oil maintained at 200°C. The stability of the oil is measured by the increase of carbon residue (Ramsbottom) and the kinematic viscosity ratio after 12 hours oxidation.

The Indiana oxidation test[3] is similar in principle. Air at 10 litres / hour is blown through 300 ml. of oil maintained at 341°F. Precipitable sludge is taken as the criterion of deterioration and periods of time are measured for the formation of (i) 10 mg. sludge per 10 g. oil and (ii) 100 mg. sludge per 10 g. oil. Viscosities may also be measured.

A modified Indiana test has been developed for oils containing additives - the 'Indiana stirring oxidation test for lubricating oils'[4]. High speed stirring provides aeration of a 250 ml. sample of oil maintained at 330°F., in the presence of copper and iron catalysts. Sludge and acidity are measured every 24 hours for a maximum of 72 hours and are taken as measures of the extent of oxidation.

In the Sligh oxidation test[5] an atmosphere of oxygen surrounds a small static oil sample kept at 200°C for two and a half hours. Asphaltic material produced is taken as the measure of oxidation, and is reported as the 'Sligh number'.

Many workers have used a technique for determining oil stability in which the oxygen absorbed by the oil is continuously recorded. Such an apparatus with oxygen bubbling through a hot oil sample in a closed circuit was first described by Dornte[6]. Low molecular weight gases and vapours are removed by an absorption and condensing system and may be estimated. The shape of the oxygen absorption versus time curve is often taken as a characteristic of the sample.

Tests also exist for measurement of the defects of an oxidised oil, and measure bearing corrosion, wear, sludge and lacquer deposition etc. The Existant Corrosivity (E.C.) test[7] is a bearing corrosion test in which no significant oxidation of the oil takes place during the test. A bearing metal specimen is immersed in 20 g. of oil at 156°C. for 20 minutes with air agitation at the rate of 6.3 ml. per minute. On the other hand the Underwood[8] and Thrust[9] tests are examples of bearing corrosion tests in which the oil is oxidised during the test period.

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. Recently radio-active piston rings have enabled wear to be estimated by determining the radio-activity of the lubricant.

A great many engine tests have been devised and many of these tests have been standardised by the Co-ordinating Research Council of America[10]. Despite, however, the large number available, little information is given in the literature on the correlation of oxidation tests with engine performance. It is accepted that some tests show little correlation with performance. Larsen, Armfield and Whitney[11,12] showed, in fact, that three oils could be placed in any of the six possible orders of merit by variation of the catalyst in an oxidation test. Matthews and co-workers[13], however, have shown that an oxidation test can provide a good indication of how an oil will perform in an engine test, but stress that the catalytic conditions used in the oxidation test should be as close as possible to those existing in the engine.

There are two important prerequisites for ultimate success in the study of the deterioration of lubricating oils at the temperatures to which they are subjected in the internal combustion engine. These are respectively, a knowledge of the chemical structure of the hydrocarbon molecules which constitute the oil, and an understanding of the mechanism of oxidation of pure hydrocarbons under those conditions. Neither of these goals has as yet been reached. Owing to the difficulty in separating different molecules of closely similar high molecular weight and physical properties, the structure of the oil is normally characterised by a number of empirical and semi-analytical techniques[14] and reported in terms of an average molecule. While the oxidation of lower molecular weight pure hydrocarbons can be studied under controlled laboratory conditions, extension of the findings to lubricating oils is made difficult by the lack of availability of pure hydrocarbons of sufficiently high molecular weight; and the knowledge that in a complicated mixture of hydrocarbons the oxidation products of one molecule will influence the oxidation of another.

I.3. Purpose of Research.

Acids and sludges are generally considered to be the most undesirable products of oxidation in lubricating oils. It is therefore surprising that the standard test for lubricating oils in this country, the Institute of Petroleum test[1], should neglect both. Another significant oil characteristic not taken into account by the standard test is the rate of oxygen absorption.

In view of this it is proposed to study, generally, the formation of sludge and acid and the absorption of oxygen, by oils oxidised under the conditions of the standard oxidation test.

At the outset a choice of methods will be made for determination of sludge and acid. Many methods of sludge measurement have been devised but not all give realistic figures for oil-soluble sludge, while colour-indicator acidity methods usually present difficulties with dark oil solutions.

The purpose of this investigation can be summarised as follows.

(1) An examination of the sludge and acid produced and the oxygen absorbed, on oxidation of lubricating oil fractions under the conditions of the Institute of Petroleum test.

(2) The relationship between sludge and acid produced and oxygen absorbed on the one hand, and oil composition on the other.

(3) The effect of changes in the standard Institute of Petroleum test conditions on the sludge and acid produced and on the oxygen absorbed, these changes being

(a) variation in the rate of air flow
(b) variation in oxidation temperature.

CHAPTER II

Molecular Structure of Lubricating Oils.

CHAPTER II

INTRODUCTION

Molecular Structure of Lubricating Oils.

Mineral lubricating oils are derived from crude petroleum, which consists of a complex mixture of hydrocarbons, plus small amounts of other organic compounds, chiefly those containing oxygen, sulphur or nitrogen. Hydrocarbons in the crude petroleum may vary in molecular size from methane to compounds of very high molecular weight and low volatility. Variation in structure is from normal paraffins to condensed-ring aromatic naphthenic compounds with alkyl side chains.

Distribution of molecules by size and type, and therefore the amount of potential lubricating oil present, varies widely with the source of the crude. Some crudes consist predominantly of gasoline and naphthas, others of asphalt, while still others contain chiefly lubricating oil distillate and residue, with gasoline, naphthas, gas oil, wax and asphalt occurring in varying amounts.

Lubricating oil hydrocarbons may be classified in three groups, viz.

I. Paraffins, or saturated hydrocarbons with straight or branched chains.

II. Naphthenes; saturated cyclic hydrocarbons of one or more rings which may have paraffin side chains.

III. Aromatics; hydrocarbons containing one or more aromatic nuclei which may have naphthene rings and/or paraffinic side chains.

The complex nature and high molecular weight of lubricating oil fractions mean that separation into pure compounds is almost impossible. Rossini and others[15] made an extensive study of the lubricating oil fraction of a Mid-Continent crude. Sixteen narrow distillation cuts were used and separations made by various methods including vacuum distillation, crystallisation, extraction and adsorption on silica gel. On analysis of the individual fractions the following conclusions regarding distribution of molecules were made:

(a) 43-51% of 1, 2 or 3 naphthenic rings with paraffinic side chains.

(b) 8.3% of 1, 2 or 3 naphthenic rings and 1 aromatic ring with paraffinic side chains.

(c) 8.1% of 2 naphthenic rings and 2 condensed aromatic rings with paraffinic side chains.

(d) 6.6% of 1 naphthenic ring and 3 condensed aromatic rings with paraffinic side chains

(e) 18-20% of normal paraffins plus possibly some isoparaffins.

(f) 8% asphaltic constituents.

The absence of a significant amount of isoparaffins was interesting since isoparaffins occur in lighter petroleum fractions. Earlier Kyropoulos[16] had compared the refractive indices and specific gravities of isoparaffins known at that time, with those of Pennsylvanian lubricating oils and concluded that these oils were composed largely of isoparaffins. Bielenberg[17] and Vlugter, Waterman and van Westen[18] showed that Kyropoulos' conclusions were erroneous and that Pennsylvanian lubricating oils were composed of cyclic hydrocarbons with long paraffinic side chains.

Mair and Willingham[19] showed that none of the narrow wax-free lubricating fractions produced from a Ponca City crude oil was richer in hydrogen than C_nH_{2n}, corresponding to monocyclic naphthenes. Any fraction consisting of bicyclic naphthenes and isoparaffins of the composition C_nH_{2n} should be easily separated by solvent treatment into a paraffin raffinate and a naphthenic extract. Thus the authors concluded that 'no appreciable percentage of isoparaffins exists in these fractions'.

Müller and Neyman-Pilat[20] made an extensive study of the composition of two paraffinic lubricating oils, one of Polish and the other of Pennsylvanian origin. Both oils were shown to be virtually free from isoparaffins.

The presence of isoparaffins in lighter Pennsylvanian oils was confirmed by Haak and van Nes[21] who found that a gas oil fraction contained about 17% of isoparaffins. The isoparaffin question is therefore still an open one, although it is now generally accepted that the percentage of isoparaffins in most lubricating oils is either negligible or does not exceed a few per cent at most.

The absence of unsaturated compounds in straight-run gasolines and gas oils suggests that these compounds are unlikely to be present in lubricating oil fractions. However, owing to the comparatively high iodine numbers of some oils, the possibility of their presence can not be dismissed 'a priori'. Brooks and Humphrey[22] have pointed out that a large percentage of unsaturated hydrocarbons was suggested by the iodine numbers of refined lubricating oils; citing the example of a medium heavy lubricating oil where an iodine number of 12 indicated roughly a mono-olefin content of 20%. However, the addition iodine numbers of lubricating oils are usually very small unless the distillation has produced some decomposition. Sachanen and Virobianz[23] showed that the bromine number of lubricating fractions produced in high vacuum from various crudes varied from 0.2 to 5.0. The highest addition numbers corresponded to unstable, high-boiling fractions of asphaltic crude oils which are appreciably decomposed at temperatures higher than 350°C.

In view of this the prevailing opinion, until recently, was that little or no olefins were present in crude oils and in straight-run distillates. A recent investigation by Fred and Putscher[24] proved that Pennsylvanian crudes contained fair proportions of olefins. This point was also further investigated by Haak and van Nes[21]. The fact remains, though, that Pennsylvanian crude probably holds an exceptional position and that olefins are present in crudes only in a few special cases.

CHAPTER III

Hydrocarbon Oxidation.

Oxidation of Lubricating Oil Fractions.

Oxidation Rates.

Kinetics of Oxidation.

CHAPTER III

INTRODUCTION

III.1. Hydrocarbon Oxidation.

In the past much study has been devoted to low temperature, liquid phase oxidation of hydrocarbons, both from the point of view of deterioration of lubricating oils in service and otherwise. Interest has been aroused in the mechanism of the oxidation reactions and the kinetics have naturally received much attention. Reviews on hydrocarbon oxidation have been published, covering many aspects of the subject.[25,26,27,28,29,30]

The difficulty of isolating primary oxidation products was the main barrier in early studies of hydrocarbon oxidation. Bone[31] assumed alcohols to be intermediate products in the oxidation of a simple hydrocarbon.

$$CH_4 \xrightarrow{O_2} CH_3OH \xrightarrow{O_2} CH_2(OH)_2 \rightleftharpoons CH_2O + H_2O$$

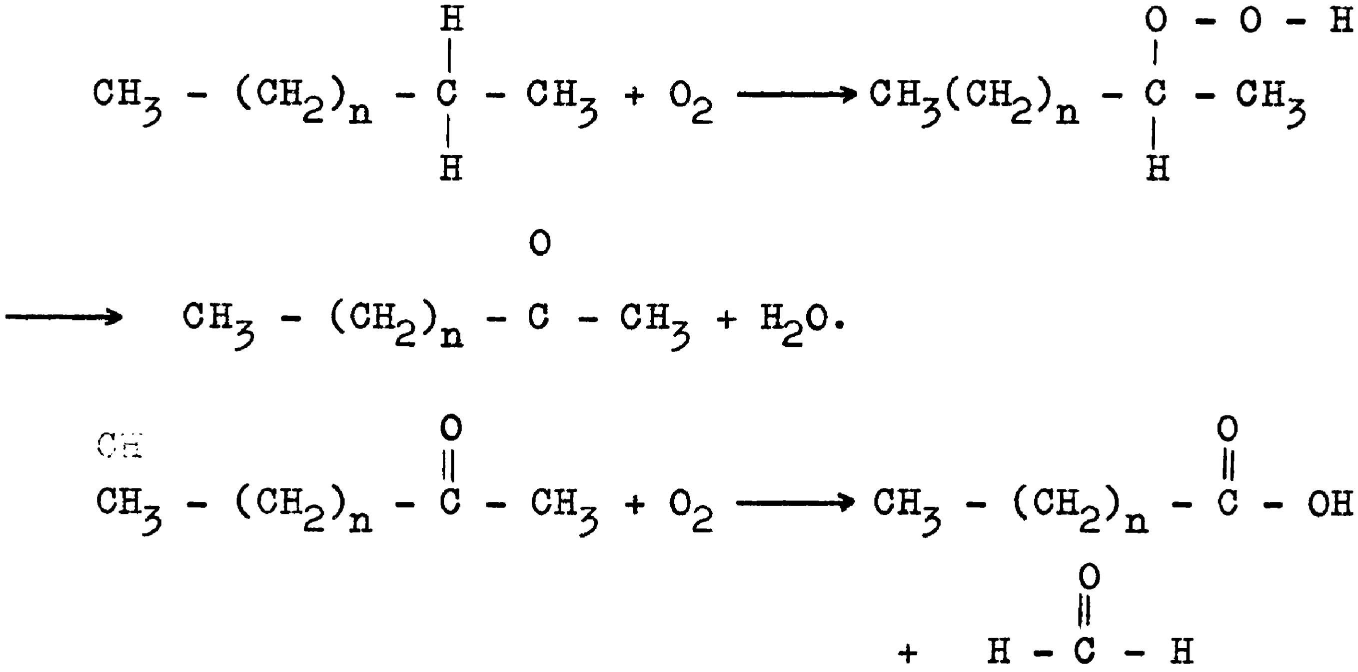
Stephens[32] maintained that this 'hydroxylation' theory proposed by Bone for high temperature oxidation in the gaseous phase was not valid for oxidation at lower temperatures in the liquid phase. Later work endorsed this view and modern theory is now based on the assumption that a hydroperoxide is the primary reaction product of hydrocarbon oxidation. Bach[33] and Engler and Wild[34] were the first to propose this mechanism which Callender[35] and Ubbelohde[36] later developed.

Chavanne and co-workers[37,38,39] studied the oxidation of some paraffins and naphthenes. For the oxidation of n-decane, n-nonane and n-octane at 120°C the main products were found to be methyl octyl-, methyl heptyl-, and methyl hexyl-ketones respectively, together with a series of carboxylic acids ranging from formic to acids containing one less carbon than the original hydrocarbon. These results indicated that a beta carbon atom was attacked primarily and agreed with the opinions of Burwell[40] who maintained that in low temperature oxidation the beta carbon atom was primarily involved, the gamma carbon next and so on towards the centre of the molecule.

Hydroperoxides were the main products encountered by George, Rideal and Robertson[41] when they oxidised high molecular weight paraffins and alkyl benzenes at 100 to 120°C. In the case of the paraffins the hydroperoxides decomposed to give ketones in very high yield. Larsen and co-workers[42] also found peroxides in high concentration in the early stages of the oxidation of decalin at 110°C. Similar findings have been reported by Balsbaugh and Oncley[43] in the case of hydrocarbons oxidised at 30 to 100°C, and by Dornte[6] and Denison[44] in the oxidation of white oils.

(a) The mechanism of the oxidation of paraffins.

From the above evidence Zuidema has suggested that the mechanism of low temperature, liquid phase oxidation of a paraffin may be as follows:



$$CH_3 - (CH_2)_n - \overset{H}{\underset{H}{C}} - CH_3 + O_2 \longrightarrow CH_3(CH_2)_n - \overset{O - O - H}{\underset{H}{C}} - CH_3$$

$$\longrightarrow CH_3 - (CH_2)_n - \overset{O}{C} - CH_3 + H_2O.$$

$$CH_3 - (CH_2)_n - \overset{O}{\overset{\|}{C}} - CH_3 + O_2 \longrightarrow CH_3 - (CH_2)_n - \overset{O}{\overset{\|}{C}} - OH + H - \overset{O}{\overset{\|}{C}} - H$$

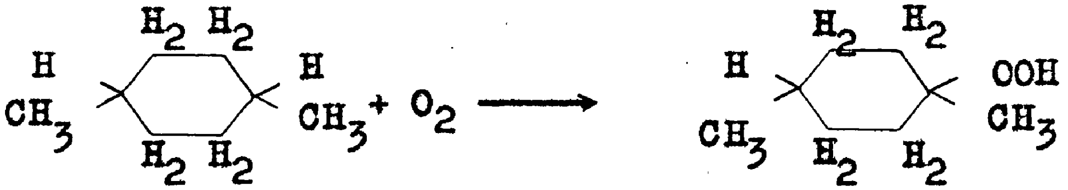
There would also be some attack on the gamma rather than the beta carbon to give the ethyl ketone, with the subsequent production of a carboxylic acid smaller by one carbon atom, and acetaldehyde. Continuation of the reaction could occur by attack of the acid at other carbon atoms. Acids, carbon dioxide and water could be produced by oxidation of the aldehydes. Alcohols could be produced by reduction of a hydroperoxide, and esters formed by condensation of an acid and an alcohol.

(b) The mechanism of the oxidation of naphthenes.

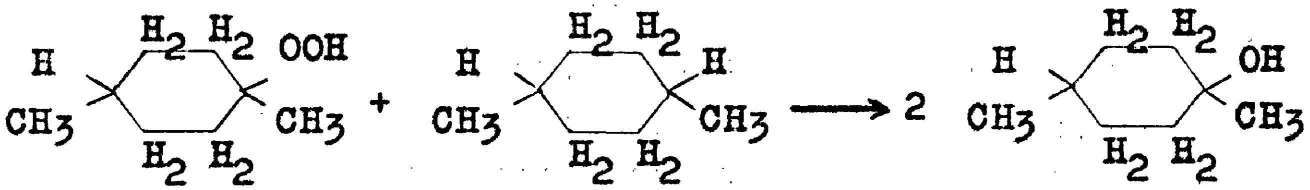
Chavanne and Bode[37] studied in great detail the oxidation of 1,4-dimethylcyclohexane at 100°C and Dupont and Chavanne[39] oxidised three cyclopentane derivatives.

In the case of the substituted cyclohexane the main product was dimethylcyclohexanol, with water, carbon dioxide, β-methyl-δ-acetylvaleric acid, acetic acid, β-methylvaleric acid, dimethylcyclohexanediol and acetonylacetone also being formed. Small amounts of hydrogen, carbon monoxide, methane, ethane and formic acid were also present.

The mechanism postulated from the above evidence is attack at a tertiary carbon atom to give a hydroperoxide as in the case of paraffin oxidation:

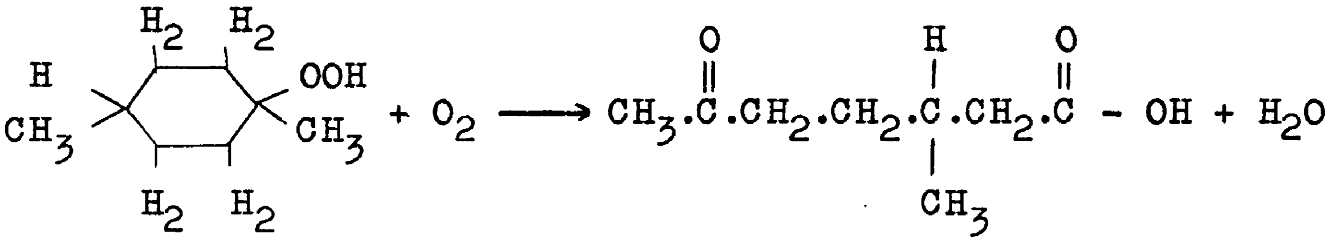


This appears to decompose, through reduction, to the alcohol:



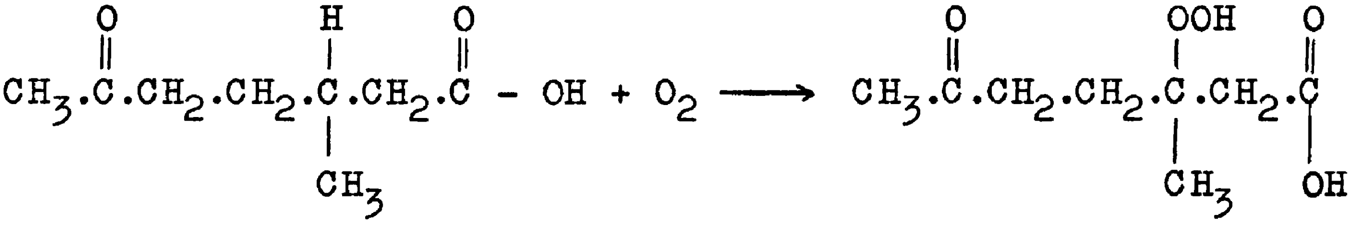
This reduction mechanism would appear here to be the main one, whereas with the paraffin hydroperoxide it was of secondary importance. Formation of the diol can be explained similarly.

Other oxidation products are formed by oxidation of the hydroperoxide itself and not the ketone as with the paraffin mechanism. Rupture of the naphthene ring then produces a product with the same number of carbon atoms as the original hydrocarbon:



β-methyl-δ-acetylvaleric acid

Further attack of this molecule at the other tertiary carbon would explain the formation of acetonylacetone.



$$\mathrm{CH_3.\overset{O}{\overset{\|}{C}}.CH_2.CH_2.\underset{CH_3}{\overset{H}{C}}.CH_2.\overset{O}{\overset{\|}{C}} - OH + O_2 \longrightarrow CH_3.\overset{O}{\overset{\|}{C}}.CH_2.CH_2.\underset{CH_3}{\overset{OOH}{C}}.CH_2.\underset{OH}{\overset{O}{\overset{\|}{C}}}}$$

Hydroperoxide

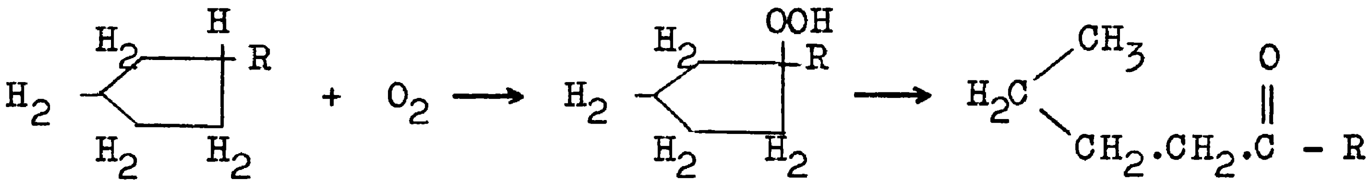
$$\longrightarrow \mathrm{CH_3.CO.CH_2.CH_2.CO.CH_3.} \quad + \quad \mathrm{CH_2.OH.COOH}$$

acetonylacetone glycolic acid

The fact that glycolic acid was not, after all, detected suggests that it may have been oxidised further to more simple products. The formation of $\overset{\beta}{\alpha}$-methylvaleric acid is explained by the oxidation of the hydroperoxide with two molecules of oxygen and a split in the naphthene ring on either side of the tertiary carbon atom.

Hydrogen, ethane and methane are probably formed by cracking.

The oxidation of the three cyclopentane derivatives, ethyl-, butyl-, and phenylcyclo-pentane by Dupont and Chavanne[39], produced ketones of the same number of carbon atoms as the original hydrocarbon. This was believed to be due to reduction of the hydroperoxide formed at the tertiary carbon atom and thus differed from the cyclohexane derivative which produced initially an alcohol.



Also produced from the ethyl and butyl derivatives were the δ -keto derivatives of heptanoic and nonanoic acids, probably by oxidation of the peroxide.

The reason for the differences between the oxidation reactions of the C_5 and C_6 naphthenes is not clear, but may well be due to there being two tertiary groups in one molecule and only one in the other. On the other hand differences in ring size or side chains may be the criterion, or even different experimental conditions of oxidation.

Nevertheless the two examples given probably indicate the general principles involved in oxidation of naphthenes.

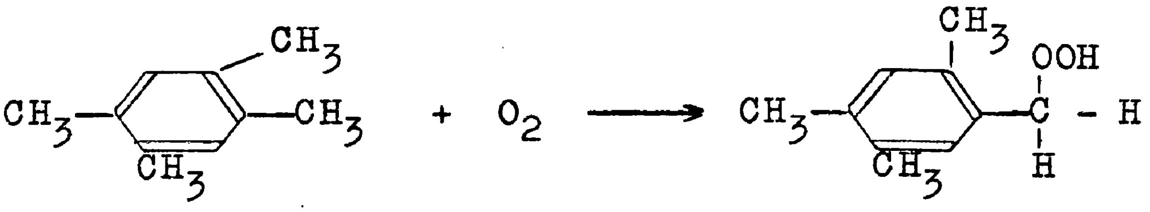
(c) The mechanism of the oxidation of aromatics.

Oxidation of aromatic hydrocarbons can be represented by the work of Stephens[45] and Stephens and Roduta[46] who oxidised a series of benzene derivatives at temperatures ranging from 80 to 140°C. They showed that at low temperatures in the liquid phase the oxygen attack always centred about a carbon atom attached to the benzene ring. This produced aldehydes from methyl benzenes, and ketones from substituted benzenes containing one or more alkyl groups larger than methyl. When the carbon atom attached to the benzene was tertiary, the ketone was found to contain the smaller of the two groups attached to the carbon atom, the other group splitting off to give a low molecular weight acid. This was found to be also true when one of the two groups was a phenyl group.

Although no peroxides were reported in this work it seems probable that the formation of a hydroperoxide group at the carbon adjacent to the benzene ring was the initiating step. Subsequent studies of the oxidation of ethylbenzene by several workers indicate that the formation of a peroxide is undoubtedly by the first step in the reaction[47].

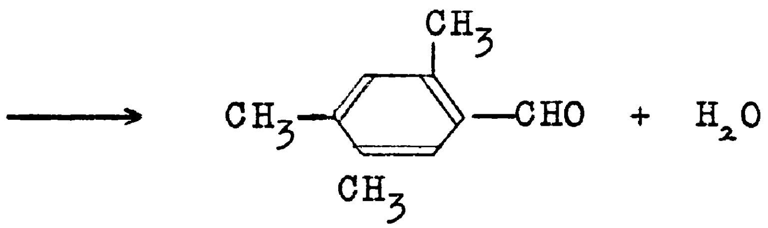
A peroxide would decompose by dehydration to the aldehyde or ketone respectively, depending on whether the starting material contained methyl or larger groups, or by the loss of a molecule of alcohol to form a ketone in the case of a tertiary hydrocarbon. Further oxidation would produce acids from both aldehydes and alcohols.

These reactions may be illustrated by considering the oxidation of durene.

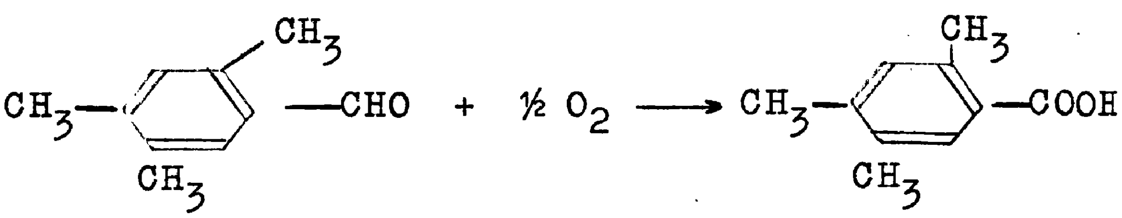


Durene

Hydroperoxide



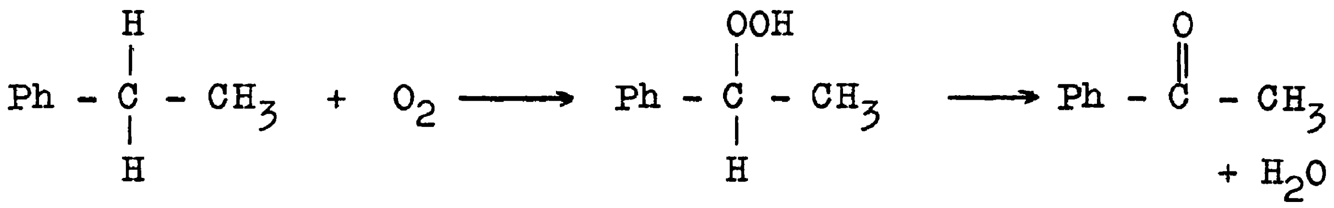
Durylic Aldehyde



Durylic Aldehyde

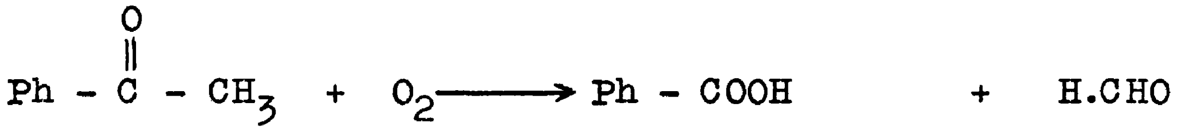
Durylic Acid

The proposed mechanism of the oxidation of ethyl benzene is as follows:



$$Ph-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 + O_2 \longrightarrow Ph-\overset{\overset{OOH}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

Ethyl benzene Hydroperoxide Acetophenone



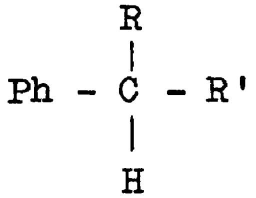
$$Ph-\overset{\overset{O}{\|}}{C}-CH_3 + O_2 \longrightarrow Ph-COOH + H.CHO$$

Acetophenone Benzoic Acid Formaldehyde

$$2\ H.CHO + O_2 \longrightarrow 2\ H.COOH$$

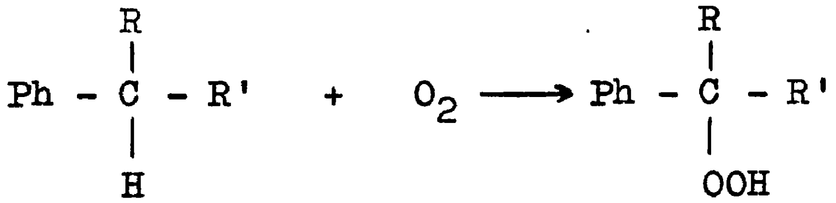
Formaldehyde Formic Acid.

If R and R' represent H or alkyl or phenyl groups in the following structure



$$Ph-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-R'$$

(where R and R' may be the same, or if not R is regarded as the smaller group), then oxidation of this type of hydrocarbon may be represented as follows:



$$Ph-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-R' + O_2 \longrightarrow Ph-\overset{\overset{R}{|}}{\underset{\underset{OOH}{|}}{C}}-R'$$

Hydrocarbon Hydroperoxide

$$\longrightarrow \mathrm{Ph} - \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}} - \mathrm{R} \qquad + \qquad \mathrm{R'OH}$$

Ketone   Alcohol or water

$$2\ \mathrm{R'OH} \quad + \quad \mathrm{O_2} \longrightarrow \mathrm{R''.COOH}$$

Alcohol   Acid

tert-Butylbenzene cannot form a hydroperoxide at the carbon atom adjacent to the benzene ring since it is a quaternary carbon. This would explain the fact that this compound is known to be very stable under oxidising conditions.

No rupture of the ring structure takes place during the normal oxidation of aromatic hydrocarbons (cf. naphthenic hydrocarbons), and oxidation always results in the production of dark insoluble condensation products.

III.2. Oxidation of Lubricating Oil Fractions.

Oxidation of lubricating fractions containing large numbers of hydrocarbons presents difficulties from the viewpoint of analysis of the products formed, and it is generally only possible to analyse for functional groups. Both Dornte[6] and Denison[44] report large quantities of peroxides when white oil is oxidised, and indeed Dornte noted that in terms of percentage oxygen absorbed white oil produced, in order of magnitude, peroxide, carbonyl, water and acid. An approximate conclusion can be arrived at from the work of Dornte[6], Fenske[48] and Hicks-Bruun and co-workers[49], who found that, on an average, water accounts for 40%, and carbon dioxide 3-10% of the oxygen absorbed when lubricating oils are oxidised.

It has been firmly established that aromatic oils give rise, on oxidation, to high percentages of asphaltenes and sludge-forming material, and refining processes have been directed largely towards their removal.

Zuidema[27] points out that the distribution of absorbed oxygen among the products in the oxidation of a lubricating oil resembles that of a pure alkylnaphthalene oxidation, and accordingly this type of compound may be the one which bears the brunt of the attack by oxygen in the complex mixture of hydrocarbons in lubricating oil.

III.3. Oxidation Rates.

(a) The physical properties of a lubricating oil which has been oxidised depend on the amount of oxidation it has undergone. The nature of the products formed and the relative amounts of these products change with the extent of the oxidation. Rates of oxidation therefore largely influence final physical properties of an oil. Oxidation rates can be assessed through oxygen absorption curves, showing the volume of oxygen absorbed by a fixed weight of sample, plotted to a base of time. Relative stabilities can be indicated by the time required for a fixed weight of oil to absorb a predetermined volume of oxygen. Dornte and co-workers[6,50,51], Larsen, Thorpe and Armfield[52], Fenske[48], von Fuchs and Diamond[53], Balsbough and Oncley[43] and Hock and Lang[54] all report investigations of this nature. Chernozhukov and Krein[55] describe an alternative method whereby oil samples are oxidised in a bomb under pressure and the resultant saponification number taken as a measure of the extent of oxidation.

(b) Zuidema[27] has co-ordinated the available data on oxidation rates and stabilities, and from this summary general trends can be indicated. The least stable compounds are those containing olefinic double bonds, benzene rings with alkyl side chains, and partially hydrogenated naphthalenes. Paraffins, naphthenes and alkyl naphthenes have intermediate stabilities, while naphthalene derivatives have been found to be the most stable class of hydrocarbons, with naphthalene itself the most stable of all. In general compounds containing a polyaromatic nucleus have proved to be extremely stable.

(c) Booser and Fenske[56] studied a number of pure hydrocarbons, a few hydrocarbon mixtures, a concentrated fraction of condensed-ring aromatics, and paraffinic-naphthenic and aromatic fractions obtained from a technical paraffin-base oil.

Oxidation rates were expressed as the number of hours required for the absorption of 100 ml. O_2 by one mol. of hydrocarbon. The following figures were obtained for a series of hydrocarbons:

hexadecene	0.35
1-methyl-4-isopropyl benzene	0.55
cis-decalin	1.1
hexadecane	2.3
1-methylnaphthalene	124
phenanthrene	over 440

More information was gained by measurement of the relative contents of the following specific groups in the oxidised products:

> acid groups, saponifiable groups, peroxides, carbonyl groups, hydroxyl groups, pentane-insoluble matter and sludge.

Aliphatic hydrocarbons gave large amounts of carbonyl compounds, rather less acid and no sludge.

Aromatic hydrocarbons, such as methylisopropyl benzene and 1-methylnaphthalene, yielded a high proportion of hydroxyl groups. Methylnaphthalene, in particular, produced much sludge, while phenanthrene yielded little else but water and carbon dioxide.

When the concentrated fraction of condensed-ring aromatics was oxidised very little acidic and carbonyl material was found, but a large amount of sludge and hydroxyl-containing compounds. On oxidation of equal parts of a mixture of hexadecane and methylnaphthalene, the stability of the mixture was found to be almost equal to that of methylnaphthalene itself, indicating that the oxidation of the relatively reactive hexadecane is inhibited by methylnaphthalene. Moreover in the resulting mixture of oxidation products the ratio of oxygen in hydroxyl groups to oxygen in other groups was found to be higher than the corresponding ratio in the oxidation products of the hexadecane and methylnaphthalene taken separately. These results would seem to show that the oxidation of mixtures of aromatic and non-aromatic hydrocarbons results in a product in which much more oxygen is found in hydroxyl groups than in other groups.

Booser and Fenske attempted to explain this by stating that the aromatic hydroxyl compounds formed from methylnaphthalene would act as inhibitors for the oxidation of hexadecane.

A contrary effect is to be found in the oxidation of a mixture of equal parts of hexadecane and cis-decalin. Initially the oxidation reaction is of the normal autocatalytic type with a rate almost equal to the arithmetic mean of the oxidation rates of the components. At a later stage, however, the rate of oxidation rises considerably above the mean rate. This must be attributed to a stimulating effect of cis-decalin or its oxidation products on the oxidation of hexadecane or its oxidation products.

Wibaut and Strang[57,58] investigated the oxidation at 125°C of a number of octane isomers and a few dimethylcyclohexanes, and observed that these hydrocarbons, after careful elimination of peroxides, possessed a relatively high resistance to oxidation. Exceptions to this rule were those isomers possessing one or more tertiary carbon atoms, provided these were not sterically shielded (e.g. 2-5-dimethylhexane).

(d) Kapff, Bowman and Lowy[59] produced, from a lubricating oil, a number of fractions differing in molecular weight and also in aromatic, naphthenic and paraffinic content as analysed by a statistical method. These fractions were oxidised and the progress of oxidation followed by measurement of acidity and viscosity increase. It was shown that acid formation was lowest in the fraction which contained the highest proportion of naphthenes. It increased with aromatic content but proved to be more susceptible to a rise in paraffinic content. Molecular weight had little influence. Increase of viscosity was more marked in high aromatic fractions.

Hibbard[60], also, separated by a chromatographic technique, a lubricating oil into fractions varying widely in their percentages of aromatic, naphthenic and paraffinic material. The fractions were analysed by a method of Deanesley and Carleton[61] and were oxidised at 280°F for 36 hours by a method developed by Burk, Hughes, Scovill and Bartleson[62]. The general conclusions reached were as follows:

1) A saturated fraction did not yield any oil-insoluble sludge, but much pentane-insoluble matter, and a great quantity of acids. A 90:10 mixture by weight of this fraction and a fraction with isolated aromatic rings behaved in a similar way. On the other hand a 90:10 mixture by weight of this fraction and a fraction with condensed-ring aromatics yielded a noticeable quantity of sludge.

2) A fraction with condensed-ring aromatics had a small capacity to produce acids and pentane-insoluble matter and showed only a slight increase of viscosity. It yielded, however, a large amount of oil-insoluble sludge.

III.4. Kinetics of Oxidation.

(a) Kinetics of hydrocarbon oxidation have been discussed at some length in various reviews and symposia. A brief summary of some of the accepted reactions will be given here.

It has been established that in the first stages of liquid phase hydrocarbon oxidation hydroperoxides are formed almost quantitatively[63]. Since the peroxide is a catalyst for the oxidation of tetralin, and since several other 'free radicals' are also immediate catalysts (i.e. reduce the induction period to zero), Waters[63] has suggested that these catalysts act by abstracting hydrogen atoms from the autoxidisable hydrocarbon, i.e.

$$X\cdot + CH_2 \longrightarrow XH + CH\cdot$$

George and Robertson[64], however, believe that the initial step in the uncatalysed oxidation process involves energy chains rather than free radicals, viz.

$$RH \longrightarrow R^*H \longrightarrow R^*$$

This question of initiation of the reaction is not quite free from controversy, but the steps in the reaction sequence are generally taken to be:

Initiation -

$$RH \xrightarrow{\text{activation}} R\cdot \quad + \quad (H\cdot)$$

Propagation -

$$R\cdot \quad + \quad O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot \quad + \quad RH \longrightarrow ROOH \quad + \quad R\cdot$$

Termination -

$$R\cdot \quad + \quad R\cdot \longrightarrow RH \quad + \quad R(-H)$$

$$RO_2\cdot \quad + \quad \cdot OH \longrightarrow ROH \quad + \quad O_2$$

$$R\cdot \quad + \quad R\cdot \longrightarrow R{-}R \qquad \text{etc.}$$

This reaction is catalysed immediately by free radicals such as phenyl radicals and more slowly (i.e. there is still an induction period) by metals. The reaction is inhibited (i.e. the induction period is increased) by small quantities of inhibitors which are usually easily oxidisable compounds such as phenols, thiols, amines etc.

(b) As stated above George and Robertson[64] believe that the initial step in the reaction sequence involves energy chains, while Waters[63], Ivanov[65] etc. support the view that the activation results in free radical formation.

Neither suggestion is completely satisfactory, particularly for uncatalysed, low temperature oxidation, and various other mechanisms have been proposed[66,67,68]. Unfortunately no direct experimental evidence has been produced to support any of these mechanisms. Irrespective of the mechanism of the initiation reaction, however, the available evidence suggests that 'without catalysts and at temperatures where the hydroperoxide is stable, the oxidation of hydrocarbons proceeds slowly to the formation of a hydroperoxide and appears to stop at this point. The chain reaction by which the oxidation proceeds further and with auto-catalytic character involves the breakdown of the hydroperoxide and the formation of free radicals'[69].

It has been shown by Waters[63] that acids, bases and metals have an effect on the mechanism of hydroperoxide breakdown. As a result products which appear early in the process of oxidation have an effect on the subsequent course of the oxidation reaction. Even with a single hydrocarbon a complex of reaction products should result. Thus with hydrocarbon mixtures the effect of the oxidation products of one hydrocarbon on the rate and extent of oxidation of another should be virtually impossible to predict.

CHAPTER IV

CHARACTERISATION OF LUBRICATING OIL MOLECULAR STRUCTURE

The n-d-M Method of Structural Group Analysis.

The v_k-n-d Method of Structural Group Analysis.

Experimental Procedure for the n-d-M Method.

CHAPTER IV

CHARACTERISATION OF LUBRICATING OIL MOLECULAR STRUCTURE

IV.1 Possibly the most useful series of techniques employed at present to characterise the structure of lubricating oils is Structural Group Analysis. The hypothetical mean molecule in the oil is considered and the distribution of carbon atoms among paraffinic, naphthenic and aromatic structure determined. In addition to carbon distribution the number of naphthenic and aromatic rings per mean molecule is given.

The method of structural group analysis from which nearly all subsequent forms have been derived is the 'direct' method, and is based on a theoretical study of hydrocarbon molecules.

A paraffin molecule of a given molecular weight will have a definite and deducible percentage of hydrogen. If naphthenic rings are introduced into this molecule each ring added results in the loss of two hydrogen atoms. A saturated molecule containing naphthenic rings will therefore have a lower hydrogen content than the paraffin of the same molecular weight. A relationship can be established between hydrogen content, molecular weight and the number of rings per molecule in a saturated hydrocarbon, viz:

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

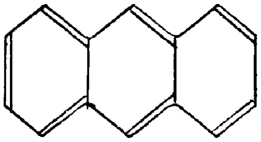
where R_N is the number of naphthenic rings per molecule.

H is the percentage of hydrogen.

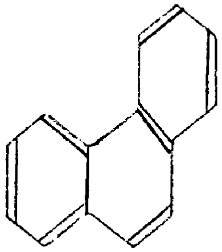
M is the molecular weight.

Where a molecule contains aromatic rings which are then hydrogenated to saturated rings, each aromatic carbon atom adds a hydrogen atom. A measure of the number of aromatic rings present is then given by the amount of hydrogen taken up on hydrogenation and an equation for this can be derived. The above equation for R_N can then be applied to the now saturated molecule except that percentage hydrogen is now a measure of total rings present in the original molecule. Naphthenic rings can be obtained from total rings and aromatic rings by difference. In this way a picture of the hypothetical mean molecule may be built up and thus the carbon distribution calculated.

Before structural group analysis methods could be derived certain assumptions had to be made regarding the number of carbon atoms per ring and to what extent ring condensation and ring linkage occurred. The choice has been Kata-condensed, six-membered rings as a basis for calculation. The reasons for this assumption, and the somewhat arbitrary nature of the choice, were discussed by van Nes and van Westen[14].

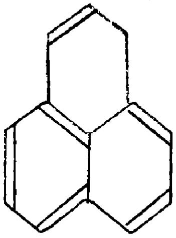


linear



angular

Kata-condensation



peri-condensation

Vlugter, Waterman and van Westen[70] first published a method for structural group analysis, known as the 'Waterman Ring Analysis'. One of the features of hydrocarbon molecules is additivity 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 and

d = density at 20°C.)

is additive for increments of C and H. It follows that 'r' is proportional to the percentage hydrogen in the hydrocarbon molecule. The number of rings per molecule can thus be obtained by measurement of specific refraction and molecular weight in a saturated oil sample.

The same authors gave a method for analysing samples containing aromatic rings[70]. The aniline point for the sample under examination was measured. This value was then compared with the aniline point for the completely hydrogenated sample of the same molecular weight and specific refraction as the original sample, this second aniline point being obtained from a graph. Using suitable factors the difference in the two aniline points was used to give the percentage of aromatic rings and to predict what the specific refraction of the sample would be were it completely hydrogenated.

The Waterman Ring Analysis, which had proved much more suitable for routine analysis than the direct method was refined by Leenderste who produced the 'density method'[14]. This eliminated aniline point measurements, and aromatic content and the specific refraction of the completely hydrogenated fraction were determined from density measurements

Analysis was now reduced to the measurement of refractive index, density and molecular weight. Attempts were made to simplify the density method and equations were evolved for carbon distribution and ring content in terms of the above three quantities, which no longer required the calculation of specific refraction. These equations are the basis of the n-d-M method of structural group analysis.

Of the three determinations required for analysis, the determination of molecular weight is the only one offering any real difficulty. More recent work by Boelhouwer and Waterman led to the V_k-n-d method[71], where measurement of kinematic viscosity replaces molecular weight measurement.

IV.2. The n-d-M Method of Structural Group Analysis.

(a) Using the physical constants refractive index (n), density (d) and molecular weight (M), van Nes and van Westen[14] describe a method for the Structural Group Analysis of mineral oil fractions. This method is based on the statistical analysis of a large number of samples.

From general equations of the type

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

$$R = a' + b'M \triangle d + c'M \triangle n$$

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

where C = percentage carbon in one type of structure.

R = mean number of rings per molecule.

$\triangle d$ = the difference between measured density (d) and the density of the limiting normal paraffin (a hypothetical paraffin containing infinite CH_2 groups in the liquid state) at the same temperature.

$\triangle n$ = a similar quantity for refractive index.

M = molecular weight.

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

In deriving the formulae van Nes and van Westen find that two different equqtions are necessary for each quantity to be calculated "because it was not possible to give one sufficiently accurate equation for the whole range". This is probably caused by the fact that the mean number of carbon atoms per ring decreases when the number of rings increases. Equations are given for 'low range' and 'high range' aromatic values.

Percentage carbon in paraffinic structure (% C_P), in naphthenic structure (% C_N) and the mean number of naphthenic rings per molecule (R_N) are estimated by difference.

The method is primarily intended for the analysis of olefin-free petroleum distillates boiling above the gasoline range. It is eminently suitable for lubricating oil fractions since based on samples containing fractions of molecular weight 194 and upwards. The method can be said to be suitable for fractions containing 75% carbon in ring structure where the aromatic rings do not exceed the naphthenic rings by more than 1½ times, and fractions having up to four rings per molecule with not more than half of them aromatic. Corrections have to be made for moderate amounts of sulphur.

The method is not suitable for individual hydrocarbons.

(b) Determination of n-d-M analysis.

Refractive index (n) and density (d) are measured at 20°C and the molecular weight (M) is determined. If the sulphur content (S) is expected to exceed a few tenths of one per cent it is also estimated. These quantities are substituted in the following equations:

$$\Delta d = d - 0.8510$$

$$\Delta n = n - 1.4750$$

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

$$v = 2.51\,\Delta n - \Delta d$$

$$w = \Delta d - 1.11\,\Delta n$$

The percentage of carbon in aromatic structure ($\% C_A$) is given by:

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

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

The percentage carbon in ring structure ($\% C_R$) is given by:

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

$$\text{for } w \text{ negative} \quad \% C_R = 1440w + \frac{10{,}600}{M} - 3S$$

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

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

$$\% C_P = 100 - \% C_R$$

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

$$\text{for } v \text{ positive} \quad R_A = 0.44 + 0.055\,M\,v.$$

$$\text{for } v \text{ negative} \quad R_A = 0.44 + 0.080\,M\,v.$$

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

$$\text{for } w \text{ positive} \quad R_T = 1.33 + 0.146M(w - 0.005S)$$

$$\text{for } w \text{ negative} \quad R_T = 1.33 + 0.180M(w - 0.005S)$$

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[14] give a series of momographs for rapid solution of the equation.

IV.3. The v_k-n-d Method of Structural Group Analysis.

A more recent method for structural group analysis of mineral oils has been devised by Boelhouwer and Waterman[71]. This, the v_k-n-d method, is based on kinematic viscosity (v_k), refractive index (n) and density (d).

This method was not used in the present work but a brief comparison is made with the n-d-M method.

The v_k-n-d method dispenses with the rather difficult measurement of molecular weight and replaces it by the determination of kinematic viscosity. As a result a considerable saving of time is made in obtaining the necessary constants. The time required for calculation from the constants is similar in both methods, but the v_k-n-d method entails the use of a curve with consequent estimation of interpolated points which may lead to inaccuracies. The n-d-M method, on the other hand, lends itself to complete solution by equations. Moreover, the v_k-n-d method is derived from less fundamental data than the n-d-M method and therefore the latter must be regarded as the more accurate.

Apart from the considerations just given, the n-d-M method was chosen for this work since it was thought desirable to know the molecular weights of the fractions, irrespective of structural group analysis.

IV.4. Experimental procedure for the n-d-M Method.

(a) Determination of 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, the instrument giving readings for the sodium D-line.

(b) Determination of density.

Densities were measured using a simple U-tube pycnometer, the design and approximate size being shown in Fig.1.

The pycnometer used was a modification of the Cup-type pycnometer recommended by van Nes and van Westen for the n-d-M method[14], and described by Lipkin *et al.*[72] 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 of the pycnometer could easily cope with any droplets of oil forced out by 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.

PYCNOMETER

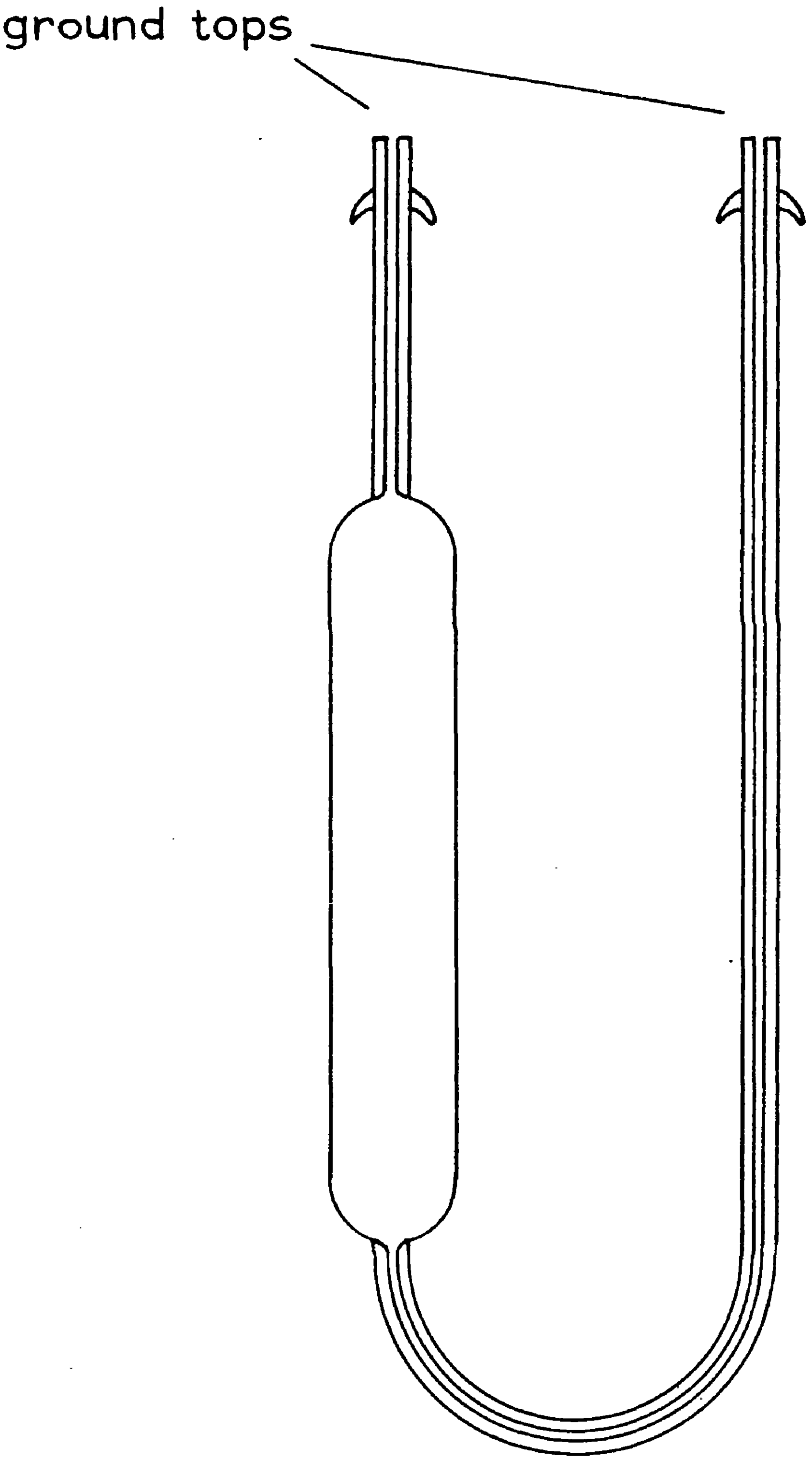


FIG. 1.

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 <u>et al</u>.[72]

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 ± 0.05°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 g./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 true density in vacuo.

According to Lipkin[72] $C = 0.0012(1 - d_A)$

where C = correction factor, d_A = apparent density.

(c) Determination of molecular weight.

(1) Molecular weights of petroleum fractions in the lubricating oil range may be determined by two possible methods. The cryoscopic method depends on the depression of the freezing point of a solvent when oil is added to it; the ebullioscopic method on the elevation of the boiling point of a solvent similarly treated. Apparatus for the cryoscopic method is much simpler than for the other but it appears that rather variable results may be obtained[73].

The ebullioscopic method is recommended[14] for n-d-M analysis and has been used in this work.

(2) If a quantity of oil is added to a suitable solvent then, under ideal conditions, the resulting rise in boiling point and the molecular weight are related by the equation

$$M = \frac{K\,c}{\Delta T} \cdot 100$$

where M = Molecular weight of oil.
c = Concentration of oil in solvent (g./g.)
ΔT = Elevation of boiling point.
K = Ebullioscopic constant.

As ideal conditions are hardly ever attained, the calculated molecular weight can vary with concentration of oil in solution. It is thus normally recommended[73,14] that the molecular weight equivalent to zero concentration be taken. This is found by plotting molecular weight or boiling point elevation at a number of concentrations and extending the best line among the points to meet the axis at zero concentration.

Determinations are carried out in an ebullioscope, an apparatus which contains boiling solvent and is fitted with a condenser. Provision is made for heating, oil addition and the direct measurement of the boiling point of the solution. Certain factors must be considered in the design and operation of ebullioscopes and these are outlined below.

(i) Any change in atmospheric pressure during a determination will affect the boiling point and give false temperature differences. This is counteracted by operating two identical ebullioscopes side by side, one of which contains only boiling solvent. Any change in boiling point of the solvent can then be noted and a suitable correction made for the boiling point elevation.

(ii) Superheating is liable to occur, but can be eliminated by the use of a Cottrell vapour lift pump which ensures a steady stream of liquid in contact with vapour flowing over the thermometer bulb.

(iii) A certain amount of solvent is always out of solution in the form of vapour and of liquid 'hold-up' in the condenser. This means that the actual concentration of the oil in the solvent is greater than that calculated. Carefully controlled heating to give a constant boiling rate overcomes this difficulty. In this way a constant 'hold-up' is obtained and is accounted for by the ebullioscopic constant for the apparatus.

(3) The ebullioscope used is shown in Fig.2., and was a modified version of the one described by Mair[73]. A Beckman thermometer (6 Centigrade degree range) was used to measure boiling point, and was fitted, by means of a cork, into the upper section of the apparatus. The cork was protected from leakage and from absorption of solvent by a coating of 'Araldite' (an epoxy resin found to be unaffected by boiling benzene). The legs of the Cottrell pump were designed to lie alongside the thermometer bulb and both pump and bulb were protected from cooled solvent dripping from the condenser by a glass guard.

A gas micro-burner was used for heating, and control was increased by a screwclip on the burner tubing. To prevent upset of the thermal equilibrium of the system each ebullioscope was protected from cold air currents by a glass

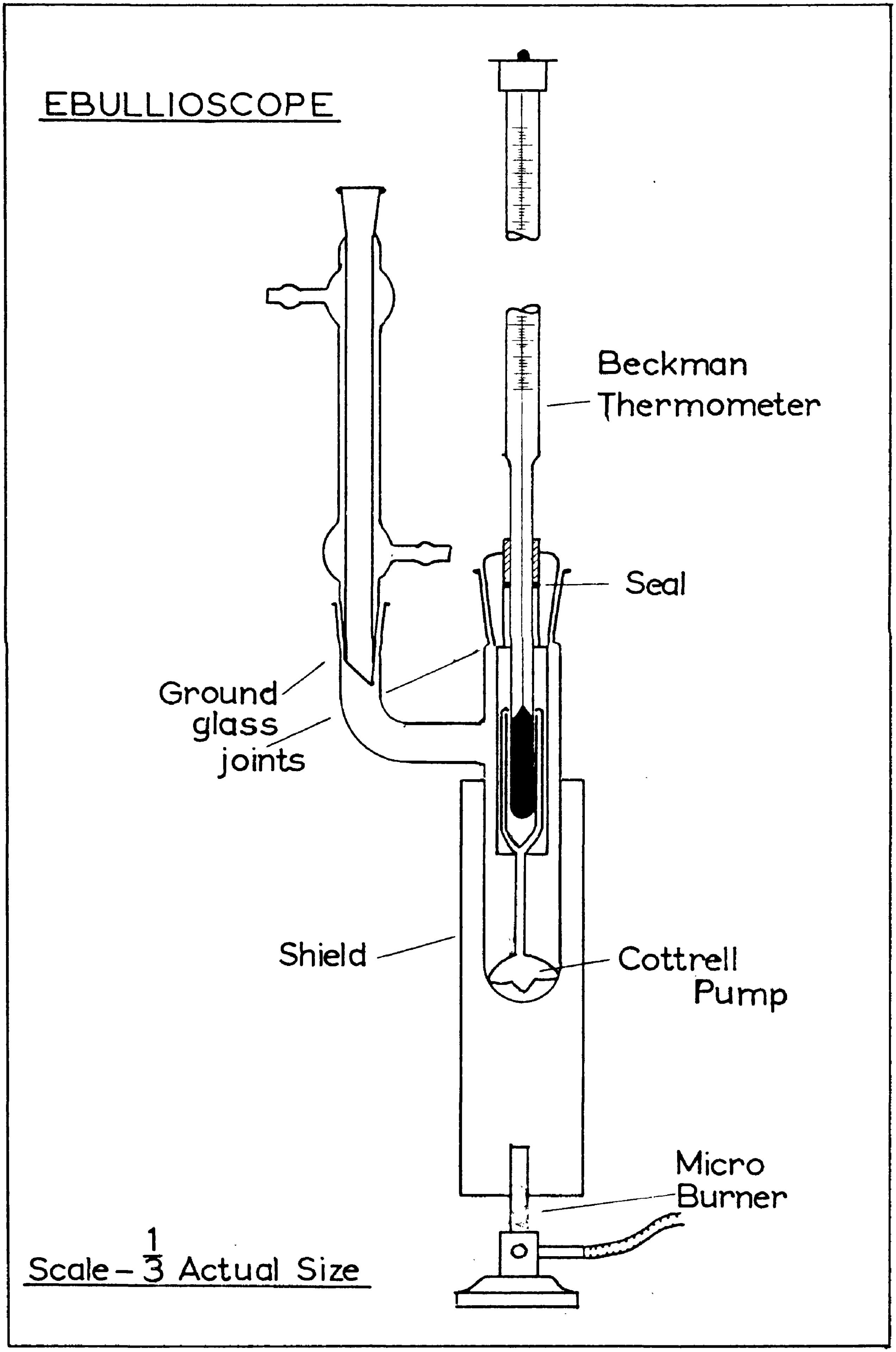

EBULLIOSCOPE
Beckman Thermometer
Seal
Ground glass joints
Shield
Cottrell Pump
Micro Burner
Scale – 1/3 Actual Size

FIG. 2.

tube, as shown in Fig.2., and the ebullioscopes were operated side by side in a glass case.

Additions of oil were made by the method suggested by van Nes and van Westen[14]. A special pipette with three symmetrically placed glass knobs was introduced into the condenser. The glass knobs ensured that the condenser was not wetted by oil drops. The pipette was weighed together with a small flask containing the oil sample before and after additions.

(4) The solvent used throughout for molecular weight determinations was benzene, and this was normally purified by distillation and drying over sodium for at least 24 hours.

Before making a determination both ebullioscopes were boiled with benzene, followed by emptying, drying and refilling with exactly 40 ml. benzene measured at 20°C. Boiling was again started and the micro-burners adjusted to give a suitable 'hold-up'. When the temperature of the thermometer in the ebullioscope used for measurements was constant to within 0.005°C the first addition was made to give a first elevation of about 0.3°C. Successive increments were added and, by steps of about 0.1°C, a final total rise of 1°C was recorded. Temperatures were read each time to the nearest 0.001°C.

Simultaneously with these readings the temperature of the pure solvent boiling in the other apparatus was read. Barometer readings were taken at the start and finish of the determination to correct the ebullioscope constant for atmospheric pressure.

The ebullioscopic constant (K) depends on the solvent used, but also to a certain extent on the characteristics of the instrument used and the procedure followed. This value (K) was found by carrying out a series of determinations on pure hydrocarbons of known molecular weight. Tetralin and naphthalene were used. The ebullioscopic constant calculated for each concentration was plotted and extrapolated to zero concentration. This value was taken as the constant at the mean atmospheric pressure (p_0) at which the calibration had been made.

An equation to correct the ebullioscopic constant for pressure changes is available[14], viz.

$$K' = K_0 + 0.24(p_0 - p)$$

p = atmospheric pressure during determination.

(5) During the last stages of this work a semi-micro ebulliometer was obtained. This apparatus dispensed with the Beckman thermometer method of measuring boiling point elevation. Instead a thermistor sensing element of low

thermal capacity was utilised, and changes of resistance of the thermistor measured by a sensitive Wheatstone bridge[74].

CHAPTER V

DATA ON LUBRICATING OILS USED.

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DATA ON LUBRICATING OILS USED.

Five 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 1. Table 2 gives the constants which were measured by the methods described, viz. refractive index, density, molecular weight, kinematic viscosity and sulphur content.

Sulphur content was determined by a micro-analytical method comprising combustion of the oil and absorption of the combustion products in hydrogen peroxide solution. The sulphuric acid thereby formed was determined by titration with sodium hydroxide solution.

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

TABLE 1.

Oil samples used.

SAMPLE	SOURCE	HISTORY (refinery treatment)
Oil 1.	Kuwait	Vacuum distillation: phenol extraction: dewaxing and clay treatment.
Oil 2.	-	Believed to be derived from a mixture of crudes: no refinery details.
Oil 3.	Persian Gulf	No refinery details
Oil 4.	Venezuela	Distillation: phenol extraction and clay treatment.
Oil 5.	Lagunillas, Venezuela	Naphthenic feed stock: vacuum distillation: caustic soda treatment: redistilled.

TABLE 2.

Constants of oil samples used.

Sample	Refractive Index 20°C	Density 20°C	Molecular Weight	Viscosity 100°F C.S.	Sulphur %	Ramsbottom Carbon Residue %
1	1.4803	0.8697	538	85.54	0.80	0.11
2	1.4854	0.8816	328	22.80	0.32	0.02
3	1.4898	0.8845	525	102.5	0.94	0.15
4	1.5016	0.9057	476	223.4	1.16	0.35
5	1.5275	0.9453	410	225.4	0.26	0.12

TABLE 3.

n-d-M analyses of oils used

Sample	% C_P	% C_N	% C_A	R_N	R_A
1	73.4	23.3	3.3	2.14	0.20
2	55.4	35.9	8.7	1.95	0.31
3	69.8	21.3	8.9	2.11	0.56
4	61.8	25.2	13.0	2.33	0.77
5	47.4	27.4	25.2	2.19	1.30

CHAPTER VI

THE STANDARD OXIDATION TEST FOR LUBRICATING OIL AND MODIFICATION TO ALLOW OXYGEN ABSORPTION TO BE MEASURED.

The Institute of Petroleum Oxidation Test.

Measurement of Oxygen Absorption in the Standard Oxidation Test.

CHAPTER VI

THE STANDARD OXIDATION TEST FOR LUBRICATING OIL AND MODIFICATION TO ALLOW OXYGEN ABSORPTION TO BE MEASURED.

VI.1. The Institute of Petroleum Oxidation Test.

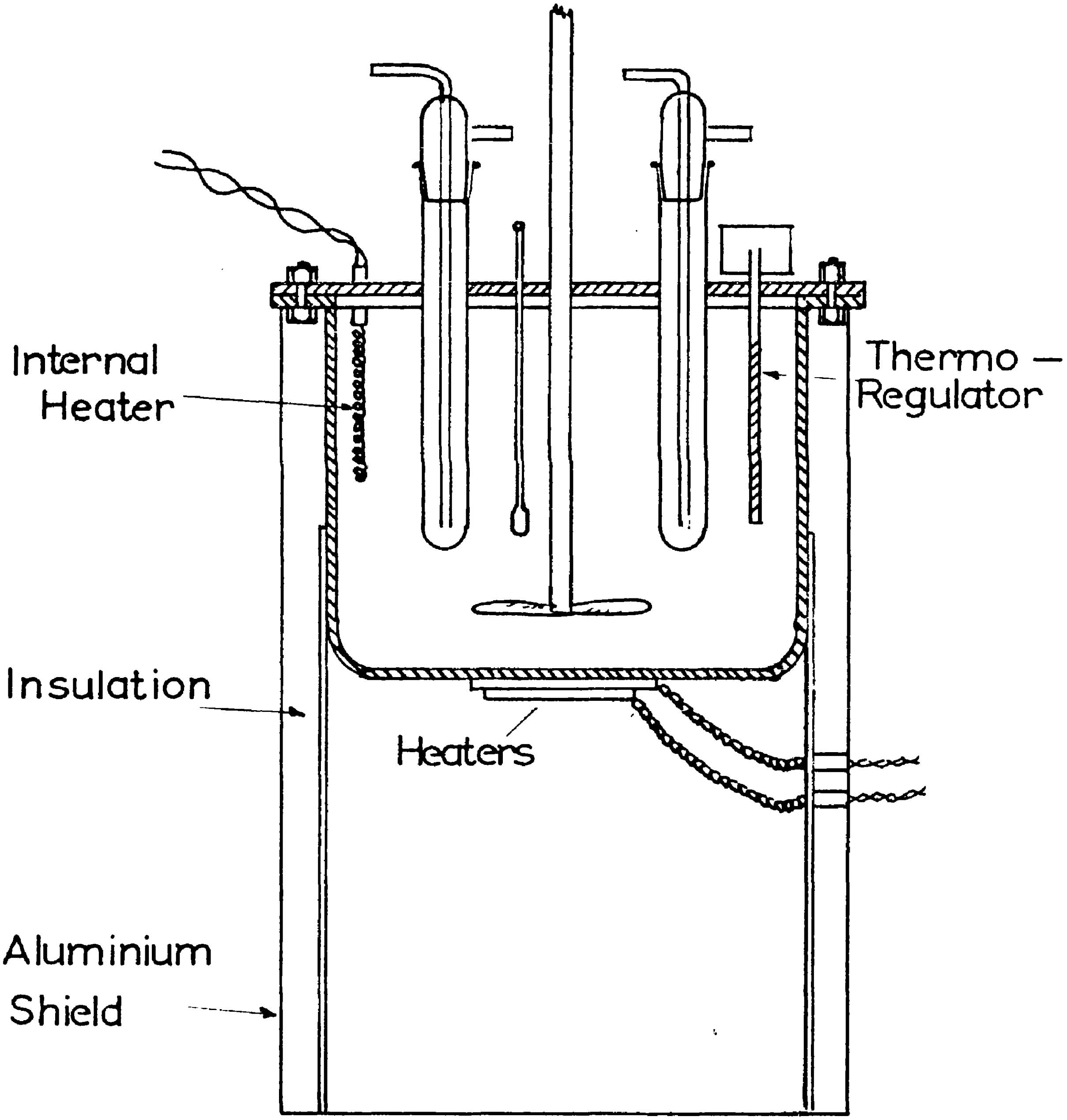
(a) The standard oxidation test for lubricating oils in Britain is that of the Institute of Petroleum - I P 48[1].

Air is passed at a rate of 15 litres per hour through a 40 ml. sample of oil heated to 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 deterioration.

The apparatus used in the work reported here is shown in Fig.3. Dimensions were according to specification and heating was effected by means of two flat external heaters of 300 and 600 watts, and one internal heater of 250 watts. Heating was begun using the two external heaters and when the required temperature was reached the 300 watt heater was kept on continuously, with the internal heater on 'control'. This

OXIDATION APPARATUS



Scale $\frac{1}{4}$ Full Size

FIG. 3.

arrangement maintained the bath at 200°C with very little temperature fluctuation.

Air was supplied by a small 'Proctor' diaphragm pump. This pump gave a non-pulsating air flow which was measured by a monometer flowmeter. The apparatus could test simultaneously four samples of oil.

(b) Kinematic viscosity measurements.

Kinematic viscosities were measured by U-tube viscometer in a thermostat at 100 ± 0.025°F by the procedure of I P 71[1] - "Viscosity-Kinematic in C.G.S. Units". The viscometers were calibrated according to British Standard Specification, B S.188.

(c) Ramsbottom carbon residue.

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

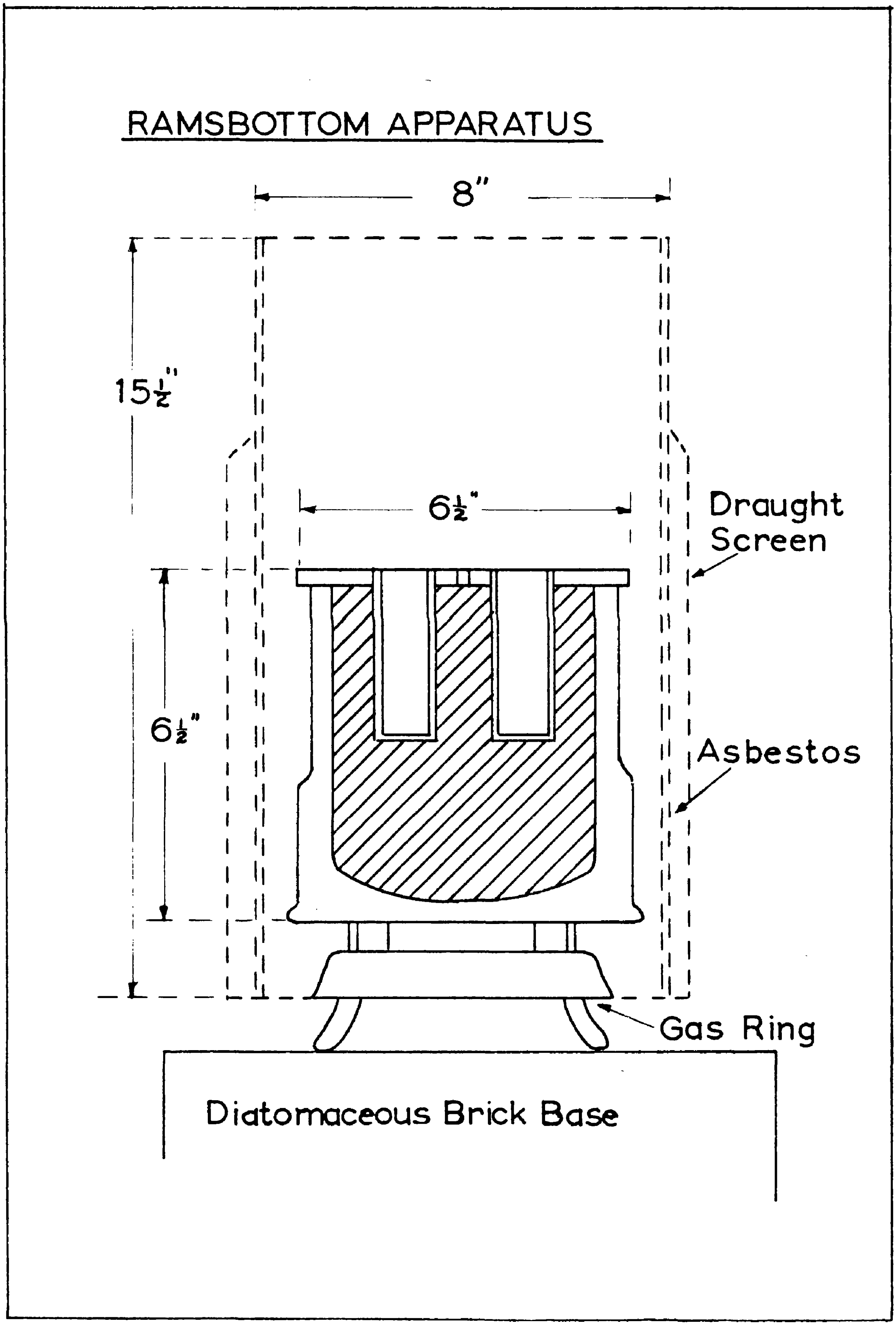

RAMSBOTTOM APPARATUS
8"
15½"
6½"
6½"
Draught Screen
Asbestos
Gas Ring
Diatomaceous Brick Base

FIG.4.

VI.2. Measurement of Oxygen Absorption in the Standard Oxidation Test.

(a) In view of the work contemplated it was important that the oxygen absorbed by the oil, during oxidation in the standard test, should be measured. In conjunction with Aitken[75] an apparatus was set up which enabled this to be done.

The I P 48 heating bath was utilised with a modified oxidation tube. In place of a boiling tube with a cork seal, as in the standard test, a tube with ground glass fittings and inlet and outlet tubes attached was used. The remainder of the system is shown in Fig.5.

Gases leaving the oxidation tube entered a water cooled condenser and trap, then passed to a further fog trap where fine oil mist was removed. From the fog trap the gases entered an absorption train which, in its final form, consisted of

(1) a U-tube filled with fine calcium chloride to remove water;

(2) a bubbler bottle filled with concentrated sodium hydroxide solution for removal of carbon dioxide and hydrocarbon gases;

(3) a U-tube of coarse calcium chloride to remove any

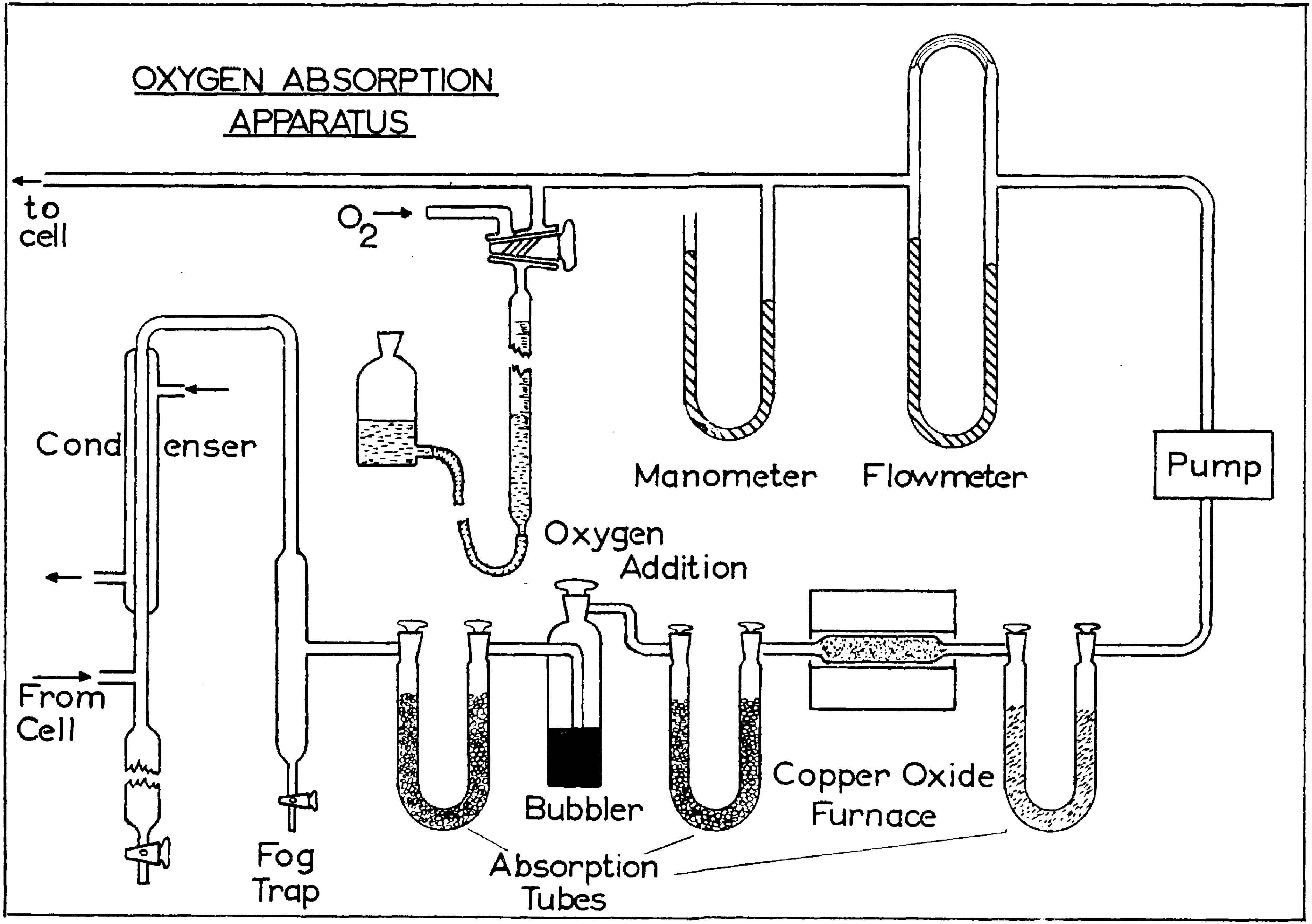

OXYGEN ABSORPTION APPARATUS
to cell
O_2 →
Cond enser
From Cell
Fog Trap
Manometer
Flowmeter
Pump
Oxygen Addition
Bubbler
Copper Oxide Furnace
Absorption Tubes

FIG.5.

water carried over;

(4) a tube filled with copper oxide at 300°C to convert any carbon monoxide to dioxide, and hydrogen to water.

(5) a U-tube, one limb filled with 'ascarite' to absorb carbon dioxide, and the other with calcium chloride to absorb water.

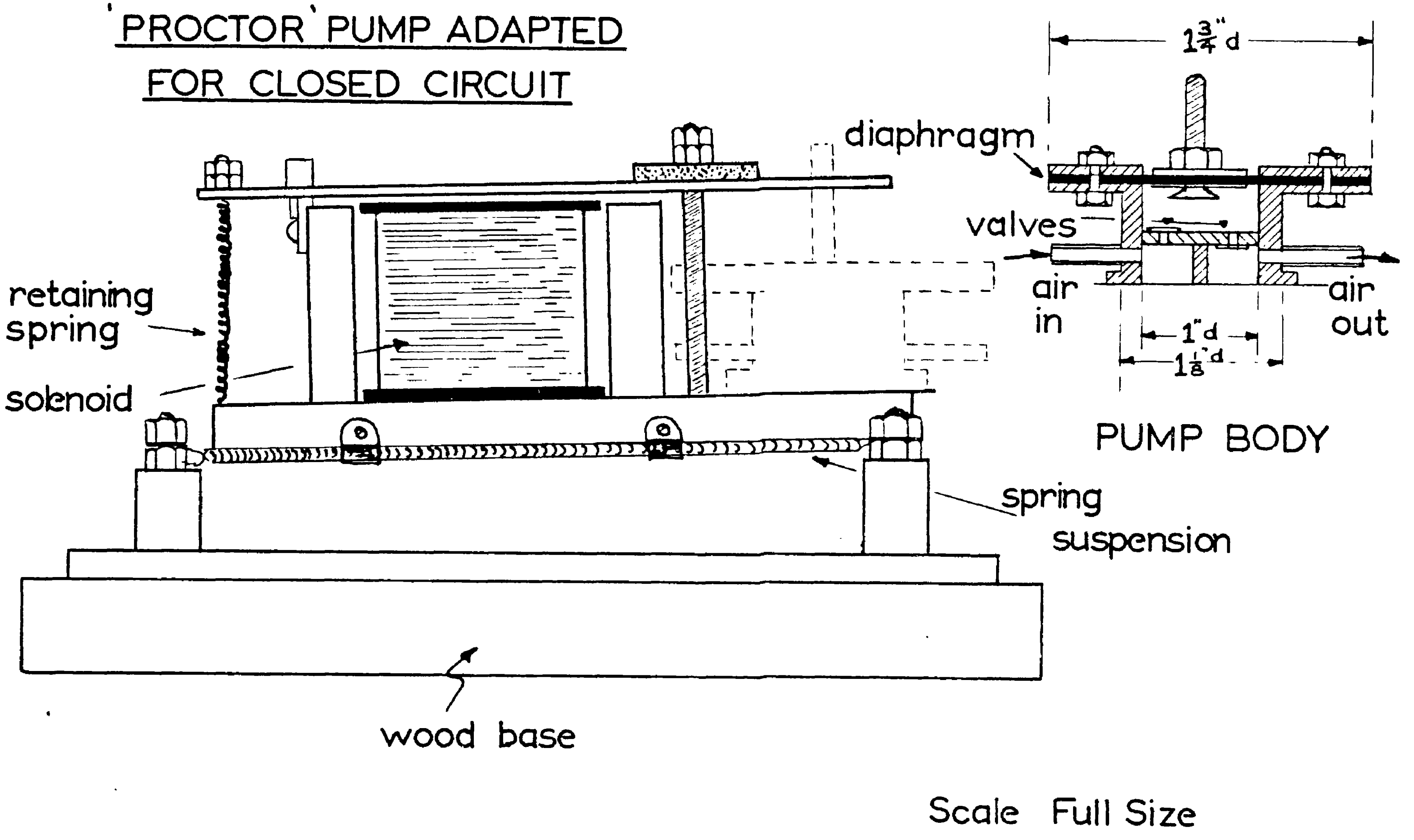
Immediately after this absorption system was placed the circulation pump, and the apparatus was completed by a flowmeter, a water-filled manometer and a system for oxygen addition.

The circulation pump was a modification of the 'Proctor' pump previously mentioned. A specially constructed body allowed the diaphragm to be sealed with 'Bostik' and resulted in a leak-proof pump, as shown in Fig.6.

Addition of oxygen was made by the three-way stopcock shown, the burette fitted with the mercury levelling bottle allowing measured volumes of oxygen at atmospheric pressure to be added.

(b) Experimental procedure.

All ground glass joints and stopcocks were first coated with silicone grease and the system tested for leaks by running, with no oil in the cell, under a few cms.Hg.



'PROCTOR' PUMP ADAPTED FOR CLOSED CIRCUIT

FIG.6.

pressure and then under a few cms.Hg. vacuum.

After verifying that no leaks were present 40 ml. of the oil to be tested were placed in the cell for twenty minutes and allowed to reach 200°C. The cell was then connected to the gas absorption circuit. At the start of the test the pump was switched on and the flow-rate adjusted to 15 litres per hour. A decrease in the pressure of the system, shown on the manometer, indicated oxygen absorption. Additions of oxygen were made, normally, between fixed marks on the manometer scale so that the mean pressure in the system was always atmospheric. All oxygen absorption volume measurements were corrected to N.T.P.

(c) Absorbents used.

The absorbents listed were those finally used but an extended series of experiments had been necessary before a satisfactory arrangement was reached. In the preliminary work it was found that gaseous organic products of oxidation rendered inactive some of the absorbents. This, in particular, led to an accumulation of unabsorbed carbon dioxide in the system. It was found, finally that a bubbler of sodium hydroxide solution removed both carbon dioxide and the organic gases and a satisfactory absorption train resulted.

CHAPTER VII

SLUDGE AND ACIDITY PRODUCED BY OIL OXIDATION

Determination of 'Sludge'.

Determination of Acidity.

CHAPTER VII

SLUDGE AND ACIDITY PRODUCED BY OIL OXIDATION.

VII.1. Determination of "Sludge".

(a) The term 'sludge', considered in connection with used oils, usually refers only 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. This may be considered dissolved sludge since it is not present in the original oil, but formed during use. Moreover, such dissolved sludge must be considered just as objectionable as insoluble sludge as it represents alteration products of the oil and can be thought of as potential insoluble sludge.

From this viewpoint the method used had to give values for oil-soluble and oil-insoluble sludge.

The method decided on was a modified version of that used by Levin and Towne[76] and consisted of the direct determination of soluble sludge and an indirect determination of insoluble sludge.

Direct determination of insoluble sludge was not seriously considered since difficulties arise in weighing the filtered sludge. A direct method of this type has, however, been used by Matthews[77] who used a cellulose-asbestos bacteriological filter in a special holder, so that solvent extraction of the oil-insolubles could be carried out without transference of the sludge. This type of method was rejected since values for both soluble and insoluble sludge were wanted; the method used in this work enabled both to be determined by a simple procedure.

Some methods for sludge determination use hydrocarbon solvents for dilution of a used or laboratory oxidised oil to cause flocculation of the sludge, which may then be easily filtered. Such methods, however, are extremely unreliable for determining insoluble sludge as the solvent usually has a complex effect; not only causing flocculation of insoluble material, but precipitating material actually in solution in the oil.

Paraffins are the poorest solvents for sludge or asphaltic material and the lower-boiling paraffins are the poorest solvents of the series. For this reason Levin and Towne[76] used a commercial pentane mixture for precipitation, pentanes being the lowest paraffins conveniently handled. Experiments showed that they did not dissolve material originally undissolved in the oil itself.

The method used comprised the determination of the pentane-insoluble matter in the original oxidised oil sample, and in a clarified sample obtained by passing the undiluted sample through 'Sterimat' filter pads similar to those used by Matthews[77]. From the difference in the two values the oil-insoluble sludge was determined.

(b) Experimental procedure.

A well-stirred, representative sample of the oxidised oil was filtered through a 'Sterimat' pad at about 75°C. This was easily done using a 6 cm. diameter pad in conjunction with an electrically-heated Buchner funnel. A slight suction was used to facilitate filtration.

On this clarified sample, as well as on a portion of the original sample, the pentane-insoluble matter was determined as follows:

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

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

where A = sludge not dissolved in pentane, original oil sample (g/10g.).

B = sludge not dissolved in pentane, clarified sample (g./10g.)

C = oil-insoluble sludge (wt.%)

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

(c) <u>Validity of method</u>.

It is obviously empirical to classify as oil-soluble sludge that portion of a clarified oil which is insoluble in commercial pentane. The use of pentane, however, was considered more desirable than liquid propane as used in the method of Hall, Levin and McMillan[78]. It was felt that propane might precipitate material, normally present in unoxidised lubricating oils, which could not rightly be called 'sludge'. The advantage of this method, although empirical, was that it did not precipitate material from any of the

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* Levin and Towne[76] used this method for oil-insoluble sludge (C) only and did not count A and B as being measures of total and oil-soluble sludges respectively.

original unoxidised oils used, but did produce insolubles at very short oxidation times with the more highly aromatic oils. For this reason the oil-soluble sludge values obtained are considered useful as indications of potential oil-insoluble sludge.

VII.2. Determination of Acidity.

(a) The determination of acidity in an oxidised lubricating oil is made difficult by its dark colour. One hour of oxidation in the apparatus described has usually been found sufficient to render the oil very dark and opaque in anything but a very thin film. Total acidity is therefore difficult to determine, separate determination of acidic groups, e.g. carboxylic acids, phenols etc., being even more complicated.

Two types of methods are normally applied to oil acidity determination. These are:

(1) Colour indicator methods in which the oil is titrated with standard alkali to a definite pH fixed by the colour change of a suitable indicator.

(2) Potentiometric methods in which the oil is titrated with standard alkali and the change in potential, indicated by a suitable pair of electrodes, plotted

against the volume of alkali used. Points of inflection on the curve or a selected pH value determine the end-point.

(b) Colour indicator methods.

The older methods of acid number determination[79,80] normally utilise standard aqueous alkali as titrant solution. The acidic constituents of the oil must therefore be dissolved in a solvent miscible with water, and makes titration into a two-phase system almost inevitable. Such methods utilise ethanol or mixtures of ethanol and solvent naphtha, with a small amount of heating and agitation to extract the acids. The colour change of the indicator (normally phenolphthalein) is observed in the aqueous alcohol layer. In many cases, especially with oxidised oils, such agitation leads to emulsion formation, and the difficulty of breaking the emulsion can considerably extend the time of reaction. The repeatability and reproducibility of such methods is not good due to incomplete extraction, reaction of alkali with atmospheric CO_2 and reaction of alkali and saponifiable material. It has been found in one case that, owing to emulsion difficulties, the titration occupied 15 minutes instead of the customary 1-2 minutes and an acid number 1.5 high was obtained[80].

A one-phase method demands either a suitable solvent combination which aqueous alkali will not split into two phases, or a non-aqueous titration in which the standard alkali is in alcoholic solution. I P 1/55, Method A, is of the first type and utilises benzene-ethanol (3:2) as a solvent and aqueous KOH solution as titrant, the indicator being alkali blue. Oils of high acid number unfortunately require enough alkali to split the system into two phases before the end-point is reached.

The newer method I P 139, which is identical with A.S.T.M. method D 974 and B.S.2834, employs a solution of KOH in <u>iso</u>propyl alcohol. The oil sample is dissolved in a mixture of benzene and <u>iso</u>propyl alcohol (1:1) containing 0.5% water, and the resulting single phase solution is titrated at room temperature with the alcoholic KOH solution to the end-point indicated by the colour change of p-naphthol-benzein solution taking place in the pH range 8.5 - 9.8 (orange in acid and green-brown in alkali). This last method has two disadvantages. In very black oil solutions the end-point is extremely difficult to see, and the solvent mixture is not always able to dissolve oil sludge which is acidic and must be determined.

Several techniques have been suggested for the better observation of end-point. These include using as a stirring rod in the titration flask a narrow bore glass tube, and observing the colour change in the tube[81]; or shaking the titration flask to produce a slight foam as the colour change takes place and observing under a white fluorescent lamp[82]. Flasks with narrow side limbs and long necks have been used to good effect[83]. A variation of this method employs a magnetic stirrer to produce a vortex in the neck of the flask during titration, the colour change being observed in the vortex[84]. Two photocells fitted to a bridge circuit and used in conjunction with two filters forms the basis of a photo-electric colorimeter which can indicate difficult end-points.

In spite of all these refinements I P 139 cannot adequately handle dark oxidised oils containing a large amount of sludge.

(c) Potentiometer methods.

In A.S.T.M. method D 664 the sample is dissolved in the mixture of benzene and isopropyl alcohol (plus water) as used in I P 139, and titrated potentiometrically with isopropyl alcoholic KOH solution using a glass/calomel electrode system. Meter readings are plotted against volumes of titrating solution and the end-points are taken at the inflections in the resulting curve. When no definite inflections are obtained end-points are taken at meter readings corresponding to the end-points in the titration of typical strong and weak acids. The meter readings are obtained from suitable buffer solutions, these being m-nitrophenol-KOH-<u>iso</u>-propyl alcohol for total acid number and collidine-HCl-<u>iso</u>-propyl alcohol for strong acid number.

A number of practical difficulties make the method extremely tedious. The electrodes and cables must be shielded carefully from other electrical influences, in particular the stirrer motor. Masses of metal in close vicinity must be adequately earthed. The battery operating the potentiometer must be frequently checked. An interval of one or two minutes must be allowed to elapse after each addition of alkali before a reading is taken. Scrupulous cleanliness of electrodes must be observed.

This method was tried with a number of oxidised oil samples and was found to be only moderately successful. With some oxidised samples points of inflection were observed indicating groups of acidic constituents, but with many only smooth curves were obtained. The potentiometric method was not really suited to the rapid determination of the total acidity of a large number of oxidised samples. Moreover the solvent used did not readily dissolve samples containing sludge.

(d) Masked fluorescent indicator method.

For rapid testing the method developed by Fenske and his co-workers[85] was found to be invaluable. It was essentially a non-aqueous titration in which two indicators were used. The method was based on a suggestion by Burshtein[86].

In a dark coloured solution of oxidised oil a titration end-point may be detected by the sudden appearance of a fluorescence. In acid oil solutions the fluorescence of fluorescein may be masked by the presence of methyl red at a pH at which it is in its red form. Thus although fluorescein still fluoresces at pH values as low as 0.5 - 1.0, this fluorescence does not become apparent until the red-to-yellow colour change of methyl red takes place (pH range 4.2 - 6.3).

In Fenske's method the oxidised oil is dissolved in a mixture of n-butyl alcohol - toluene (1:1). This has been found to be a superior solvent to that used in the A.S.T.M. methods. No difficulty should be experienced in dissolving the precipitated matter of the most heavily oxidised oils.

A solution of methyl red is prepared in butanol - toluene solvent (0.1%) and the fluorescein in ethanol (0.1%).

The oil solution, with indicators added (2 - 4 ml. methyl red solution; 0.2 - 0.3 ml. fluorescein solution), is titrated with a standard solution of sodium butoxide prepared by reacting sodium with n-butanol. On the acid side of the neutral point the methyl red masks the green fluorescence which develops strongly when the solution becomes alkaline. Observation of the end-point is aided by illuminating the titrating vessel strongly from the side and using a dark background to reduce transmitted light.

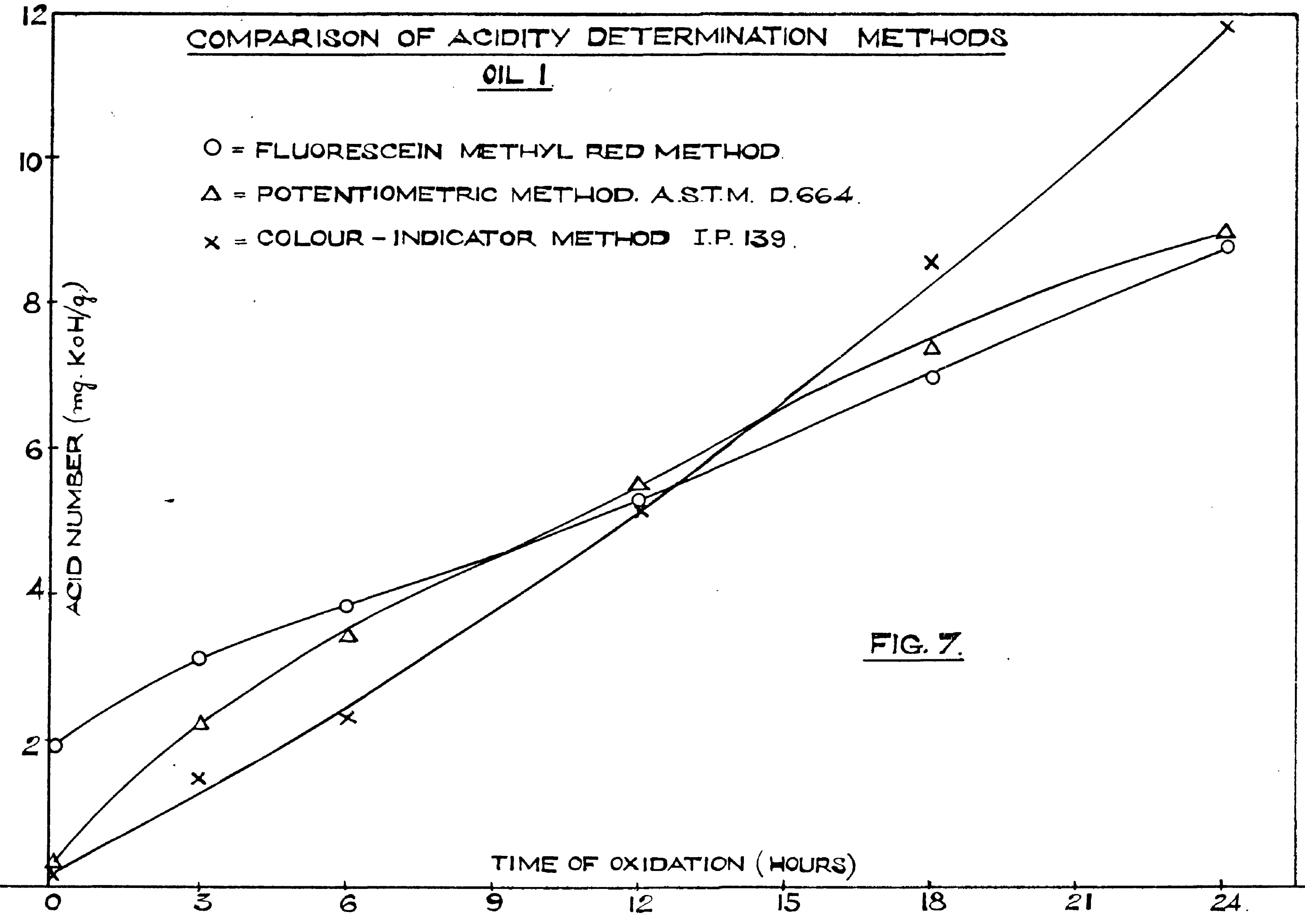
The reliability of this method was tested by comparing results with those given by the Standard potentiometric (A.S.T.M. D 664) and colour indicator (I P 139) methods. Samples of oils 1 and 5 (Table 1.) containing no additives were oxidised for periods up to 24 hours and the total acid numbers determined on a series of sub-samples. Quadruplicate acid number determinations were carried out on every oxidised sample by each of the three methods. The results are given in Tables 4 and 5.

The arithmetic mean was calculated for each set of four results and is included in the tables together with the range in value obtained. The mean results are plotted for comparison in Figs.7 and 8.

TABLE 4.

Acid No. determinations on oxidised samples of oil No.1.

OXIDATION TIME (HOURS)	ACID NUMBER DETERMINATION No. 1	2	3	4	MEAN VALUE	RANGE
Fluorescein-methyl red method						
0	2.3	1.7	1.5	2.1	1.9	0.8
3	2.9	2.8	3.2	3.5	3.1	0.6
6	4.0	3.5	3.9	3.9	3.8	0.5
12	5.5	5.2	5.1	5.4	5.3	0.4
18	7.2	7.1	6.8	7.2	7.0	0.4
24	8.9	8.7	8.7	8.7	8.8	0.2
Potentiometric method A.S.T.M. D 664						
0	0.2	0.3	0.4	0.3	0.3	0.2
3	2.1	2.1	2.2	2.5	2.2	0.4
6	3.6	3.3	3.3	3.4	3.4	0.3
12	5.5	5.8	5.4	5.4	5.5	0.4
18	7.4	7.1	7.5	7.5	7.4	0.4
24	8.7	9.0	9.2	9.1	9.0	0.5
Colour-Indicator method I P 139						
0	0.3	0.1	0.1	0.2	0.2	0.2
3	1.3	1.6	1.6	1.5	1.5	0.3
6	2.5	2.3	1.9	2.5	2.3	0.6
12	4.7	5.2	5.5	5.5	5.2	0.8
18	8.9	8.1	8.4	8.9	8.6	0.7
24	11.2	11.9	12.2	11.9	11.8	1.0



COMPARISON OF ACIDITY DETERMINATION METHODS

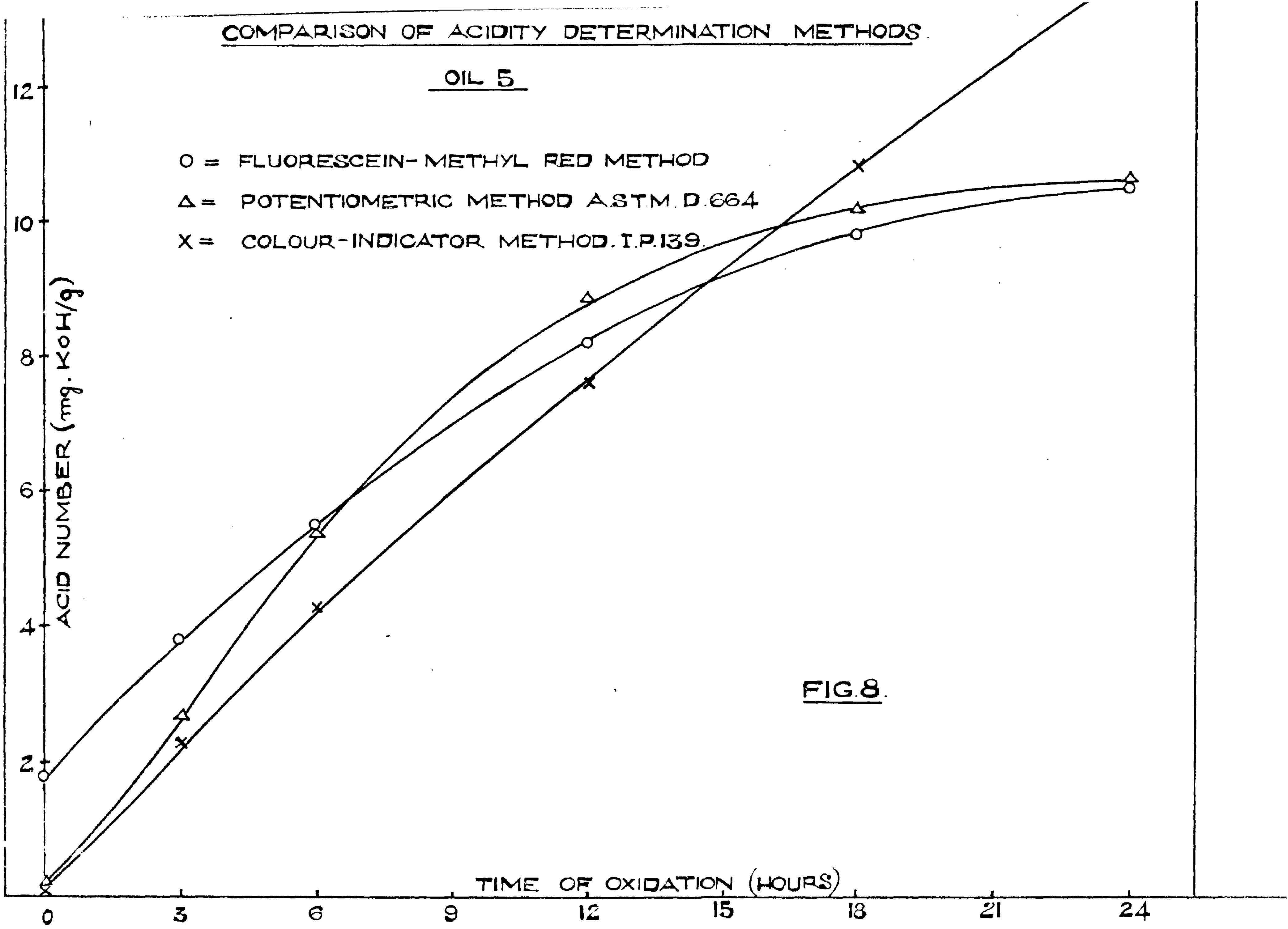
OIL I.

FIG. 7.

TABLE 5.

Acid No. determinations on oxidised samples of oil No.5.

OXIDATION TIME (HOURS)	ACID NUMBER DETERMINATION No. 1	2	3	4	MEAN VALUE	RANGE
Fluorescein-methyl red method						
0	1.4	1.7	2.1	2.0	1.8	0.7
3	3.9	3.6	3.8	4.1	3.8	0.5
6	5.7	5.4	5.2	5.7	5.5	0.5
12	8.4	8.1	8.2	8.2	8.2	0.3
18	9.8	9.7	9.8	10.0	9.8	0.3
24	10.6	10.5	10.4	10.4	10.5	0.2
Potentiometric method A.S.T.M. D 664						
0	0.1	0.3	0.2	0.1	0.2	0.2
3	2.5	2.7	2.7	2.7	2.7	0.2
6	5.5	5.4	5.5	5.2	5.4	0.3
12	8.8	8.9	9.2	8.8	8.9	0.4
18	10.0	10.3	10.2	10.3	10.2	0.3
24	10.3	10.7	10.7	10.6	10.6	0.4
Colour-Indicator method I P 139						
0	0.1	0.2	0.1	0.1	0.1	0.1
3	2.1	2.2	2.5	2.1	2.3	0.4
6	4.3	4.1	4.7	4.2	4.3	0.6
12	7.2	7.6	7.9	7.8	7.6	0.7
18	10.4	11.0	10.6	11.3	10.8	0.9
24	13.4	13.9	13.2	14.4	13.7	1.2



COMPARISON OF ACIDITY DETERMINATION METHODS.

OIL 5

FIG.8.

It can be seen from the tables that there is relatively good agreement among the results given by the three methods. The range in value, however, which may be taken as a measure of the uncertainty of the true result, decreases with increasing oxidation time for the fluorescein - methyl red method, increases slightly for the potentiometric method, and increases strongly in the case of the standard colour-indicator method. These differences are due to the fact that the standard indicator end-point is more easily seen in the lighter coloured oils obtained at short oxidation times. As oxidation time is increased the progressive darkening of the oil makes the fluorescent end-point easier to observe. It was found that the addition of a neutral black dye to insufficiently dark oils greatly facilitates the observation of the fluorescent end-point and reduces the range of value to that given by heavily oxidised oils.

In Figs.7 and 8 it can be seen that for the lighter coloured oils the potentiometric method gives higher acid numbers than the standard colour-indicator method. The reason for this probably lies in the difference between the pH for the standard indicator end-point and the pH of the buffer used in the potentiometric method. It is convenient to adopt the potentiometric method as a standard for comparison, since it is less dependent on personal judgement of end-point.

Uncertainty of a colour-indicator end-point leads in general to over titration and a high result. In Fig.7 for oxidation time of less than about twelve hours the fluorescein - methyl red method gives a high result, but for longer oxidation periods the standard colour-indicator method gives values considerably in excess of those obtained by the other two methods. In Fig.8 the same trends are shown at slightly different oxidation times. It would therefore appear that for insufficiently dark oils the fluorescein - methyl red end-point is inferior to that of p-naphthol-benzein, but for black oils the fluorescent end-point is far superior; and the result obtained is at least as accurate as that given by the potentiometric method.

The butanol-toluene solvent and titration with a sodium butoxide solution has been applied to D 664 and I P 139 methods. With very heavily oxidised oils improved results were obtained owing to better dissolution of sludges precipitated during the oxidation.

Other combinations of colour indicators and fluorescent materials were also examined. It was found that methyl red / eosin had similar characteristics to the methyl red / fluorescein system. A combination of bromo-cresol purple and rhodamine B was found to be useful for light coloured oil solutions, but decreased in accuracy as solutions became darker.

CHAPTER VIII

THE EFFECT OF OIL COMPOSITION ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED, ON OXIDATION UNDER THE CONDITIONS OF THE STANDARD TEST FOR LUBRICATING OILS.

I - REFINED LUBRICATING OILS FROM DIFFERENT CRUDE SOURCES

Absorption of Oxygen.

Sludge Produced on Oxidation.

Acidity Produced on Oxidation

Carbon Residue Increase and Viscosity Ratio.

CHAPTER VIII

THE EFFECT OF OIL COMPOSITION ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED, ON OXIDATION UNDER THE CONDITIONS OF THE STANDARD TEST FOR LUBRICATING OILS.

I. REFINED LUBRICATING OILS FROM DIFFERENT CRUDE SOURCES.

VIII.1. The modified Institute of Petroleum apparatus, described in Chapter VI, was used at the outset to determine the oxygen absorbed under the conditions of the standard test. Various products obtained were estimated, the main interest being in the sludge and acid obtained.

Oxidation was carried out on the five oils described in Table 1, and oxidation times up to 24 hours were used. The normal maximum time for any one 'run' was 6 hours, longer oxidations than this being effected in two or more stages. A preliminary test had shown that no significant differences could be detected between oxidation for interrupted periods and continuous oxidation.

Each oil was first subjected to a 24 hour oxidation test during which absorption of oxygen was measured. Oxidations were next conducted for various shorter periods of time but without the measurement of oxygen absorbed. Although I P 48 stipulates 12 hours oxidation for the standard test it was decided to extend the time to 24 hours so that the effect of time on oxidation could be better studied.

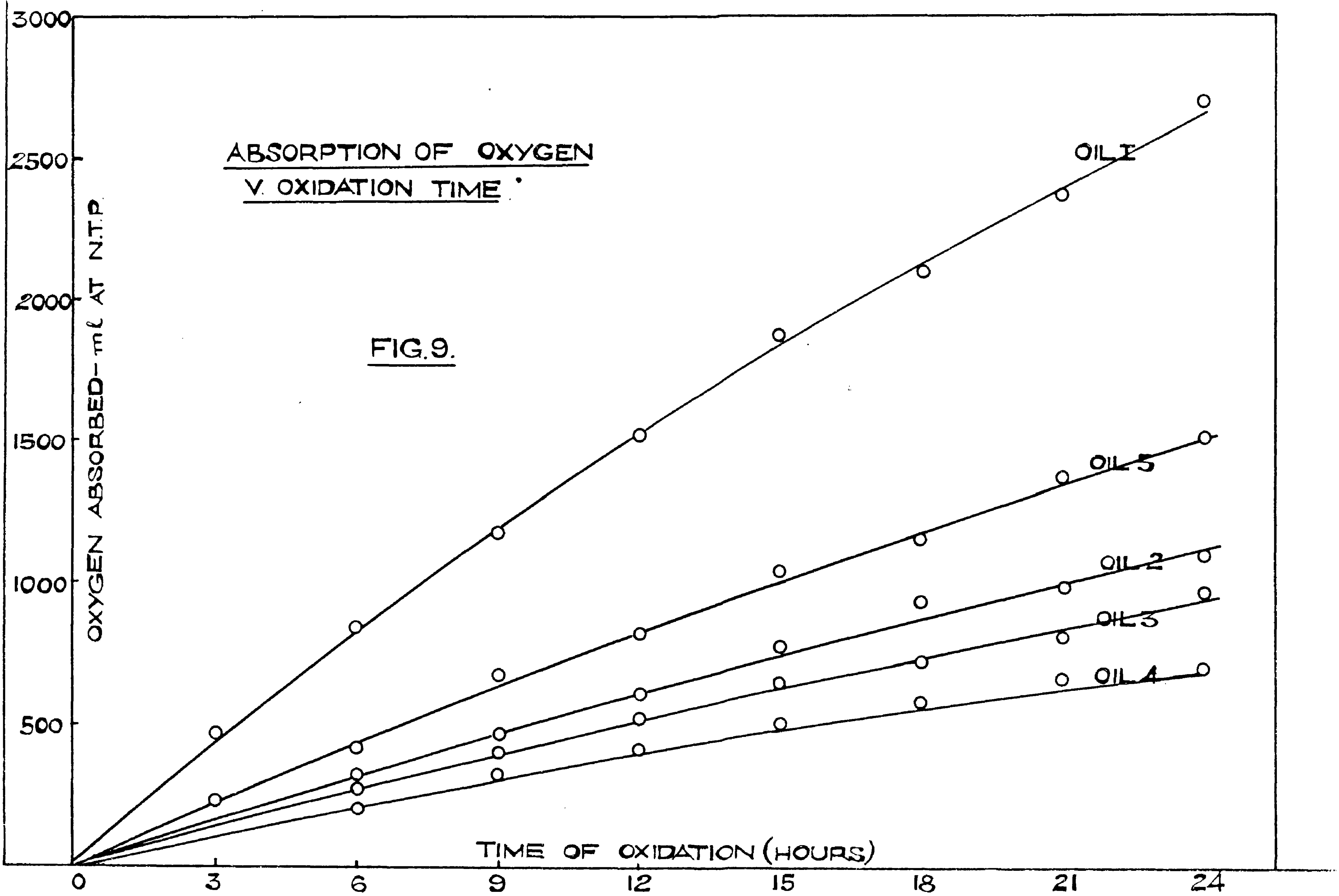
After oxidation the following characteristics were determined:

1. the quantity of oil-insoluble sludge.
2. the quantity of oil-soluble sludge.
3. the acidity of the oxidised oil.
4. the acidity of the clarified oil.
5. the acidity of the completely desludged oil.

VIII.2. Absorption of Oxygen.

(a) The oxygen absorption curves for 24 hours oxidation are shown in Fig.9, and can be seen to be almost linear, i.e. oxygen is absorbed at a constant rate. For this reason comparison of amount of oxygen absorbed is, to all intents, synonymous with comparison of absorption rates.

It has been shown by Dornte[6,50,51] and other workers that on plotting oxygen absorbed against time four distinct types of curves may be obtained; 1) Autocatalytic - where rate of absorption increases with time; 2) Autoretardant - where the rate decreases with time; 3) Linear - where the



ABSORPTION OF OXYGEN
V. OXIDATION TIME

FIG. 9.

rate is constant and; 4) Initially autocatalytic followed by autoretardant. It must be stressed, however, that one curve (of types 1-4) is not an absolute characteristic of the oil being tested. It has been shown by von Fuchs and Diamond[53] that a given oil may exhibit autocatalysis or autoretardation depending on the temperature of oxidation. It will, indeed, be shown later in this work that certain of the oils studied here may give an autocatalytic type of curve under other oxidation conditions. Regarding the linear absorption / time relationships found under the standard test conditions, it may be significant that most workers studying absorption rates have worked at lower temperatures than 200°C. As will be seen this may tend to produce relationships other than linear.

(b) No real correlation is apparent between rate of oxygen absorption on the one hand and viscosity ratio and carbon residue increase on the other. (Table 6). The only slight point of similarity is that oils 2 and 3 which have low absorption rates give low values for the other two quantities.

TABLE 6.

Oil Sample	Oxygen Absorbed in 12 Hours (ml. at N.T.P.)	Viscosity Ratio at 12 Hours	Increase in % Carbon Residue at 12 Hours	% C_A
No. 1	1520	1.56	1.04	3.3
No. 2	600	1.22	0.42	8.7
No. 3	520	1.22	0.61	8.9
No. 4	400	1.42	1.09	13.0
No. 5	820	3.18	3.24	25.2

(c) If aromatic content of the five oils is considered it is seen that the three oils which absorb least oxygen have values for % C_A in the range 8.7 to 13.0, while the oil of least aromatic content (% C_A = 3.3) is easily the most reactive. Oil 5 with aromatic content of 25.2% shows somewhat lower absorption but is still substantially higher than the three oils first mentioned. At this stage no real conclusions can be arrived at regarding the influence of oil composition on the amount of oxygen absorbed, but the tendency seems to be towards a minimum absorption with medium aromatic content.

An interesting point is that von Fuchs and Diamond[53] and Fenske *et al.*[48] on measuring oxygen absorption rates for various lubricating oil blends found an 'optimum aromaticity', i.e. a particular blend of certain aromatic content which proved to be more stable than the blends with higher or lower content of aromatics. This same phenomenon was indicated in the work of Clark[87] who studied the dielectric stability of insulating oils. Dielectric stability and oxidation stability are known to be closely related.

VIII.3 Sludge Produced on Oxidation.

(a) Three different sludge values were measured for each oxidised oil sample, viz. total sludge, oil-insoluble sludge and oil-soluble sludge. Table 7 shows the values obtained.

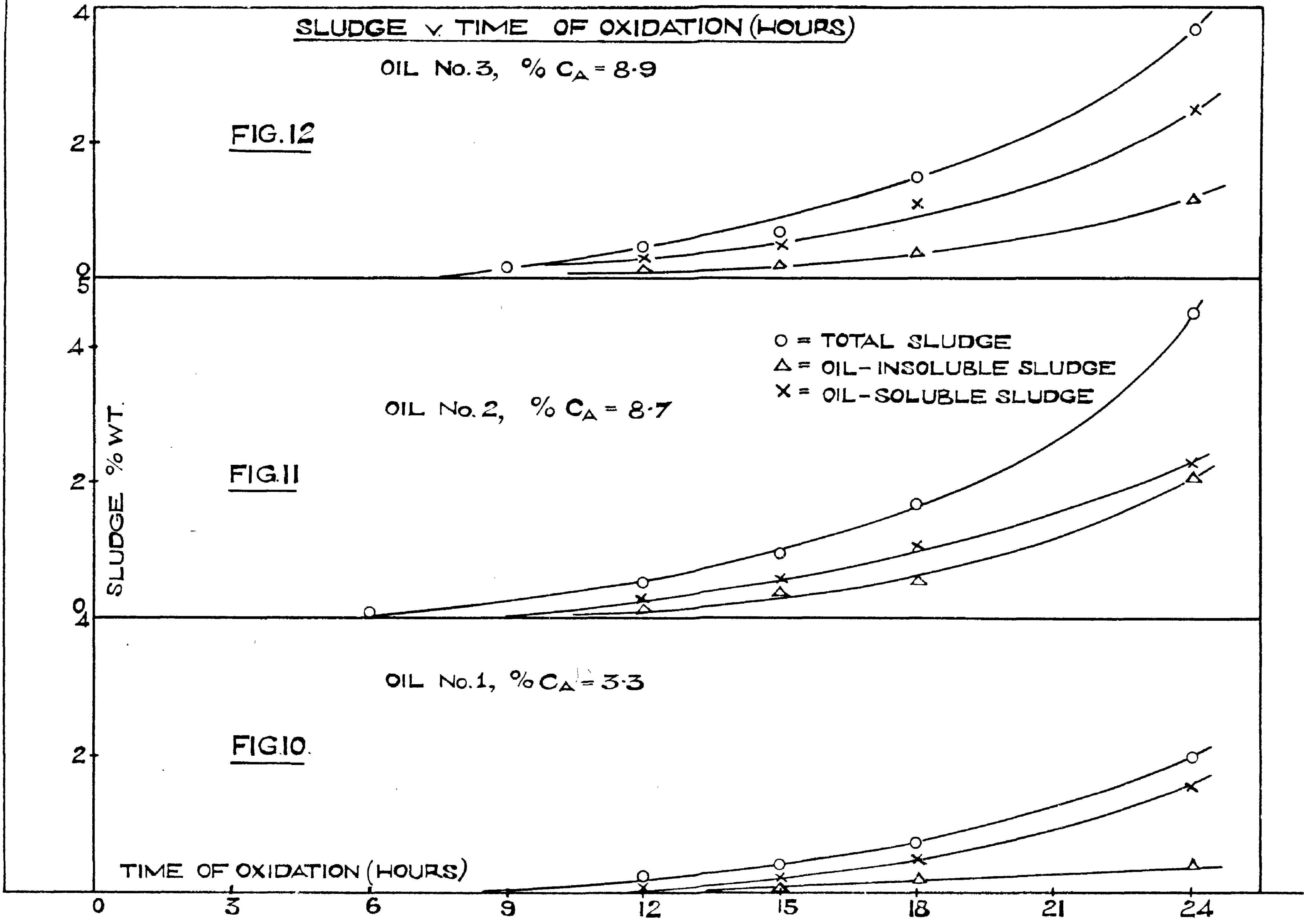
These determinations were made by the modified method of Levin and Towne[76]. Oil-soluble sludge is often described as "pentane-insoluble" sludge but here the former name is used. The results obtained have been plotted against time of oxidation and are shown in Figs.10 to 14.

(b) Only the more aromatic oils (4 and 5) were found to produce sludge at all times of oxidation, and in general, total sludge increased with percentage of aromatics in the oil. This effect was reported by Waterman, Leenderste and Palm[88] in an investigation of the sludge-forming properties

TABLE 7.

Sludge (% wt.) produced on oxidation

Oil Sample	Type of Sludge	Time of Oxidation (Hrs.) 3	6	12	15	18	24
No.1. % C_A = 3.3	Soluble	-	-	0.1	0.3	0.5	1.6
	Insoluble	-	-	trace	0.1	0.2	0.4
	Total	-	-	0.2	0.4	0.7	2.0
No.2. % C_A = 8.7	Soluble	-	0.1	0.3	0.6	1.1	2.3
	Insoluble	-	-	0.2	0.4	0.6	2.2
	Total	-	0.1	0.5	1.0	1.7	4.5
No.3. % C_A = 8.9	Soluble	-	0.1	0.3	0.5	1.1	2.5
	Insoluble	-	trace	0.1	0.2	0.4	1.2
	Total	-	0.2	0.4	0.7	1.5	3.7
No.4. % C_A = 13.0	Soluble	trace	0.2	0.6	0.9	1.2	1.6
	Insoluble	0.2	0.3	0.8	1.2	1.4	3.7
	Total	0.3	0.5	1.4	2.1	2.6	5.3
No.5. % C_A = 25.2	Soluble	0.1	0.4	0.6	1.2	1.3	1.3
	Insoluble	0.3	0.6	0.9	1.5	2.5	6.3
	Total	0.4	1.0	1.5	2.7	3.8	7.6



SLUDGE v TIME OF OXIDATION (HOURS)

SLUDGE v. TIME OF OXIDATION (HOURS)

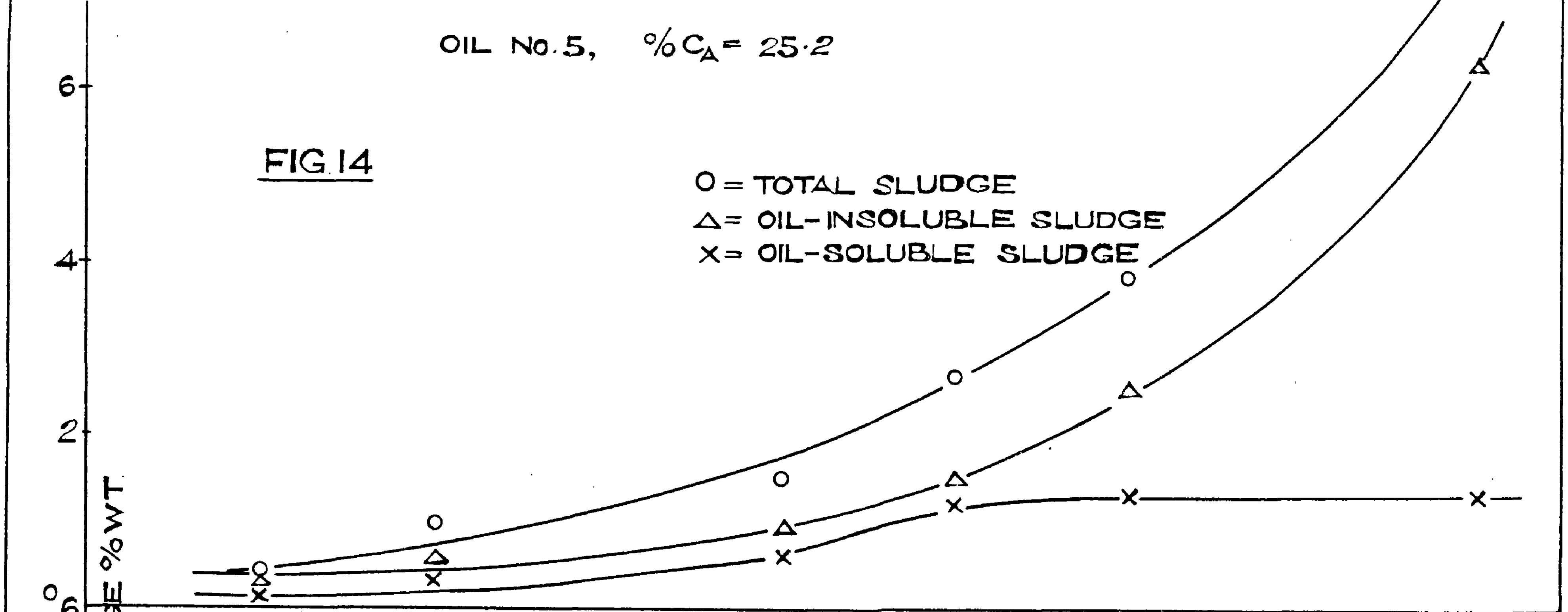


FIG 14

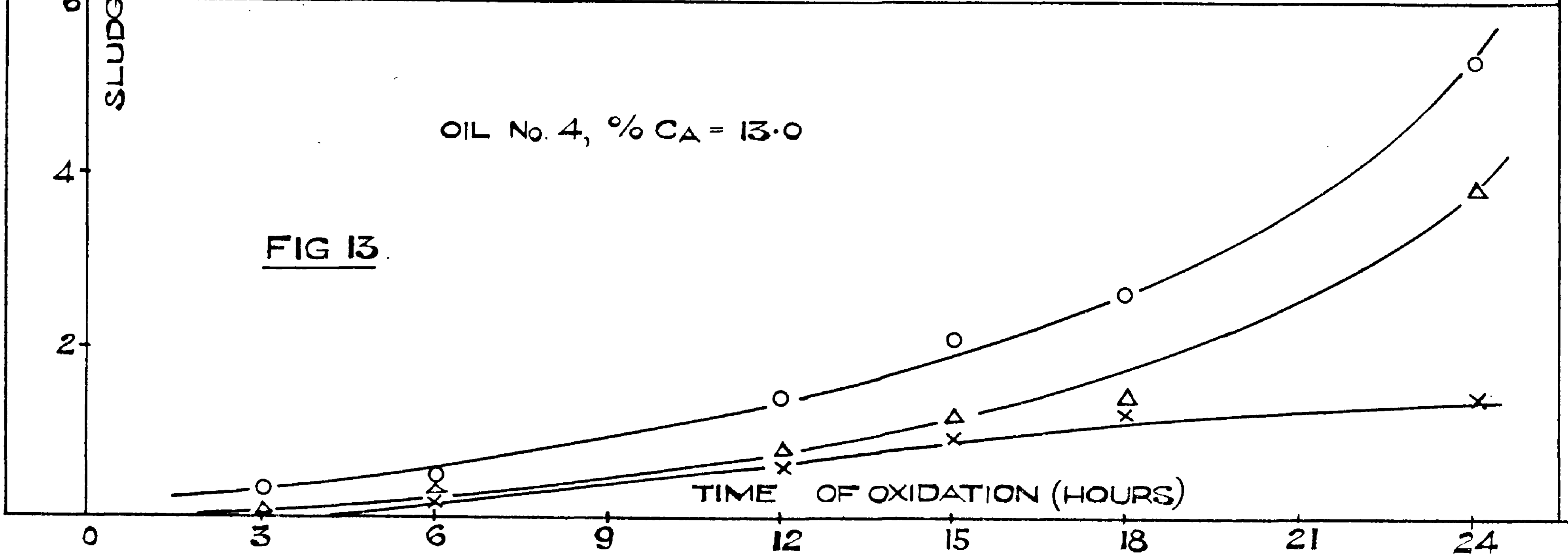


FIG 13.

of hydrocarbons. Hibbard[60], Booser and Fenske[56] and other workers noticed similar effects with lubricating oil fractions, oxidised, however, at lower temperatures than 200°C.

It can be seen from Figs.10-14 that the rate of sludge formation of both soluble and insoluble sludge shows an increase with time of oxidation, i.e. autocatalytic. An exception is seen with the two higher aromatic oils where oil-soluble sludge is formed at a constant rate and then assumes an approximately constant value.

The lower aromatic oils (Figs.10, 11 and 12) produced more soluble than insoluble sludge while oils 4 and 5 (13.0% and 25.2% C_A respectively) gave almost equal amounts of both types of sludge until 12-15 hours oxidation. On further oxidation oil-insoluble sludge increased rapidly whereas soluble sludge remained almost constant.

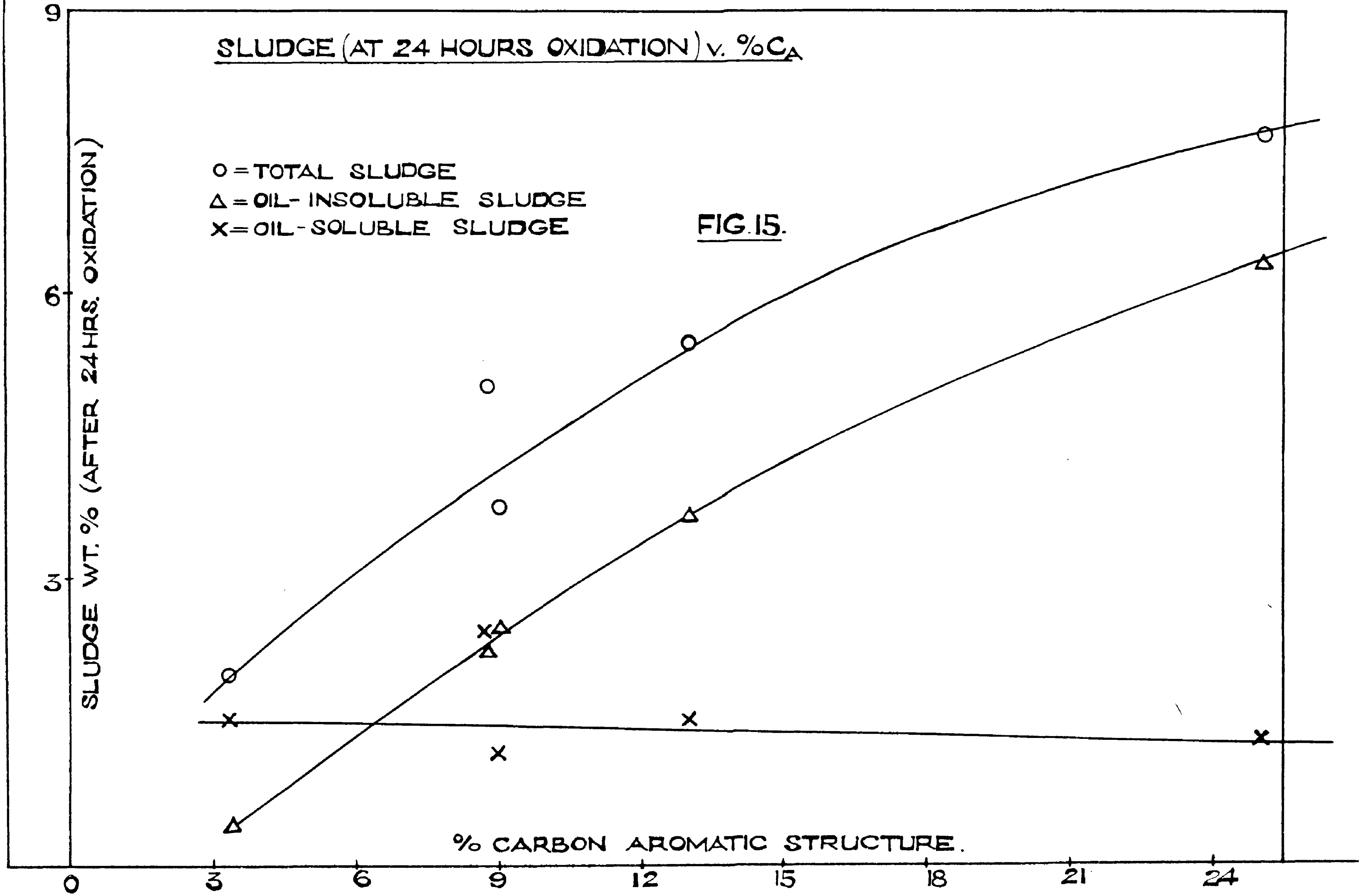
It is known that paraffinic and naphthenic compounds do not form sludges and it is therefore reasonable to suppose that aromatic content is the criterion for sludge formation. It may also be assumed that oil-soluble sludge is a precursor of insoluble sludge, requiring further reaction before precipitation, during which time more soluble sludge will have been formed. This would explain why oils low in aromatic content require longer oxidation times before the appearance of sludge, a smaller number of aromatic molecules being available for reaction. Also, as is shown by oils 1, 2 and 3, soluble sludge is present before there is any noticeable quantity of insoluble sludge. This can be explained if there is a time lag before the soluble ⟶ insoluble sludge conversion occurs. With high aromatic oils 4 and 5 such a time lag must be less than three hours.

It has sometimes been suggested that sludge formation is a result of condensation and/or oxidation of acids. This contention scarcely seems tenable since sludge is often not formed by oxidation of hydrocarbons yielding the greatest amounts of acid, e.g. paraffins, naphthenes and white oils. Aromatics, on the other hand, which yield small amounts of acid produce large amounts of sludge. Since it is known, however, that with aromatic materials a large proportion of the oxygen absorbed goes to produce hydroxyl compounds then it is possible that aromatic hydroxyl compounds are necessary for insoluble sludge production. This seems a feasible explanation for the differences, outlined above, between low and high aromatic oils. Moreover it provides an explanation of other experimental facts described later.

This hypothesis also offers an explanation for the apparent decline in the rate of formation of soluble sludge on sustained oxidation of oils 4 and 5. If, with these higher aromatic oils, the concentration of aromatic hydroxyl compounds increases as oxidation proceeds, then sufficient hydroxyl or phenolic material would be available for reaction. The approximately constant amount of soluble sludge suggests equilibrium between the reactions, oil ⟶ soluble sludge and soluble sludge ⟶ insoluble sludge.

The relationship between sludge formed and % C_A also adds support to the argument. Fig.15 shows that, for 24 hours oxidation, insoluble sludge increases almost linearly with aromatic content of the oils. Oil-soluble sludge, however, decreases slightly as aromatic content increases. Comparison of this figure with the absorption / % C_A pattern mentioned in VIII.2. indicates that sludge formation is not a function of oxygen absorbed, since sludge shows no minimum with oils 2, 3 or 4. From the evidence sludge is rather a function of aromatic content.

It was proposed to examine this hypothesis regarding sludge formation by the determination of phenols in the various oxidised oils. Considerable efforts were made to the estimation of phenols as weak acids, by potentiometric titration of oxidised oils in basic solvents. Little success was achieved and the attempt was abandoned.



SLUDGE (AT 24 HOURS OXIDATION) v. $\%C_A$

FIG. 15.

VIII.4. Acidity Produced on Oxidation.

(a) All the oxidised oils were examined for acidity, this being determined by the fluorescein / methyl red method already described.

For each oxidised oil three acid values were determined; (a) the acidity of the oxidised oil as obtained; (b) the acidity of the oxidised oil less oil-insoluble sludge and (c) the acidity of the oxidised oil less insoluble and soluble sludge. These different acid values are here referred to as acidities of (a) "oxidised oil", (b) "clarified oil" and (c) "desludged oil". Acidity of the oxidised oil (a) may also be designated "total acid".

The results obtained are shown in Table 8 and Figs.16 to 20. It can be seen that the rate of acid formation is approximately constant, tending to decrease a little with time. Oil 1 differs from the others in that a more definite reduction of rate with time is evident.

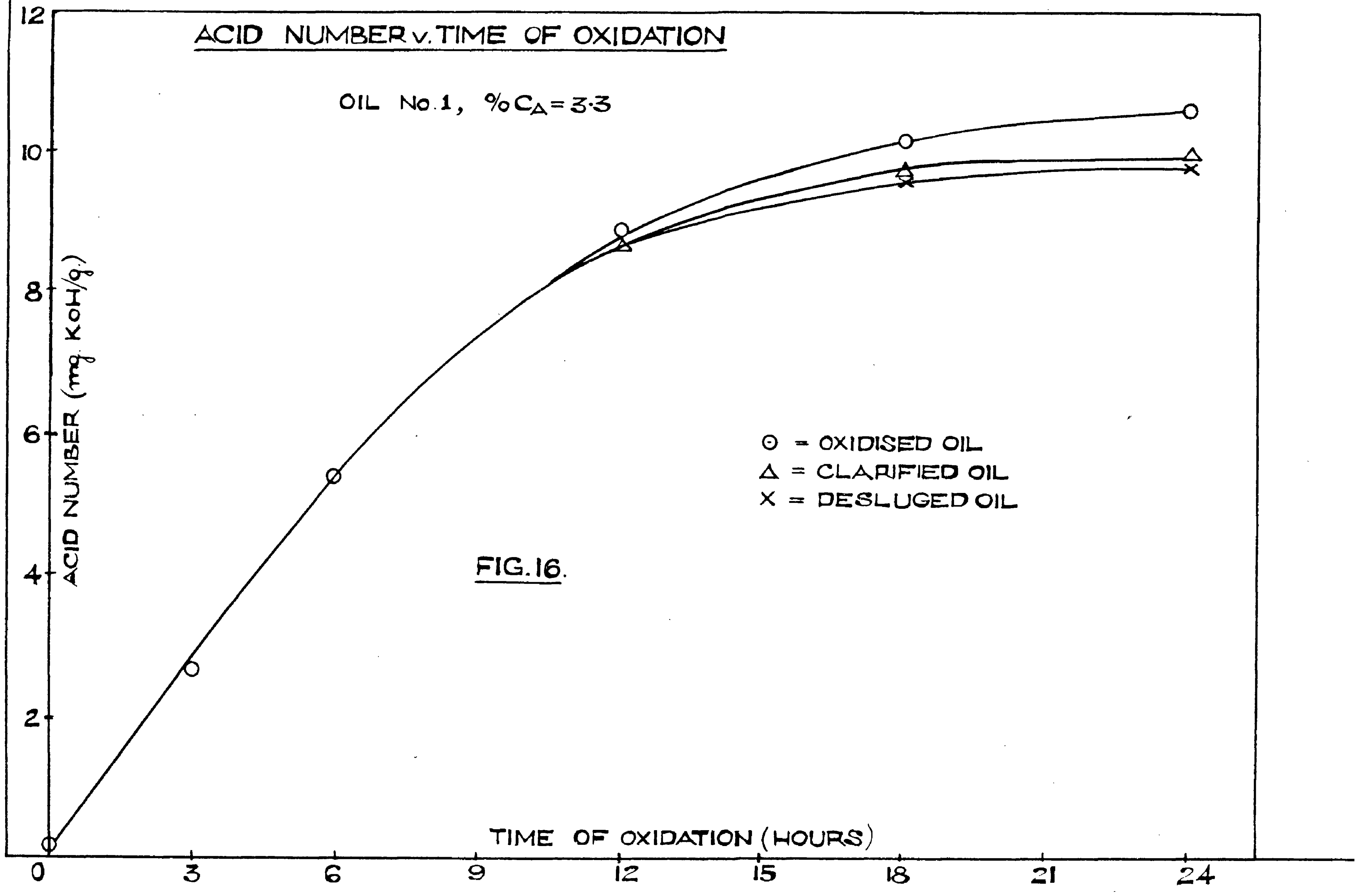
On comparing the <u>total</u> acid formed by the five oils no apparent relationship with composition is observed. Indeed four of the five oils have total acid numbers in the range 9.0 - 10.6 (mg.KOH/g.) at 24 hours oxidation. The exception is oil 2 with a total acid number less than 5.0.

However, acid values of the clarified and desludged

TABLE 8.

Acid (mg.KOH/g.) produced on oxidation

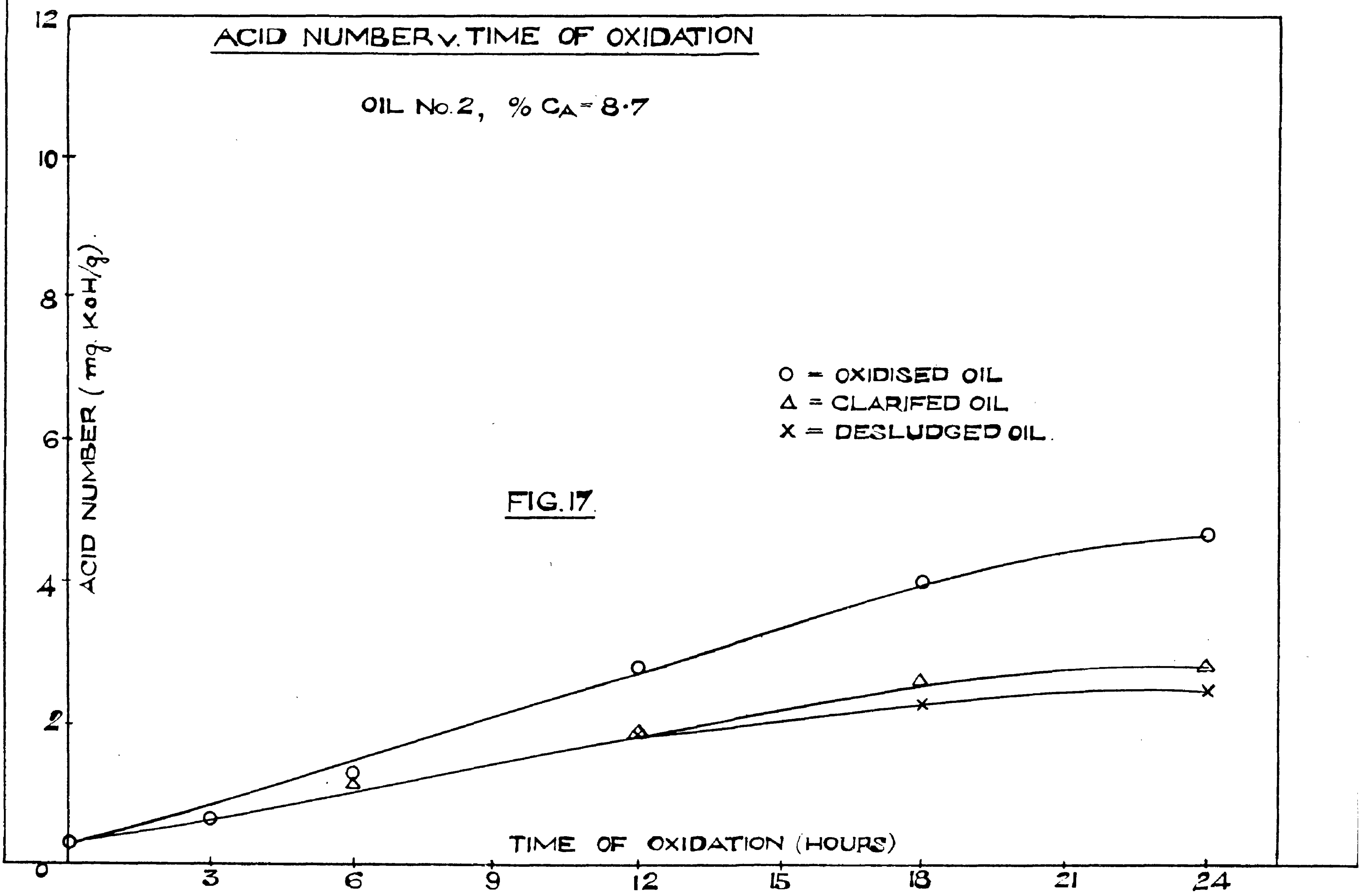
Oil Sample	State of Oil for Acidity Determination	Time of Oxidation (Hrs.) 0	3	6	12	18	24
No.1.	Oxidised	0.2	2.7	5.4	8.9	10.2	10.6
	Clarified	0.2	2.7	5.4	8.6	9.7	10.0
	Desludged	0.2	2.7	5.4	8.6	9.6	9.8
No.2.	Oxidised	0.3	0.6	1.3	2.8	4.0	4.7
	Clarified	0.3	0.6	1.1	1.8	2.6	2.8
	Desludged	0.3	0.6	1.1	1.8	2.3	2.5
No.3	Oxidised	0.3	1.3	2.9	6.0	7.7	9.2
	Clarified	0.3	1.3	2.9	5.4	6.8	7.7
	Desludged	0.3	1.3	2.9	5.2	6.5	7.4
No.4.	Oxidised	0.3	0.8	2.3	4.5	7.4	9.6
	Clarified	0.3	0.6	1.0	2.4	4.1	5.5
	Desludged	0.3	0.6	1.0	2.0	3.7	4.8
No.5.	Oxidised	0.3	2.2	3.4	5.5	7.4	9.0
	Clarified	0.3	0.5	1.2	1.8	2.3	2.8
	Desludged	0.3	0.5	0.7	1.5	1.5	1.8



ACID NUMBER v. TIME OF OXIDATION

OIL No.1, $\%C_A = 3{\cdot}3$

FIG.16.



ACID NUMBER v. TIME OF OXIDATION

OIL No. 2, % C_A = 8·7

FIG. 17.

ACID NUMBER v. TIME OF OXIDATION

OIL No 3. $\% C_A = 8{\cdot}9$

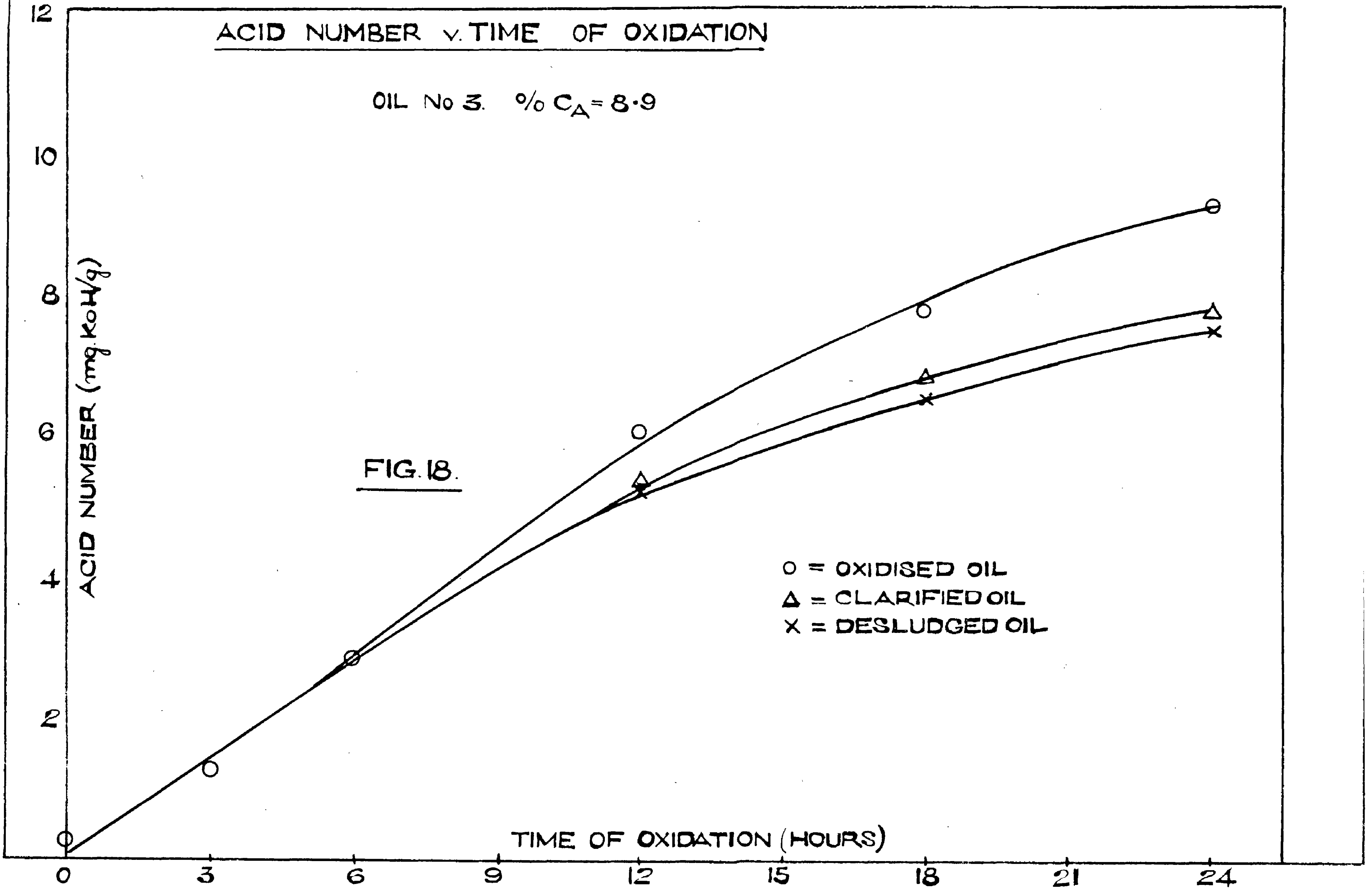
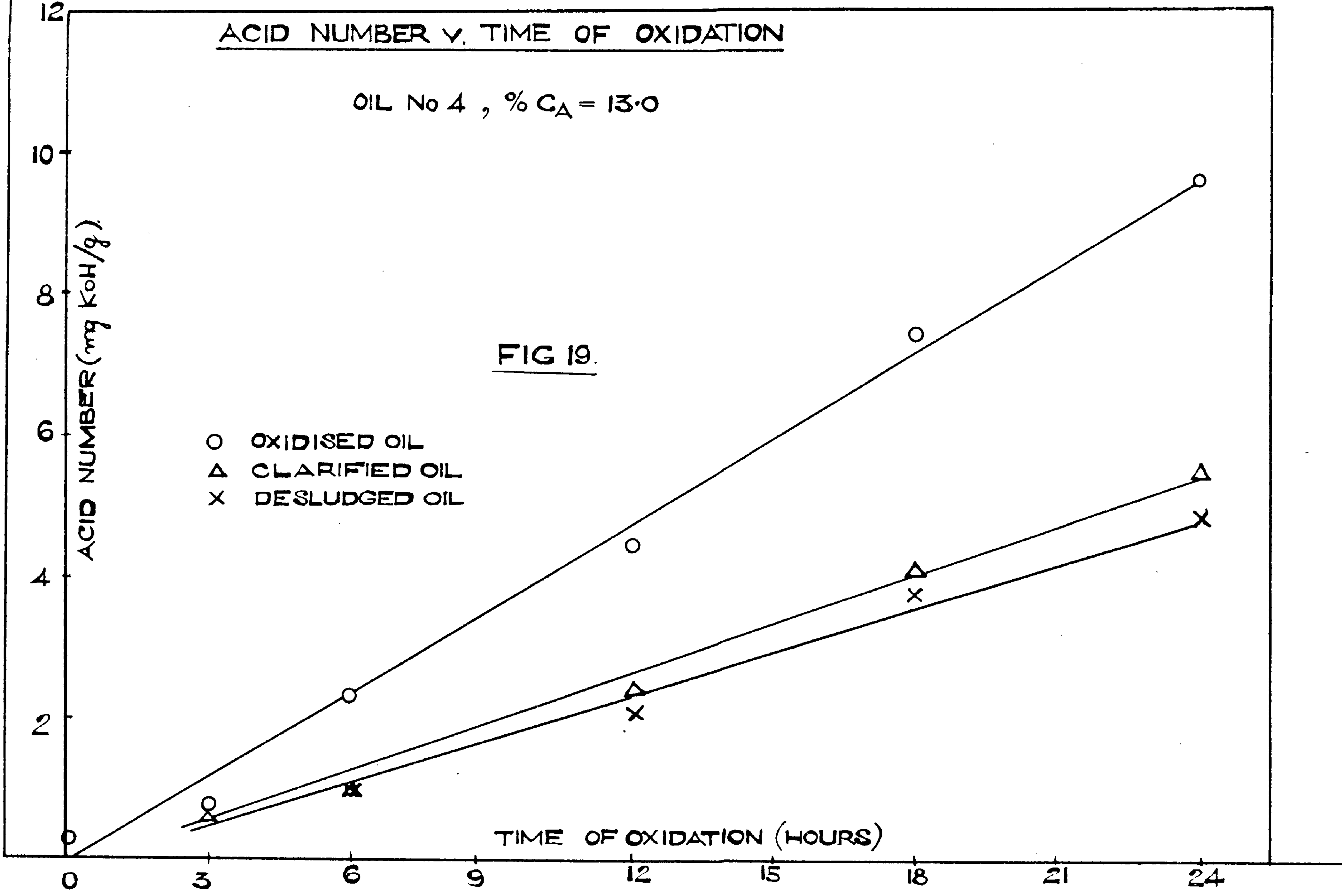


FIG. 18.



ACID NUMBER V. TIME OF OXIDATION

OIL No 4 , % C_A = 13·0

FIG 19.

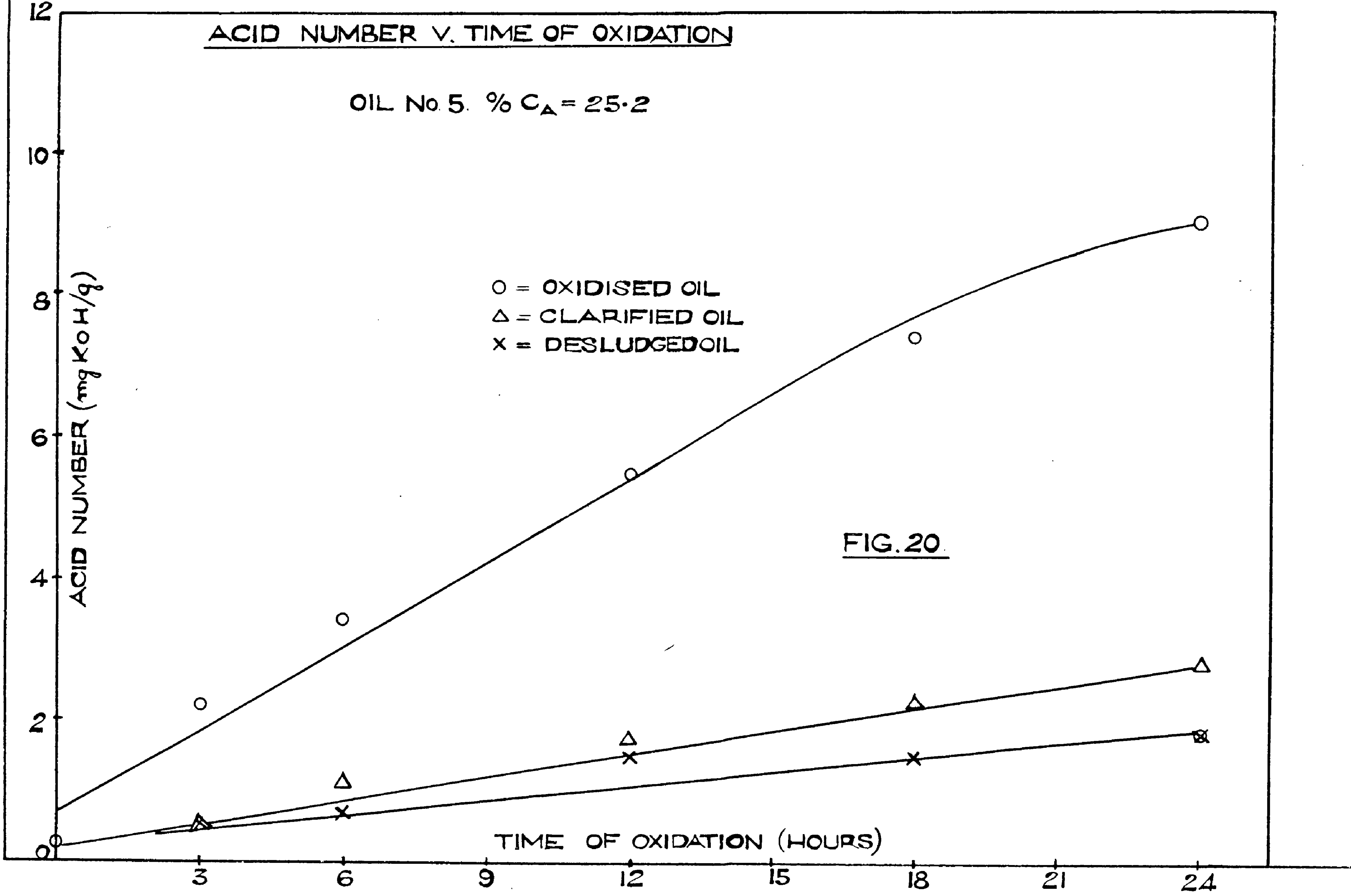

ACID NUMBER V. TIME OF OXIDATION
OIL No. 5. % C_A = 25·2
○ = OXIDISED OIL
△ = CLARIFIED OIL
× = DESLUDGEDOIL
ACID NUMBER (mg KOH/g)
TIME OF OXIDATION (HOURS)
0
2
4
6
8
10
12
3
6
9
12
15
18
21
24

FIG. 20

samples show a much greater difference and some semblance of a relationship may be observed. As may be expected clarified oils show less acidity than the original oxidised oils and desludged oils lower values still, indicating that both insoluble and soluble sludges are acidic in nature. Ventsel[89] reports that sludge has a higher acid number than the oil in which it is formed, and accordingly the acid number of a used oil is reduced by filtration.

The results also indicate that the removal of insoluble sludge produces a greater reduction in acid number of the oil than does removal of soluble sludge, even although, in some cases, a greater weight of soluble sludge has been removed.

The change in acid number due to removal of insoluble sludge shows an increase with increase of aromatic content of the original oil. In fact a plot of the difference in acid number at 24 hours between oxidised and clarified oils against % C_A proves to be linear. This, together with the fact that the content of insoluble sludge has already been shown to be proportional to % C_A suggests that the plot of the percentage weight of insoluble sludge at constant oxidation time, against acidity decrease on its removal may also be linear. This is shown to be so in Fig.21. The corresponding acidity change values for soluble sludge are also plotted.

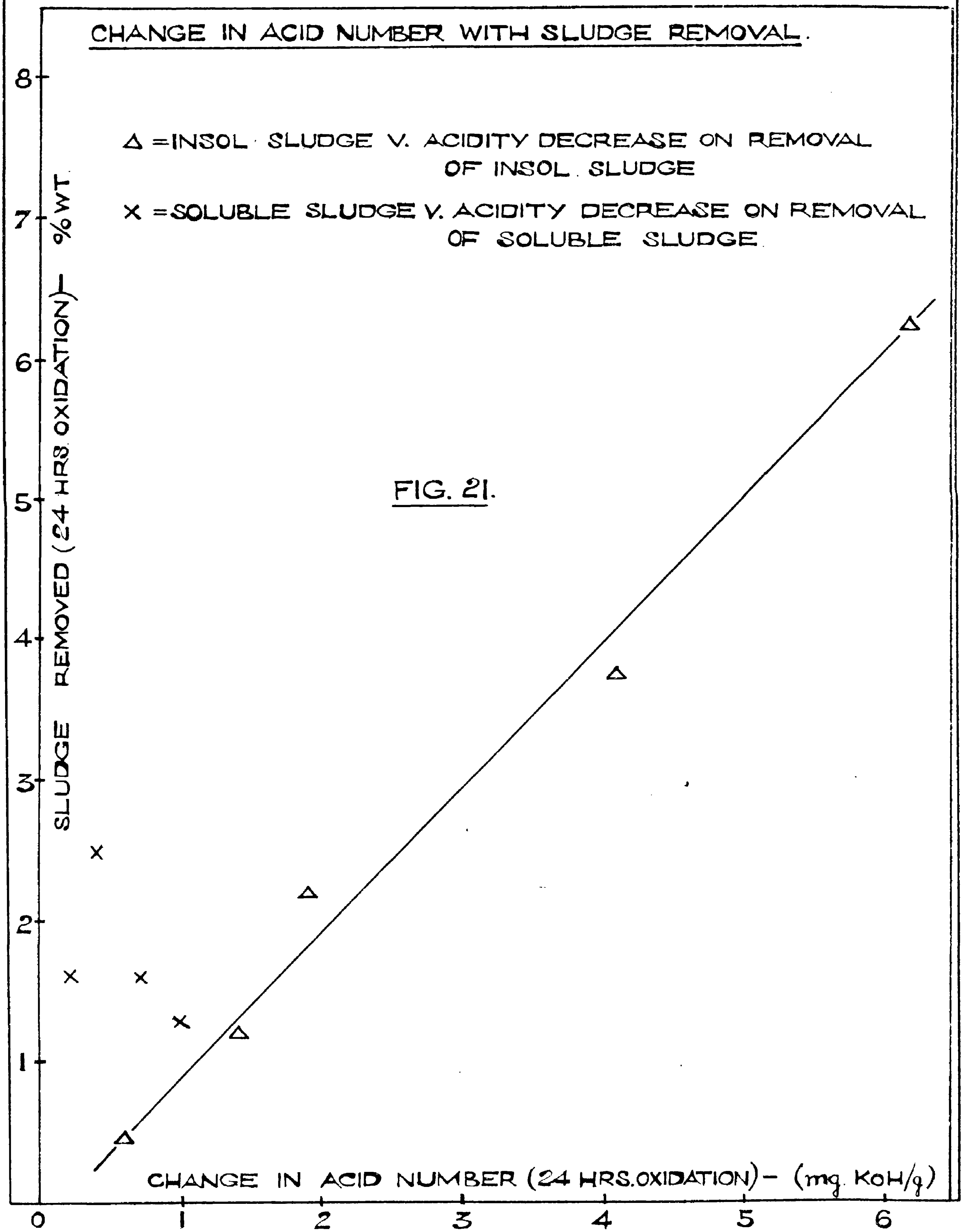


FIG. 21.

CHANGE IN ACID NUMBER WITH SLUDGE REMOVAL.

The linear relationship for insoluble sludge indicates that it may tend to a constant. The acidities of soluble and insoluble sludges have been calculated and are tabulated in Table 9. These results seem to indicate that the acidity of insoluble sludge passes through a maximum at some intermediate value of oxidation time between zero and 24 hours oxidation. The maximum is not definite for all oils and is rather doubtful due to the difficulty of obtaining accurate acidities at such low values. Results for Oils Nos.2 and 4, however, seem to confirm a maximum.

The maximum acidity for insoluble sludge is important in that a steady decrease in acidity with oxidation time, and no maximum, would infer that sludge was formed from acid. The presence of a true maximum suggests that sludge forms first and itself produces acids as oxidation progresses. Decrease of acidity after the maximum could certainly be explained as an acid ⟶ sludge reaction, but this is not considered as being very probable. The acidity/sludge relationship is no doubt very complex and the decrease in acidity of insoluble sludge could be caused by more than one factor. One which may influence the decrease on prolonged oxidation is progressive increase in molecular weight without a corresponding increase in the number of acid groups.

In the case of soluble sludge acid numbers are so low

TABLE 9

Acid Number of Sludge and Desludged Oil (mg.KOH/g.)

As_i = Acid number of insoluble sludge
As_s = Acid number of soluble sludge
A_o = Acid number of desludged oil.

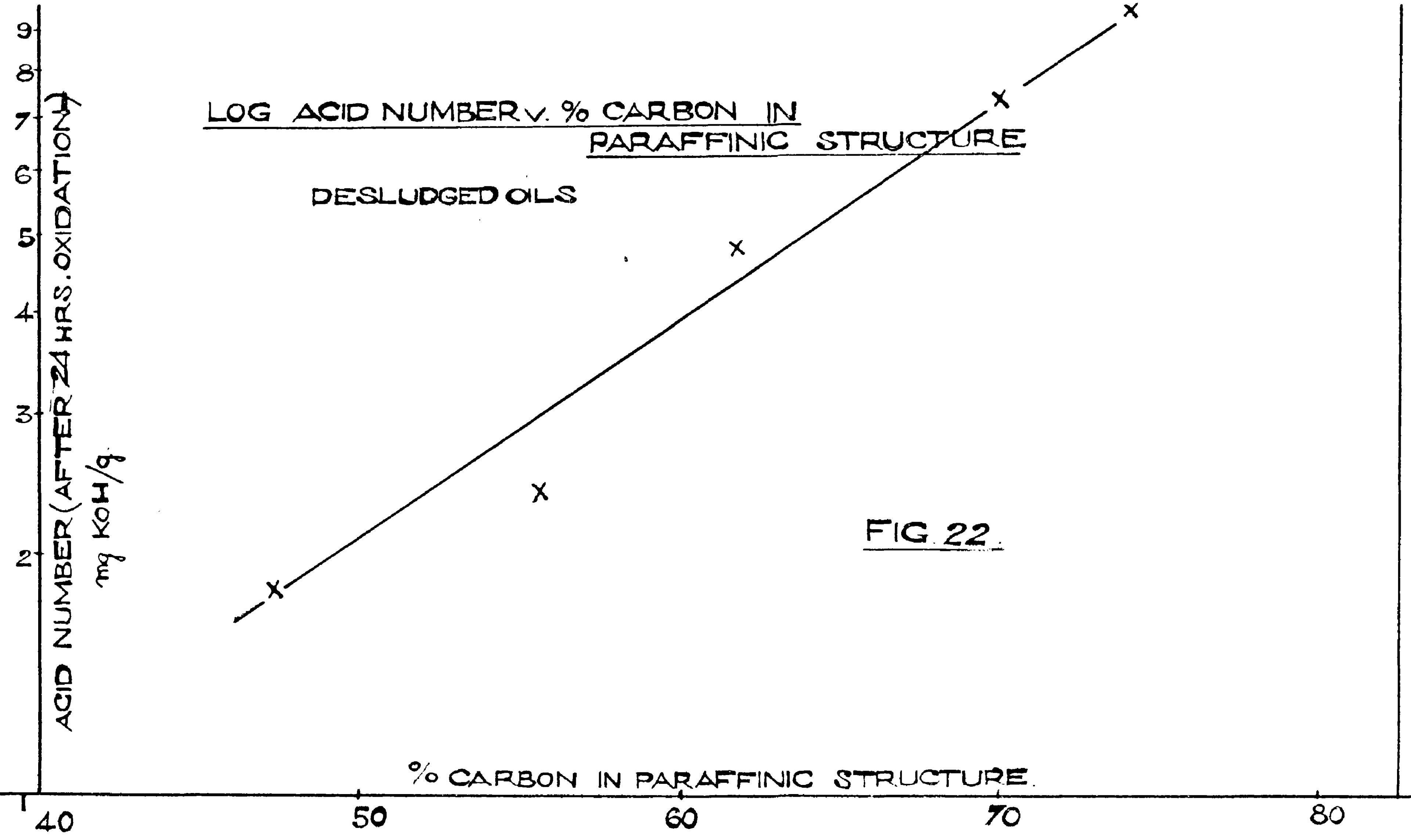
Sample	Time of Oxidation (Hrs.)					
	0	3	6	12	18	24
Oil No.1.						
As_i	-	-	-	300	250	150
As_s	-	-	-	-	20	13
A_o	0.2	2.7	5.4	8.6	9.6	9.8
Oil No.2.						
As_i	-	-	100	250	167	86
As_s	-	-	-	-	27	13
A_o	0.3	0.6	1.1	1.8	2.3	2.5
Oil No.3.						
As_i	-	-	-	300	225	125
As_s	-	-	-	40	27	12
A_o	0.3	1.3	2.9	5.2	6.5	7.4
Oil No.4.						
As_i	-	67	163	175	236	111
As_s	-	-	-	44	33	44
A_o	0.3	0.6	1.0	2.0	3.7	4.8
Oil No.5.						
As_i	-	283	244	247	240	98
As_s	-	-	83	25	61	77
A_o	0.3	0.5	0.7	1.5	1.5	1.8

as to make accuracy doubtful. The acidity of soluble sludge is much less than that of insoluble sludge but the acidity *vs.* time relationship is seen to follow the same general pattern.

Table 9 indicates that the acidity of sludge measured on the basis of mg.KOH/g. of *sludge* is very much higher than the same measurement for an oxidised oil; this being particularly true of insoluble sludge. The acidity of the sludge measured as a percentage of total acidity of the oxidised oil is not, however, so high. Distribution of acidity among desludged oil, soluble sludge and insoluble sludge is given in Table 10. It can be seen that, in most cases, the oil contributes more acidity to the oil/sludge mixture than do the sludges. An exception is oil No.5 (and to some extent oil No.4) in which large amounts of sludge are produced.

Fig.22 shows the plot of log acid number against % C_P (for 24 hours oxidation) for desludged oils. It may be seen to be linear. The desludged oil shows a 90% increase in acidity for every 10% increase in C_P.

Acidity of the desludged oils (at a given oxidation time) would thus appear to be related to composition of the oil, viz. paraffinic content. This is understandable when it is considered that paraffins have a greater tendency to form acids than any other type of hydrocarbon.



LOG ACID NUMBER v. % CARBON IN PARAFFINIC STRUCTURE

DESLUDGED OILS

FIG. 22.

TABLE 10

Acidity Distribution

(% w/w of total acidity in terms of mg.KOH/g.)

Sample	Time of Oxidation (Hrs.)					
	0	3	6	12	18	24
Oil No.1.						
Desludged oil	100	100	100	96.5	94.1	92.5
Insoluble sludge	-	-	-	3.5	4.9	5.7
Soluble sludge	-	-	-	-	1.0	1.8
Oil No.2.						
Desludged oil	100	100	84.5	64.3	57.5	53.2
Insoluble sludge	-	-	15.5	35.7	35.0	40.5
Soluble sludge	-	-	-	-	7.5	6.3
Oil No.3.						
Desludged oil	100	100	100	86.6	84.5	80.5
Insoluble sludge	-	-	-	10.0	11.7	16.3
Soluble sludge	-	-	-	3.4	3.8	3.2
Oil No.4.						
Desludged oil	100	75.0	43.5	44.5	50.0	50.0
Insoluble sludge	-	25.0	56.5	46.7	44.5	42.7
Soluble sludge	-	-	-	8.8	5.5	7.3
Oil No.5.						
Desludged oil	100	22.7	20.6	27.3	20.3	20.0
Insoluble sludge	-	77.3	64.7	67.3	69.0	69.0
Soluble sludge	-	-	14.7	5.4	10.7	11.0

It is also evident that total acidity as such bears little or no relationship to composition of the oil, unless sludge values are taken into account. Total acid number, however, may be a valuable characteristic for an oxidised oil, combining as it does the effect of sludge formation and acid formation in one determination.

VIII.5. Carbon Residue Increase and Viscosity Ratio.

No attempt was made to determine carbon residue increase and viscosity ratio at different oxidation times. These quantities are part of the Institute of Petroleum oxidation test, and by definition of that test, should be determined at 12 hours oxidation.

Aitken[75], however, has found that, with a refined lubricating oil, carbon residue increase plotted against a base of time produces a linear graph.

Table 6 shows the results obtained at 12 hours oxidation for the five oils oxidised. If oil No.1 is neglected an increase in both quantities with aromatic content of the oil is apparent.

CHAPTER IX

THE EFFECT OF OIL COMPOSITION ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED, ON OXIDATION UNDER THE CONDITIONS OF THE STANDARD TEST FOR LUBRICATING OILS

II - OIL FRACTIONS OBTAINED BY SOLVENT EXTRACTION

Solvent Extraction of Oils.
Analysis of Raffinates.
Analysis of Extracts.
The Effect of the Extraction Process.
Absorption of Oxygen.
Sludge Produced on Oxidation.
Acidity Produced on Oxidation.
The Effect of Structure on Carbon Residue Increase
The Effect of Oil Composition on Viscosity Ratio.

CHAPTER IX

THE EFFECT OF OIL COMPOSITION ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED, ON OXIDATION UNDER THE CONDITIONS OF THE STANDARD TEST FOR LUBRICATING OILS.

II. OIL FRACTIONS OBTAINED BY SOLVENT EXTRACTION.

IX.1. Since the amounts of sludge and acid produced by the oxidation of lubricating oil under the conditions of the I P test appear to be related to the oil composition, it was decided to study this further by preparing several fractions of different composition from the same crude source. Three of the oils (Nos.3, 4 and 5) were used and fractionation was effected by furfural extraction.

IX.2. Solvent Extraction of Oils.

The three oils separated into fractions of different composition were No.3 (% C_A = 8.9), No.4 (% C_A = 13.0) and No.5 (% C_A = 25.2). The method employed was as follows.

Equal volumes of oil and reagent grade furfural were thoroughly shaken together in a separating funnel and allowed to stand for at least three hours. The phases were then separated by running off the lower extract. Solvent was removed from the extract by distillation at atmospheric pressure followed by steam distillation. The steam distillation was continued until the distillate produced a negative response to Youngsberg's test for furfural[90]. Youngsberg discovered that traces of an aqueous solution of furfural produce a red colouration when added to a solution of aniline in glacial acetic acid. Water resulting from the steam distillation was removed by normal distillation. This treatment produced an extract containing less than 0.00001 % furfural[90].

A portion of the raffinate was then taken and the solvent removed by steam distillation alone, this being possible because of the small amount of solvent taken into solution by the raffinate.

The remainder of the raffinate was again shaken up with its own volume of furfural and left to settle out. Extract and raffinate were then treated as before. Six raffinates were obtained in this way for oils 3 and 4, and seven for oil No.5. Final traces of water were removed from extracts and raffinates by treatment with anhydrous sodium sulphate.

IX.3. Analysis of Raffinates.

Refractive index and density, both at 20°C, were determined for each raffinate. Molecular weights were also measured, by the ebullioscopic method. The results obtained are shown in Tables 11, 12 and 13.

TABLE 11.

Raffinates of Oil 3.

Oil Sample		n	d	M
Original oil	R_o	1.4898	0.8845	525
1st Stage Raffinate	R_1	1.4812	0.8690	538
2nd " "	R_2	1.4794	0.8649	542
3rd " "	R_3	1.4780	0.8639	545
4th " "	R_4	1.4771	0.8623	545
5th " "	R_5	1.4763	0.8610	550
6th " "	R_6	1.4759	0.8605	550

TABLE 12.

Raffinates of Oil 4.

Original oil	R_o	1.5016	0.9057	476
1st Stage Raffinate	R_1	1.4914	0.8891	499
2nd " "	R_2	1.4871	0.8810	507
3rd " "	R_3	1.4820	0.8733	513
4th " "	R_4	1.4780	0.8650	517
5th " "	R_5	1.4750	0.8570	520
6th " "	R_6	1.4740	0.8548	520

TABLE 13.

Raffinates of Oil 5.

Original oil	R_o	1.5275	0.9453	410
1st Stage Raffinate	R_1	1.5152	0.9296	438
2nd " "	R_2	1.5082	0.9200	445
3rd " "	R_3	1.5043	0.9147	448
4th " "	R_4	1.5020	0.9111	453
5th " "	R_5	1.5001	0.9085	453
6th " "	R_6	1.4986	0.9061	458
7th " "	R_7	1.4972	0.9043	462

The n-d-M method of structural group analysis was employed for analysis of the raffinates. Tables 14-16 show the results.

TABLE 14.

n-d-M Analysis of Oil 3 Raffinates

Sample	% C_A	% C_N	% C_P	R_A	R_N	$\frac{\% C_P}{\% C_N}$
R_0	8.9	21.3	69.8	0.56	2.11	3.28
R_1	5.8	21.8	72.4	0.35	1.85	3.32
R_2	4.6	21.6	73.8	0.30	1.75	3.42
R_3	3.2	22.8	74.0	0.25	1.75	3.24
R_4	2.7	23.1	74.2	0.25	1.75	3.21
R_5	2.3	22.8	74.9	0.20	1.80	3.28
R_6	2.0	24.4	75.1	0.10	1.85	3.08

TABLE 15.

n-d-M Analysis of Oil 4 Raffinates

R_0	13.0	25.2	61.8	0.77	2.33	2.45
R_1	8.0	28.5	63.5	0.55	2.25	2.23
R_2	5.5	28.0	66.5	0.40	2.10	2.37
R_3	4.5	28.2	67.3	0.25	2.10	2.38
R_4	3.2	25.0	71.8	0.15	1.95	2.87
R_5	2.6	21.9	75.5	0.15	1.70	3.44
R_6	2.2	21.8	76.0	0.15	1.55	3.48

TABLE 16

n-d-M Analysis of Oil 5 Raffinates

R_0	25.2	27.4	47.4	1.30	2.19	1.73
R_1	18.2	32.7	49.1	1.00	2.48	1.50
R_2	13.5	35.5	51.0	0.82	2.60	1.44
R_3	12.5	35.5	52.0	0.70	2.64	1.46
R_4	11.5	35.5	53.0	0.60	2.71	1.49
R_5	10.3	35.7	54.0	0.53	2.76	1.51
R_6	9.0	36.5	54.5	0.48	2.77	1.49
R_7	8.7	36.5	54.8	0.46	2.79	1.50

IX.4. Analysis of Extracts.

Only the first extract from each oil was completely dried, ready for further investigation. A simple method of analysis was required and the density - density coefficient method of Lipkin and Martin[91] was used. Ideally this method applies only to mixtures of aromatics with alkyl side chains and was primarily intended to determine the proportion of rings to chains. Aromatic fractions containing naphthene rings are known to cause low results, therefore the method is not entirely reliable in this case, since naphthene rings are, no doubt, present to a small extent in the extracts. Nevertheless for the purpose required here the method was considered suitable. The n-d-M method could not be applied since refractive indices were impossible to measure on the dark, viscous liquids obtained.

For the analysis only density and density coefficients had to be determined, application of these values to a chart giving values for weight percent aromatic rings, number of rings per molecule and molecular weight. Three graphs were available, viz. for condensed ring aromatics, for non-condensed ring aromatics and for mixtures having an equal volume of these two types. Lipkin and Martin recommend the last graph for higher boiling straight-run products because "it is believed that both condensed and non-condensed rings may be present."

Densities were determined at 20°C and at another temperature (100°F = 37.8°C). Due to the very viscous nature of the extracts the pycnometer method, used for other oils and raffinates, was unsuitable. Since densities were greater than unity in all cases the following procedure was employed:-

A specific gravity bottle was weighed, first empty, then filled with distilled water at 20°C and finally filled with distilled water at 37.8°C. It was then re-weighed empty, half-filled with extract, weighed, topped up with distilled water, placed in a thermostat bath at 20°C and again weighed. The bottle was finally placed in a water bath at 37.8°C and then weighed. From this data densities and density coefficients were calculated.

The results obtained by this procedure and the analyses from the graph of Lipkin and Martin are shown in Table 17.

TABLE 17

Analyses of Extracts

Source of Extract	Density 20°C	Density 37.8°C	Density Coefficient	% C_A	Molecular Weight
Oil 3	1.0157	1.0037	68.5×10^{-5}	69	280
Oil 4	1.0385	1.0259	70.8×10^{-5}	80	240
Oil 5	1.0621	1.0491	73.1×10^{-5}	91	180

IX.5. The Effect of the Extraction Process

It is not the purpose of this work to study the furfural extraction as such, as it was only intended to provided a means of obtaining a few fractions from a parent oil. At the same time a brief summary of the results shown in Tables 14-16 would appear to be valid.

Aromatic content of the raffinates decreases stage by stage, showing a marked decrease from R_o (original oil) to R_1 and diminishing progressively. Thus the quantity of aromatic material removed at each stage would seem to be a function of the aromatic content at the beginning of that stage.

The percentage of carbon in paraffinic material increases as extraction proceeds, but % C_N is rather more irregular. It shows an increase with oils 3 and 5, but with oil No.4, after an increase in the first stage, it gradually falls off. Again with the mean number of naphthenic rings per molecule (R_N) we find an increase only in the case of oil 5, the other two oils showing a decrease from stage to stage. This behaviour indicates that a certain amount of naphthenic or naphthenic/aromatic material is soluble in furfural. Because of this the ratio of % C_P to % C_N tends to vary considerably, except for oil 5 where a much narrower range of values is apparent.

Molecular weights of the raffinates increase as extraction proceeds, indicating that material lower in molecular weight has been removed. This is confirmed by the results of the extract analysis.

IX.6. Absorption of Oxygen

(a) Volumes of oxygen absorbed by the raffinates on 12 hours oxidation are shown in Table 18. The values for the three original oils are also included. Since the absorption/time graphs approximated in all cases to a straight line comparison of ml. O_2 absorbed at 12 hours is synonymous with comparison of absorption rates. For this reason volumes of oxygen absorbed are referred to when actual rates are implied.

TABLE 18

Oxygen Absorbed by Raffinates.

Sample	Oxygen Absorbed (mls.) at 12 Hours Oxidation					
	Oil 3	% C_A	Oil 4	% C_A	Oil 5	% C_A
R_0	520	8.9	400	13.0	820	25.2
R_1	740	5.8	635	8.0	650	18.2
R_2	880	4.6	715	5.5	435	13.5
R_3	1100	3.2	960	4.5	400	12.5
R_4	1280	2.7	1180	3.2	375	11.5
R_5	1320	2.3	1200	2.6	440	10.3
R_6	1340	2.0	1220	2.2	480	9.0
R_7	-		-		550	8.7

It is seen from Table 18 that the fractions from oils 3 and 4 show increased rates of absorption with decrease of aromatic content. Oil 5 gives an initial decrease with a subsequent rise in the case of the last three raffinates (R_5, R_6 and R_7). These results appear to have no definite relationship to composition of the raffinates, only indicating a general trend towards increased reactivity with decrease of aromatic content. Only oil 5 shows a minimum absorption (at about 12% C_A). This minimum effect or 'optimum aromaticity' was mentioned in the previous chapter as having been observed by von Fuchs and Diamond[53] and Fenske[48] with lubricating oil blends.

If, however, oxygen absorbed at 12 hours oxidation is plotted against % C_A for all raffinates and for the three original oils, then an interesting curve is obtained. This is shown in Fig.23. Here a definite correlation between absorption rate and oil composition is apparent. This figure indicates that at low values of C_A absorption rates are high, decreasing to a minimum at about 12% C_A, then increasing with increasing aromatic content. Unfortunately only oil 5 covered a sufficient range of aromatic content to produce a true minimum 'per se'.' The following evidence serves, in some degree, to confirm that less initial refining of oils 3 and 4 would have produced the same effect.

ABSORPTION OF OXYGEN BY RAFFINATES v. %C_A

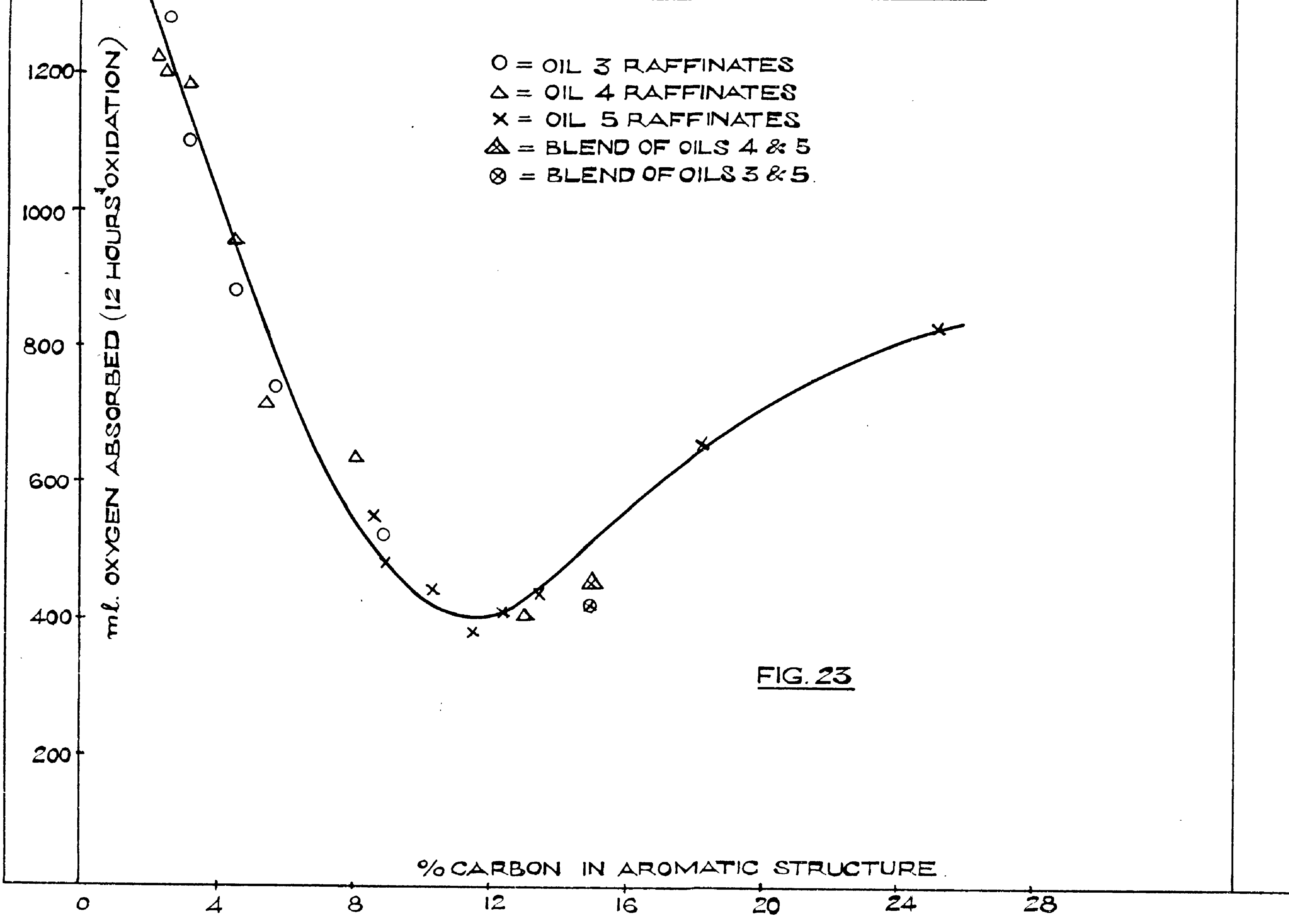


FIG. 23

Blends were produced of original, unextracted oils 3 and 5, and oils 4 and 5 such that the calculated aromatic content in each case was 15%. These blends were then oxidised for 12 hours and the absorption measured. The values are shown plotted in Fig.23 and are seen to agree fairly well with the curve obtained from the raffinates.

This 'optimum aromaticity' was also observed by Aitken[75] who found a minimum absorption at about 10% C_A for a heterogeneous selection of oils of different origin.

(b) It can be assumed, in view of this evidence, that somewhere in the region of 10-12% C_A a change in the oxidation-absorption mechanism takes place during oxidation at 200°C. Many workers have observed great differences in the rate of oxygen absorption among the three main types of hydrocarbons. George and Robertson[64] and Booser and Fenske[56] show in particular that mixtures of various groups of hydrocarbons can show different characteristics where rate of oxidation is concerned. This can be summarised as follows:

(i) The rate of oxidation may be the arithmetic mean of the rates of oxidation of the components.

(ii) The rate of oxidation may drop appreciably below the arithmetic mean, thus revealing an inhibiting effect of one of the components on the other.

(iii) The rate may be higher than the arithmetic mean: this may be called <u>stimulated oxidation</u>.

Obviously cases (i), (ii) and (iii) refer more to binary mixtures, or at most to simple mixtures of a few hydrocarbons, but at the same time must be applicable to more complicated petroleum fractions. An explanation of the minimum reactivity found at about 12% C_A can be advanced on the basis of these findings.

At low values of C_A (less than 12%) it may be assumed that inhibition is brought about by aromatic hydroxyl compounds produced on oxidation. It will be shown later that little or no sludge is produced by these raffinates with low aromatic content. If the argument regarding the role of aromatic hydroxyl compounds in sludge formation (VIII.3.) is correct then only fairly small amounts of phenolic compounds could be present. Several workers have shown, however, that small amounts of inhibitor may influence greatly the reactivity of an oil. Larsen, Thorpe and Armfield[43] attributed the extreme stability of naphthalene aromatics to the effectiveness, as inhibitors, of the naphthols produced on oxidation. They also found that naphthalene derivatives added to other substances produced a stabilising effect. Chernozhukov[92] and Chernozhukov and Krein[55,93] also noted that small amounts of naphthalene, phenanthrene and anthracene produced a marked improvement on the stability of a paraffinic oil.

It would appear, then, that, up to 12% C_A, the decrease in reactivity might well be due to a progressive increase of inhibition caused by increasing content of aromatic material.

The increased activity above this critical value of 12% C_A is probably produced by stimulated oxidation of aromatics by the presence of other hydrocarbons. These effects have been discussed by George and Robertson[64]. Along with this stimulation there is probably a natural increase due to the increase in the number of α-carbon atoms in substituted aromatics. This has been shown by Stephens[45], George and Robertson[64] and Booser and Fenske[56] to give increased reactivity.

The 'optimum aromaticity' producing a minimum absorption is therefore probably due, on the one hand (below 12% C_A) to an increase in inhibition by aromatics on the oxidation of the other hydrocarbon types, and on the other hand (above 12% C_A) to the aromatics being preferentially oxidised. It can be assumed that the inhibition effect on paraffinic and naphthenic material still persists above the critical aromatic value.

(c) Oxygen absorbed on oxidation of extracts.

One extract from each oil was prepared and analysed as described previously. These extracts were oxidised for 12 hours in a similar manner to the raffinate fractions and the absorption figures obtained are shown in Table 19. These results are not shown plotted in Fig.23 but the absorption rates of these highly aromatic fractions were rather lower than would be expected on consideration of the curve shown in Fig.23.

TABLE 19

Oxygen Absorbed by Extracts.

Source of Extract	Oxygen Absorbed in 12 Hours.	$\%C_A$
Oil 3	475 mls.	69
Oil 4	505 mls.	80
Oil 5	620 mls.	91

IX.7. Sludge Produced on Oxidation.

Determinations of total sludge, oil-insoluble sludge and oil-soluble sludge were made on all the oxidised raffinates. The values obtained are shown in Table 20.

It was immediately apparent that, whereas original oils 4 and 5 produce more insoluble than soluble sludge the oxidised raffinates from these oils show the opposite effect. This is more obviously portrayed in Figs.24 to 26 which show sludge plotted against % C_A. Oil 3 and its raffinates show more soluble than insoluble sludge in all cases.

TABLE 20.

Sludge produced by Raffinates on 12 hrs. oxidation

Sample	Type of Sludge	Sludge % wt.		
		Oil 3	Oil 4	Oil 5
R_o	Soluble	0.30	0.60	0.60
	Insoluble	0.10	0.80	0.90
R_1	Soluble	0.25	0.50	0.50
	Insoluble	0.05	0.40	0.70
R_2	Soluble	0.20	0.35	0.40
	Insoluble	trace	0.20	0.55
R_3	Soluble	0.15	0.30	0.35
	Insoluble	-	-	0.45
R_4	Soluble	0.12	0.25	0.40
	Insoluble	-	-	0.30
R_5	Soluble	0.10	0.20	0.35
	Insoluble	-	-	0.25
R_6	Soluble	0.07	0.15	0.30
	Insoluble	-	-	0.20
R_7	Soluble	-	-	0.20
	Insoluble	-	-	0.10

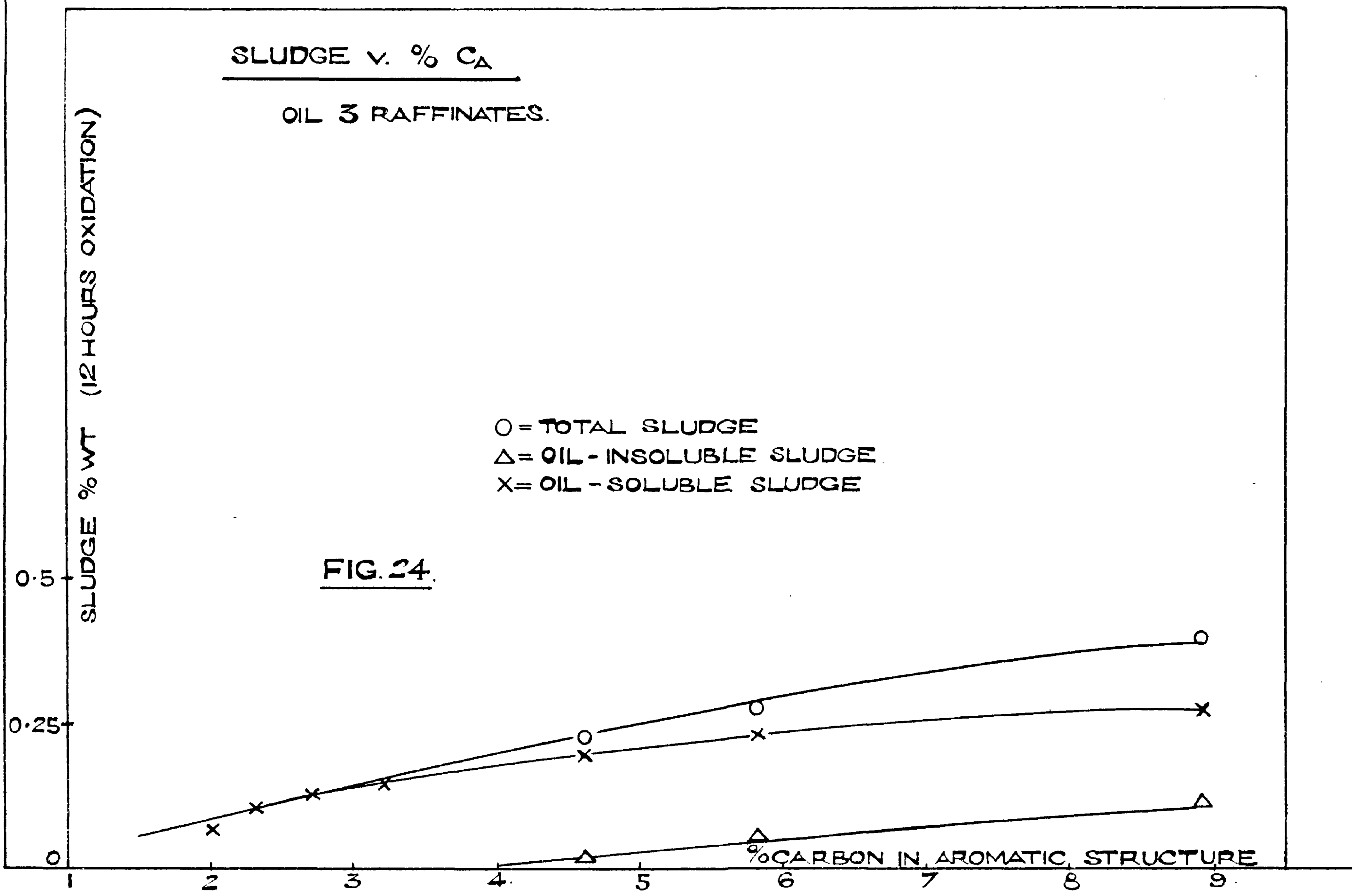
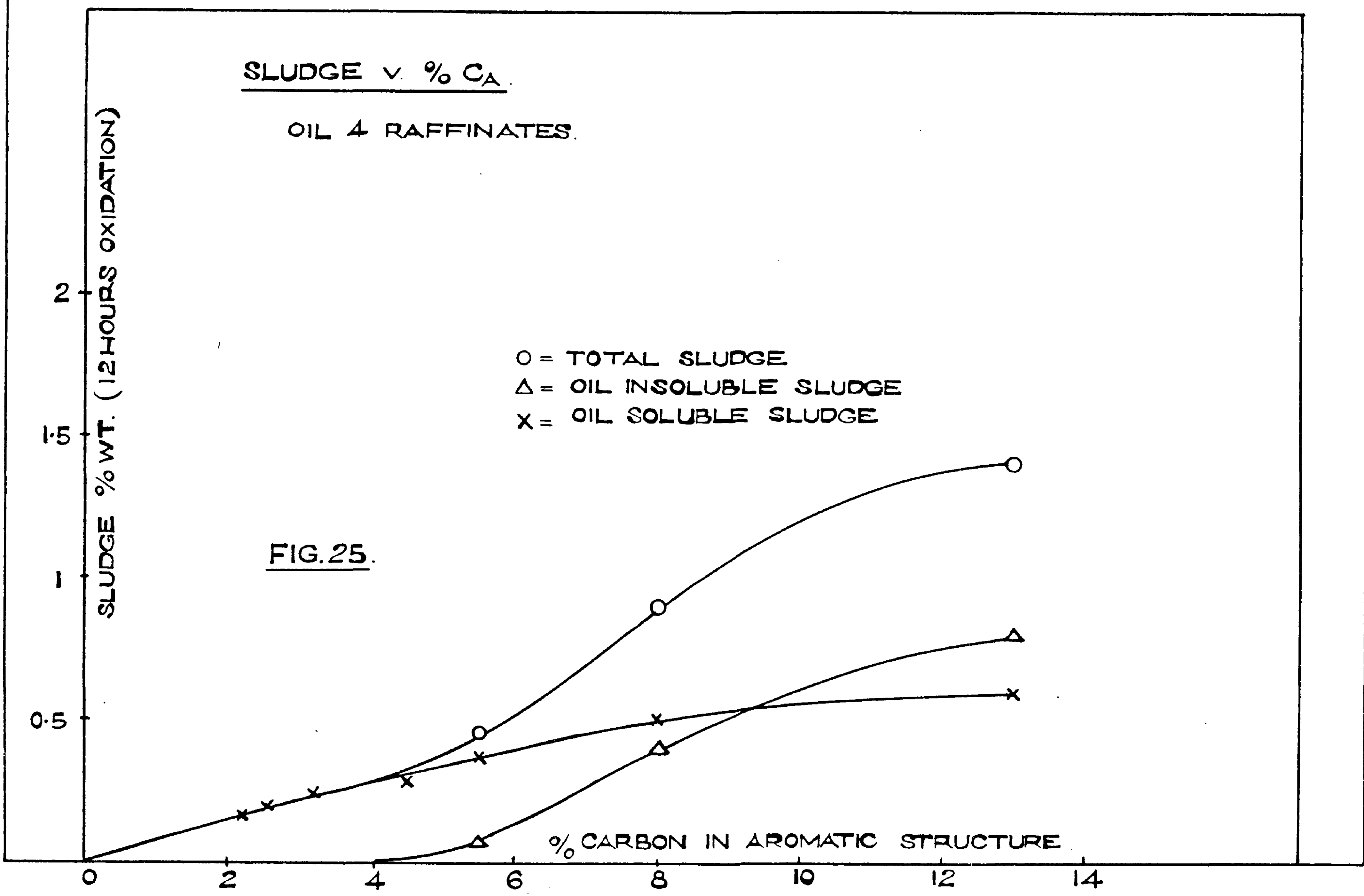


FIG. 24.

SLUDGE v. % C_A
OIL 3 RAFFINATES.
O = TOTAL SLUDGE
△ = OIL - INSOLUBLE SLUDGE
X = OIL - SOLUBLE SLUDGE
SLUDGE % WT (12 HOURS OXIDATION)
0·5
0·25
0
%CARBON IN AROMATIC STRUCTURE
1
2
3
4
5
6
7
8
9



SLUDGE v. % C_A.

OIL 4 RAFFINATES.

FIG. 25.

The general trend from this work is that total sludge increases with aromatic content in a more or less linear fashion. Distribution of soluble and insoluble sludge also varies with aromatic content. Oils of higher aromatic content yield more insoluble than soluble sludge while very low aromatic oils produce no insoluble sludge at all.

It may be stated very generally that for 12 hours oxidation under the standard conditions of the I P test;

1. Total sludge increases with increasing aromatic content
2. The proportion of oil-soluble sludge decreases with increasing aromatic content.
3. Oil-insoluble sludge is not produced with very low aromatic oils, but does appear as % C_A increases to about 4 %.

This work confirms the results obtained with Oils 1-5 described in section VIII.3., but gives no further correlation between distribution of sludge (soluble and insoluble) and structure of the oil. For this reason the discussion in VIII.3. applies also to the results presented here.

IX.8. Acidity Produced on Oxidation.

It was initially proposed to determine the acidities of all the oxidised fractions in a similar manner to that reported in VIII.4., viz. acid values of oxidised oil, clarified oil and desludged oil. The raffinates, however, being progressively more paraffinic in nature produced less sludge than the three original oils. As a result it was found that acid values were, in most cases, very similar, regardless of whether sludge had been removed or not. There was thus insufficient difference in the three possible acid values for the results to be given any significant interpretation.

The only results reported are acid values of the totally desludged raffinates, and these are shown in Table 21. As can be seen in Figs.27 and 28 a straight line is obtained in each case by plotting log acid number against % C_P. This is a similar result to that obtained with the five original unextracted oils and serves to confirm the relationship between acid value and composition of the oil.

TABLE 21.

Acid Values of Desludged Raffinates

Sample	Acid Number (mg.KOH/gm.)		
	Oil 3	Oil 4	Oil 5
R_0	9.1	9.4	4.8
R_1	9.0	9.2	4.6
R_2	8.2	6.2	4.2
R_3	8.2	4.0	3.8
R_4	7.8	3.9	2.8
R_5	7.2	2.4	2.4
R_6	5.4	2.0	2.0
R_7	-	-	1.5

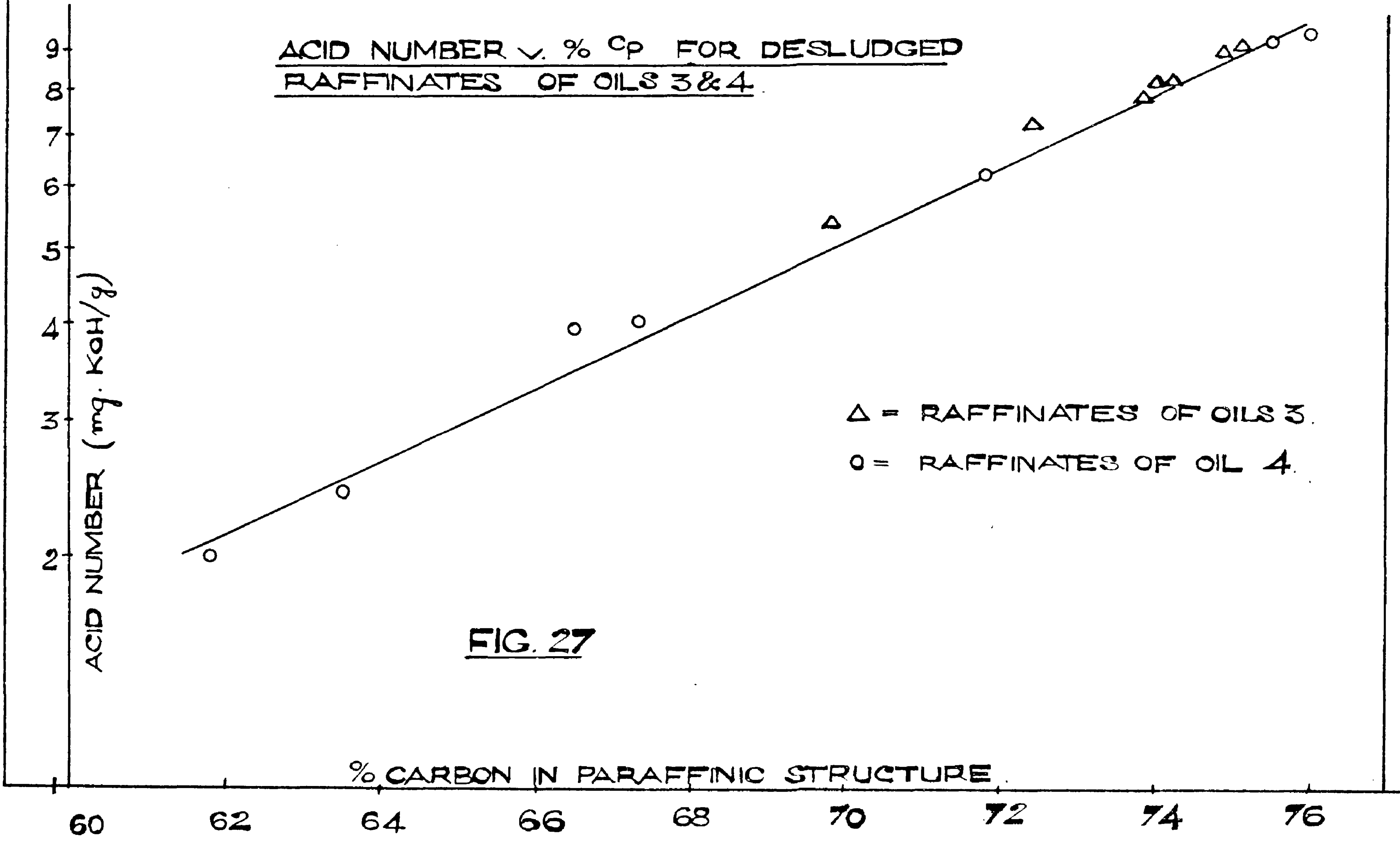


FIG. 27

ACID NUMBER v. % Cp FOR DESLUDGED RAFFINATES OF OILS 3&4
Δ = RAFFINATES OF OILS 3
o = RAFFINATES OF OIL 4
ACID NUMBER (mg. KOH/g)
9
8
7
6
5
4
3
2
% CARBON IN PARAFFINIC STRUCTURE
60
62
64
66
68
70
72
74
76

ACID NUMBER v % C_P FOR DESLUDGED RAFFINATES OIL 5

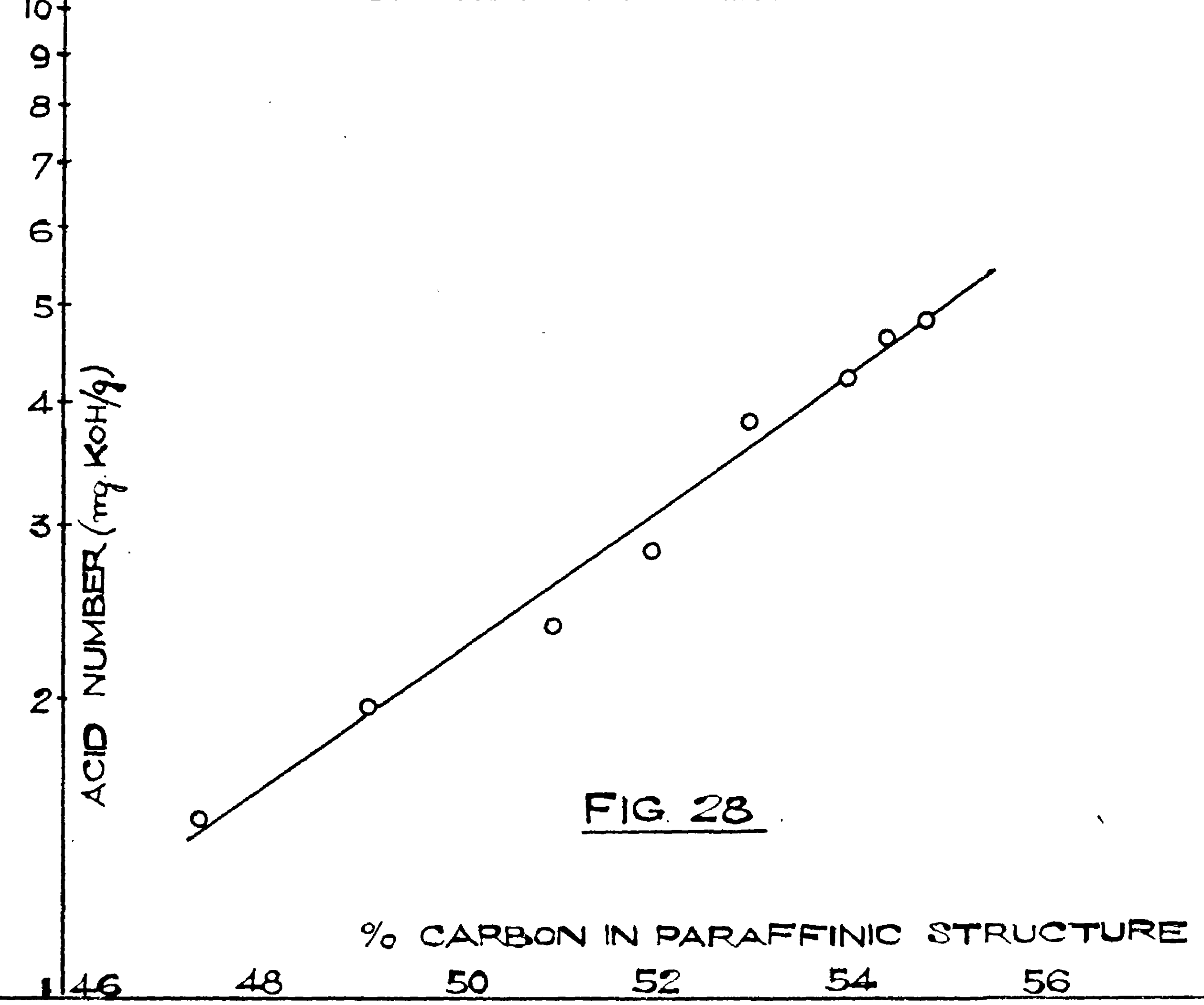


FIG. 28

It is seen that although log acid number of desludged oil is related to C_P a different slope is obtained in most cases. The increase in acid number for a rise of 10% C_P is nearly 100% for the five original oils (VIII.4.), 300% for raffinates of oils 3 and 4 and almost 400% for raffinates of oil 5. Moreover the fractions from oils 3 and 4 show similar acid values for the same paraffinic content, whereas fractions from oil 5 have roughly the same order of acidities as the others for much lower values of C_P.

IX.9. The Effect of Structure on Carbon Residue Increase.

Ramsbottom carbon residues were determined for the raffinate fractions before and after oxidation. From these measurements increase in percentage carbon residue was estimated, as specified in I P 48. Table 22 shows the results obtained. Increase of carbon residue is denoted by Δ CR.

Raffinates of oils 4 and 5 show a decrease in Δ CR with progressive extraction. Oil 3 raffinates, on the other hand, give an increase of Δ CR as aromatics are removed. The results obtained plotted against % C_A are shown in Fig.29, which indicates that above about 9% C_A a linear relationship exists between % C_A and increase in carbon residue on oxidation. At lower values of C_A a considerable scatter of points is shown.

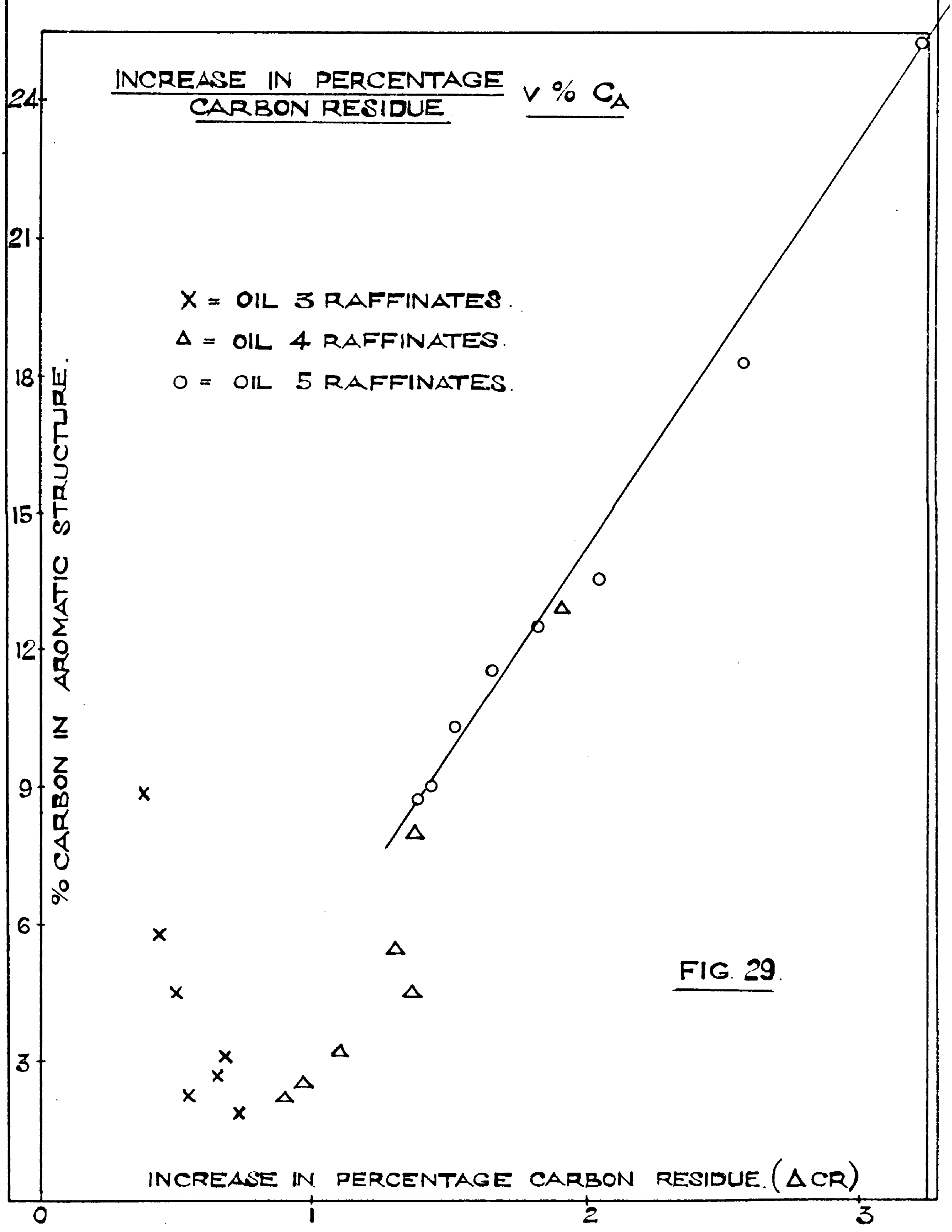

INCREASE IN PERCENTAGE CARBON RESIDUE v % C_A
X = OIL 3 RAFFINATES.
Δ = OIL 4 RAFFINATES.
O = OIL 5 RAFFINATES.
% CARBON IN AROMATIC STRUCTURE.
INCREASE IN PERCENTAGE CARBON RESIDUE. (ΔCR)
24
21
18
15
12
9
6
3
0
1
2
3

FIG. 29.

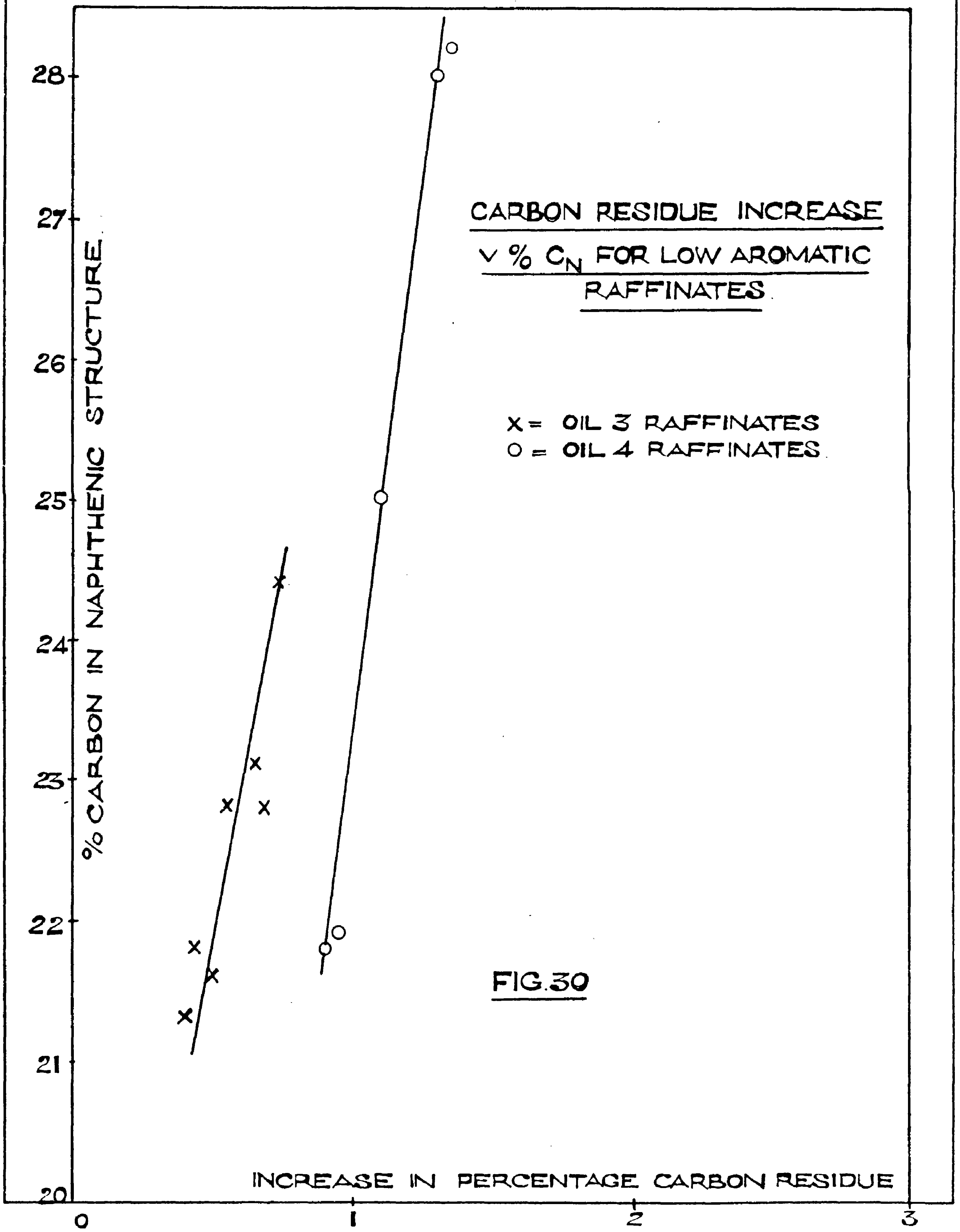
It can be demonstrated, however, that the Δ CR values for low aromatic fractions bear a relationship to C_N. Fig.30 shows, in addition, that two separate straight lines are obtained; one for fractions derived from oil 3 and one for fractions from oil 4.

TABLE 22.

Carbon Residue Increase on Oxidation of Raffinates.

Sample	Increase in Percentage Carbon Residue (Δ CR)		
	Oil 3	Oil 4	Oil 5
R_0	0.38	1.90	3.24
R_1	0.43	1.37	2.56
R_2	0.50	1.30	2.04
R_3	0.68	1.37	1.82
R_4	0.65	1.10	1.65
R_5	0.55	0.96	1.52
R_6	0.73	0.90	1.44
R_7	-	-	1.39

It was described in a previous section relating to oxygen absorption how some change in the type of reaction or reaction mechanism appears to take place about 10% C_A. The results just quoted seem to give some confirmation of this.



CARBON RESIDUE INCREASE v % C_N FOR LOW AROMATIC RAFFINATES.

FIG.30

With high aromatic oils (above 10% C_A) Δ CR increases with aromatic content of the oil, and this is probably connected with the fact that higher aromatic oil fractions yield high amounts of sludge. Sludge itself has been shown to increase with C_A. Various workers have shown that the coke-forming properties of petroleum products (Conradson and Ramsbottom carbon tests) are related to the content of neutral resins and asphaltenes, these two substances being almost synonymous with sludge. Smith[94] suggested that the carbon residue of a crude is roughly proportional to the percentage of asphalts present in it. Vassilieff[95] showed that neutral resins from crude oils produce 20% and asphaltenes about 70% of coke in the Conradson test.

More saturated fractions show a definite relationship between ΔCR and C_N. This is difficult to understand since $C_N = 100 - (C_P + C_A)$, so that ΔCR shows a decrease with increase of $(C_P + C_A)$. From the point of view of producing sludge (or carbon residue) it would be expected that C_P and C_A would counteract each other, i.e. an increase of C_P should produce less carbon residue, an increase of C_A more.

That the criterion is C_N seems to be proved by the fact that extraction of oil 4 causes C_N and C_A to decrease, while C_P increases; whereas with oil 3, C_A alone decreases, C_N and C_P both increasing. This indicates that both oils have shown different characteristics on extraction so it can be taken that neither C_A nor C_P alone influence carbon residue increase.

While accepting the fact that low aromatic oils produce carbon residue in amounts related to C_N, no explanation can be advanced on the basis of the known reactivities or sludge producing characteristics of individual hydrocarbons.

Two parallel lines were obtained by graphing Δ CR against C_N. This indicates that although Δ CR values differ for low aromatic oils the effect of increase in C_N is the same.

IX.10. The Effect of Oil Composition on Viscosity Ratio.

With oils 1-5 it was found that a roughly linear relationship was apparent between oil composition and viscosity ratio at 12 hours oxidation.

Kinematic viscosities at 100°F were determined for the raffinate fractions before and after oxidation. After oxidation the oils were clarified by filtration before viscosity measurements were made. This procedure is not exactly in accordance with the standard test, but the test for 1957 onwards (I P 48/57) states that anomalous results are likely to be obtained if solid products are formed under the conditions of the test. With the raffinates oxidised, comparatively little sludge was obtained (and in some cases none at all) but clarification was carried out where necessary. Any viscosity increase is thus in the desludged oils.

The viscosity ratios obtained are shown in Table 23.

Fig.31 shows that viscosity ratio tends to increase more or less linearly with aromatic content of the oils. Again, as with certain other measurements of stability, a different pattern is obtained for low aromatic fractions. Below about 9% C_A viscosity ratio appears to be almost constant, i.e. independent of composition.

TABLE 23.

Viscosity Ratio of Raffinates.

Sample	Viscosity Ratio		
	Oil 3	Oil 4	Oil 5
R_0	1.38	1.85	3.18
R_1	1.35	1.62	2.65
R_2	1.42	1.40	2.28
R_3	1.47	1.46	1.91
R_4	1.38	1.41	1.71
R_5	1.52	1.55	1.60
R_6	1.49	1.38	1.54
R_7	-	-	1.50

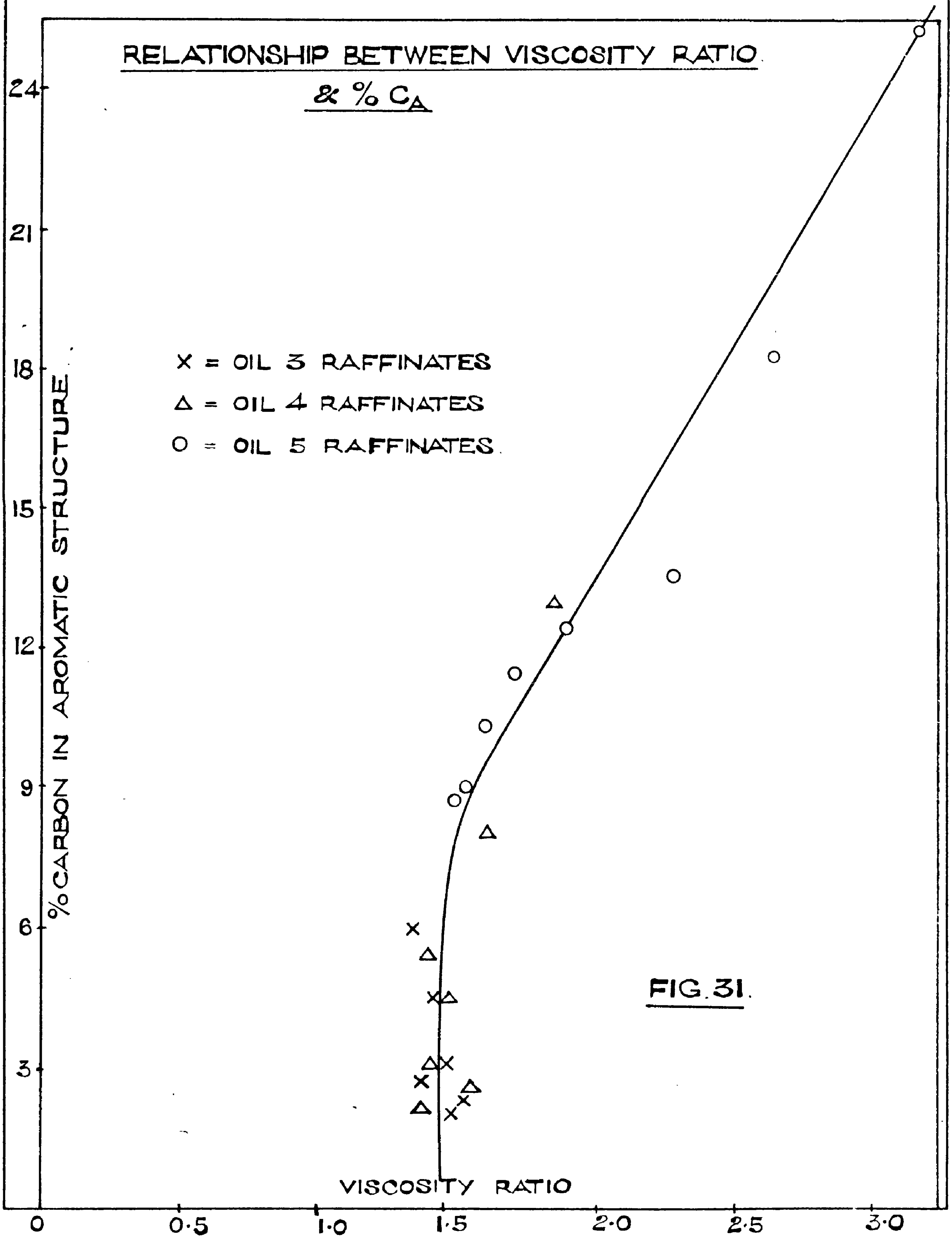

RELATIONSHIP BETWEEN VISCOSITY RATIO
& % C_A
X = OIL 3 RAFFINATES
Δ = OIL 4 RAFFINATES
O = OIL 5 RAFFINATES
%CARBON IN AROMATIC STRUCTURE
VISCOSITY RATIO
24
21
18
15
12
9
6
3
0
0·5
1·0
1·5
2·0
2·5
3·0

FIG. 31.

Increase of viscosity ratio with increasing aromatic content seems a reasonable finding since soluble sludge shows a general increase with C_A. Hicks-Bruun and co-workers[49] attributed increase in viscosity on oxidation mainly to dissolved sludge, with resins (not precipitated by pentane) causing a similar, but smaller, increase. Various workers have shown that neutral resins are slowly formed from heavy polycyclic aromatics. This indicates that increase of viscosity due to the presence of resins would also be a function of aromatic content.

The tendency towards a more constant viscosity ratio below about 9% C_A coincides with a value for soluble sludge of 0.5% by weight. Resins were not determined on the oxidised fractions but this change in viscosity ratio at low aromatic content may well be the result of several factors. The reduction of sludge (and resin content if any) would decrease the viscosity ratio but a counter effect could be caused by the formation of acids which, according to Hicks-Bruun, also have the effect of increasing viscosity, although to a lesser degree than either sludge or resins.

CHAPTER X

THE EFFECT OF REDUCED AIR FLOW ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED, ON OXIDATION OF LUBRICATING OILS UNDER THE CONDITIONS OF THE STANDARD INSTITUTE OF PETROLEUM TEST.

The Effect of Air Rate on Oxygen Absorption

The Effect of Air Rate on Acid and Sludge Produced on Oxidation.

The Effect of Air Rate on Viscosity Ratio and Carbon Residue Increase.

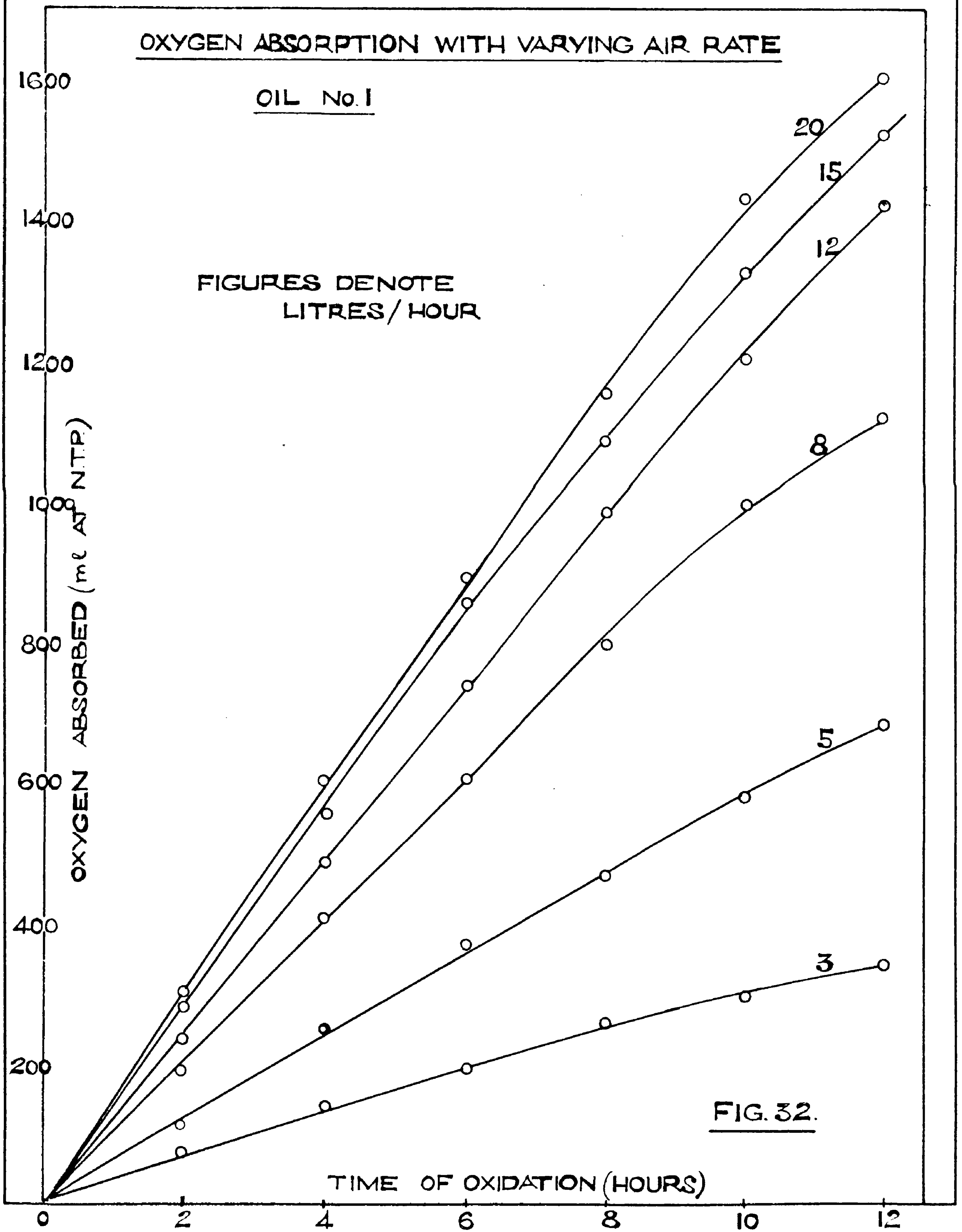
CHAPTER X

THE EFFECT OF REDUCED AIR FLOW ON THE OXYGEN ABSORBED, AND ON THE PRODUCTS OBTAINED ON OXIDATION OF LUBRICATING OILS UNDER THE CONDITIONS OF THE STANDARD INSTITUTE OF PETROLEUM TEST.

X.1. In the I P test the standard air flow used in 15 litres /hour and it was felt that while a reduction in the air flow rate, with other conditions of the standard test constant, would undoubtedly produce a decrease in oxidation, it would be of interest to see whether all oils would show the same relative changes. For this reason oxidation was carried out on oils 1-5 at 200°C and for a total oxidation time with some exceptions, of 12 hours. Air rates used ranged from 3 to 20 litres per hour.

X.2. The Effect of Air Rate on Oxygen Absorption.

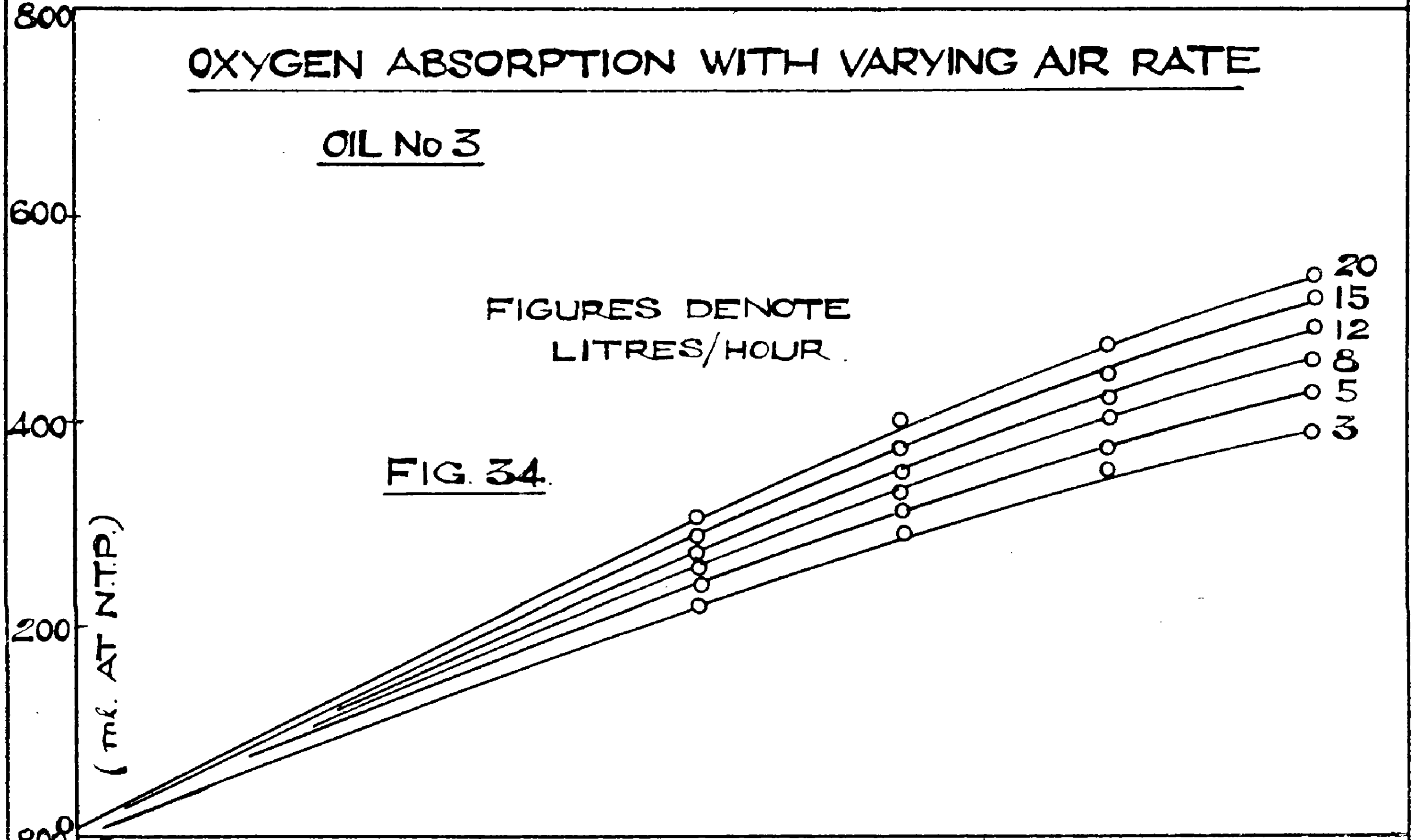
The volumes of oxygen absorbed during 12 hours oxidation by the five oils are shown in Table 24. Oils 1 and 5 show by far the greatest changes in absorption, the other three oils exhibiting relatively little difference. Figs.32 to 36 show rather more clearly the oxygen absorptions for different air rates.



OXYGEN ABSORPTION WITH VARYING AIR RATE

OIL No. I

FIG. 32.



OXYGEN ABSORPTION WITH VARYING AIR RATE

FIG. 34.

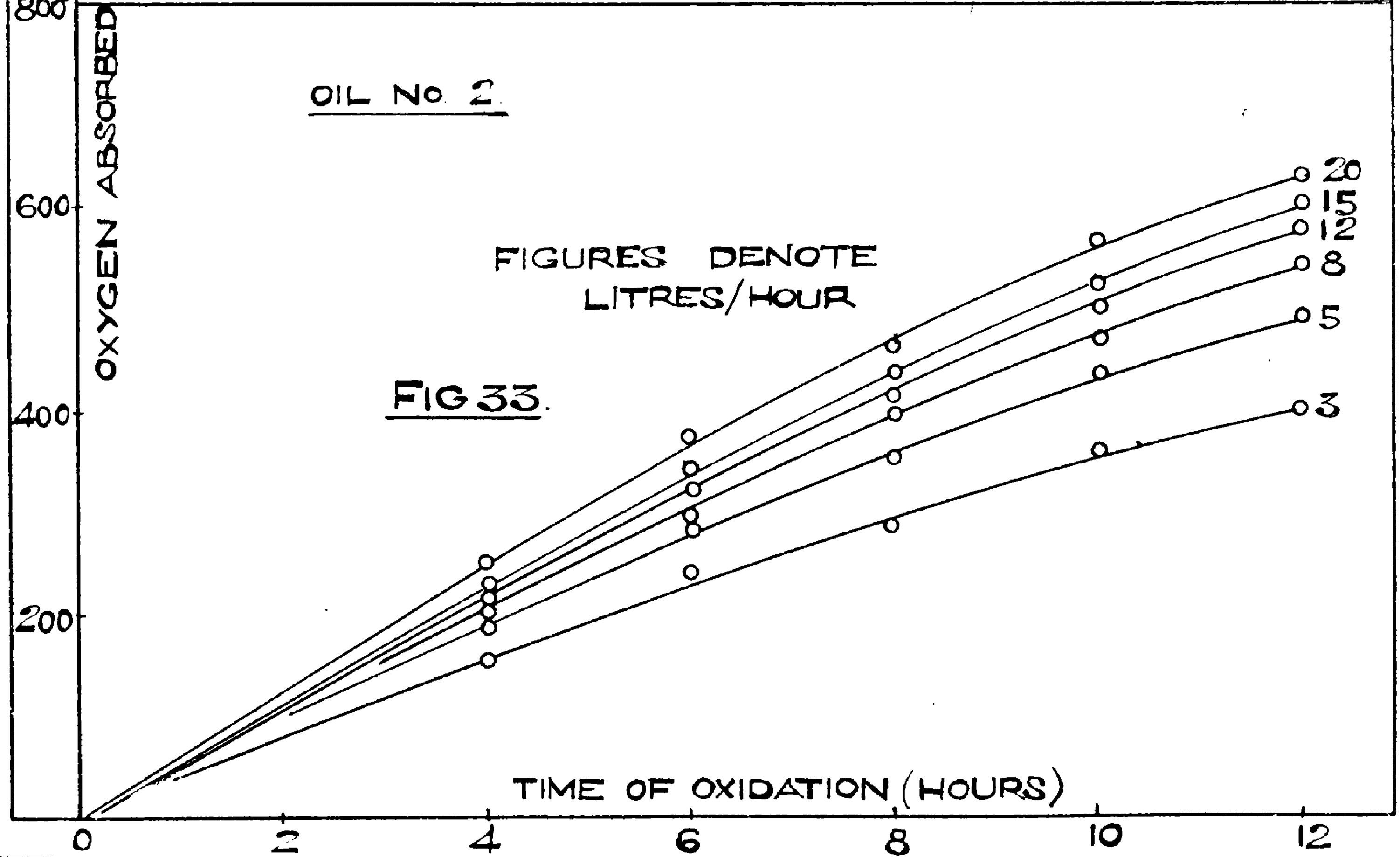


FIG 33.

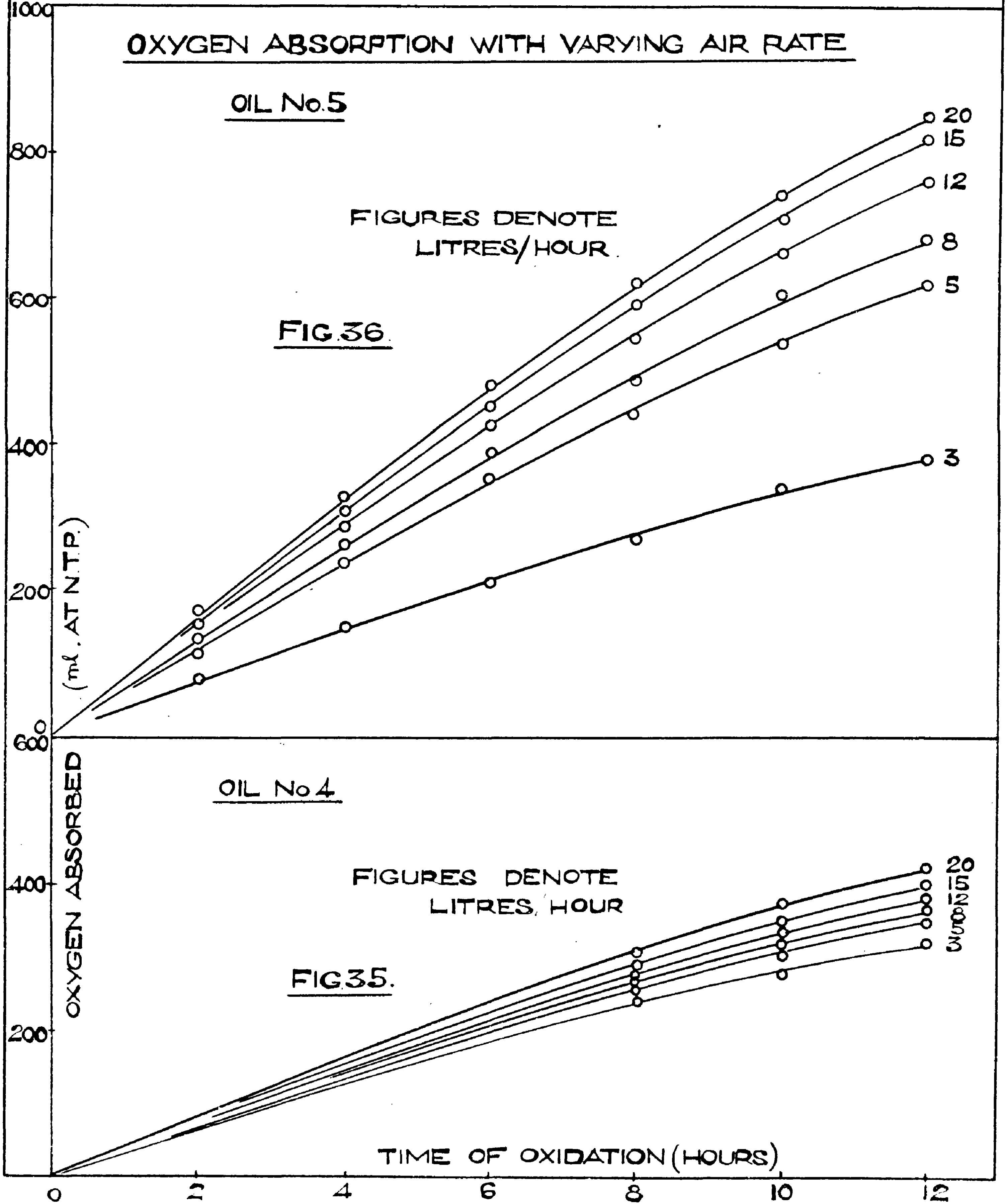

OXYGEN ABSORPTION WITH VARYING AIR RATE

FIG.36

FIG.35.

TABLE 24.

Oxygen absorbed with different air rates at 12 hours.

Sample	mls. of Oxygen Absorbed at different air rates litres/hour					
	3	5	8	12	15	20
Oil 1	340	680	1120	1420	1520	1600
Oil 2	400	490	540	575	600	630
Oil 3	390	430	460	490	520	540
Oil 4	320	350	370	380	400	420
Oil 5	380	620	680	760	820	850

These results indicate that oils with a low oxygen absorption under standard test conditions, i.e. at 15 litres/hour, do not suffer from a diminished rate of oxygen supply until a fairly low air rate is reached. This suggests that oils with low reaction rates (oils 2, 3 and 4) are controlled by their chemical oxidation rates, and absorption of oxygen, which is low in any case, remains at a fairly constant rate until only a small amount of air is provided. On the other hand the more reactive oils 1 and 5, having a higher chemical oxidation rate, are soon affected by diminished oxygen access.

A possible explanation of this phenomenon is that diffusion of oxygen is a rate-limiting factor; diffusion not being sufficiently great with oils 1 and 5 to enable the 'natural' chemical rate of oxidation to be maintained. Evidence that this might be the case is provided by the fact that at the lowest air flow rate (3 litres/hour) there is little difference in the amount of oxygen absorbed by any of the oils. It can be assumed that, at this low rate of oxygen provision, the chemical rates no longer have control and that an almost constant rate of diffusion of oxygen determines the oxygen uptake for each oil. Surface properties of the various oils, controlling bubble size, would account for the fact that absolutely identical rates of absorption were not obtained at 3 litres/hour air flow.

It is significant that constant rates of absorption were not obtained with any of the oils, even at 20 litres/hour. This indicates that complete saturation has not been effected although the standard test conditions of 15 litres/hour may, in fact, not differ appreciably from saturated conditions.

X.3. The Effect of Air Rate on Acid and Sludge Produced on Oxidation.

Acid and sludge measurements were carried out on the oils oxidised with varying rates of air flow. Total sludge

ACID & SLUDGE WITH VARYING AIR RATE – OIL 1

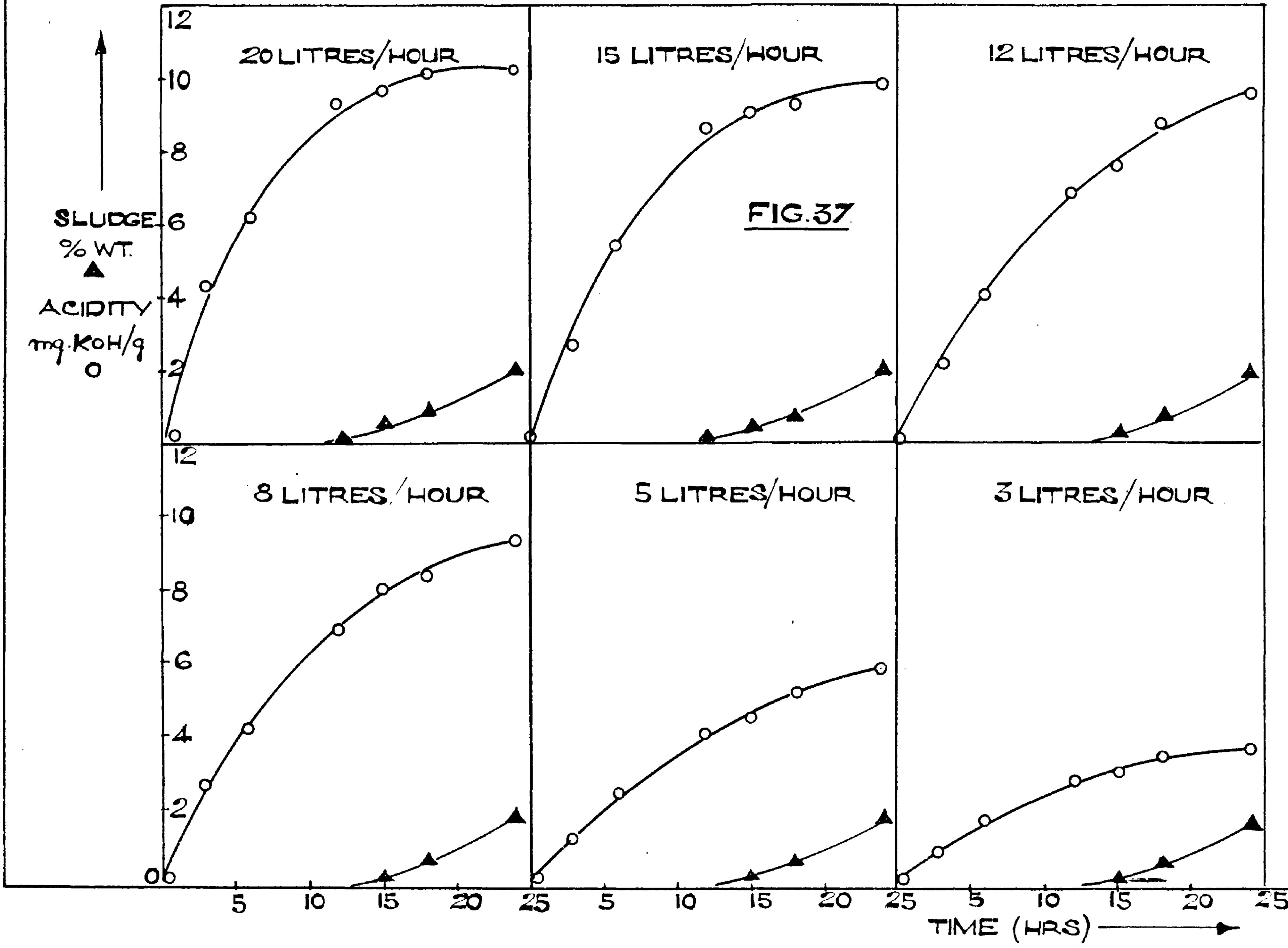


FIG.37

ACID & SLUDGE WITH VARYING AIR RATE - OIL 2.

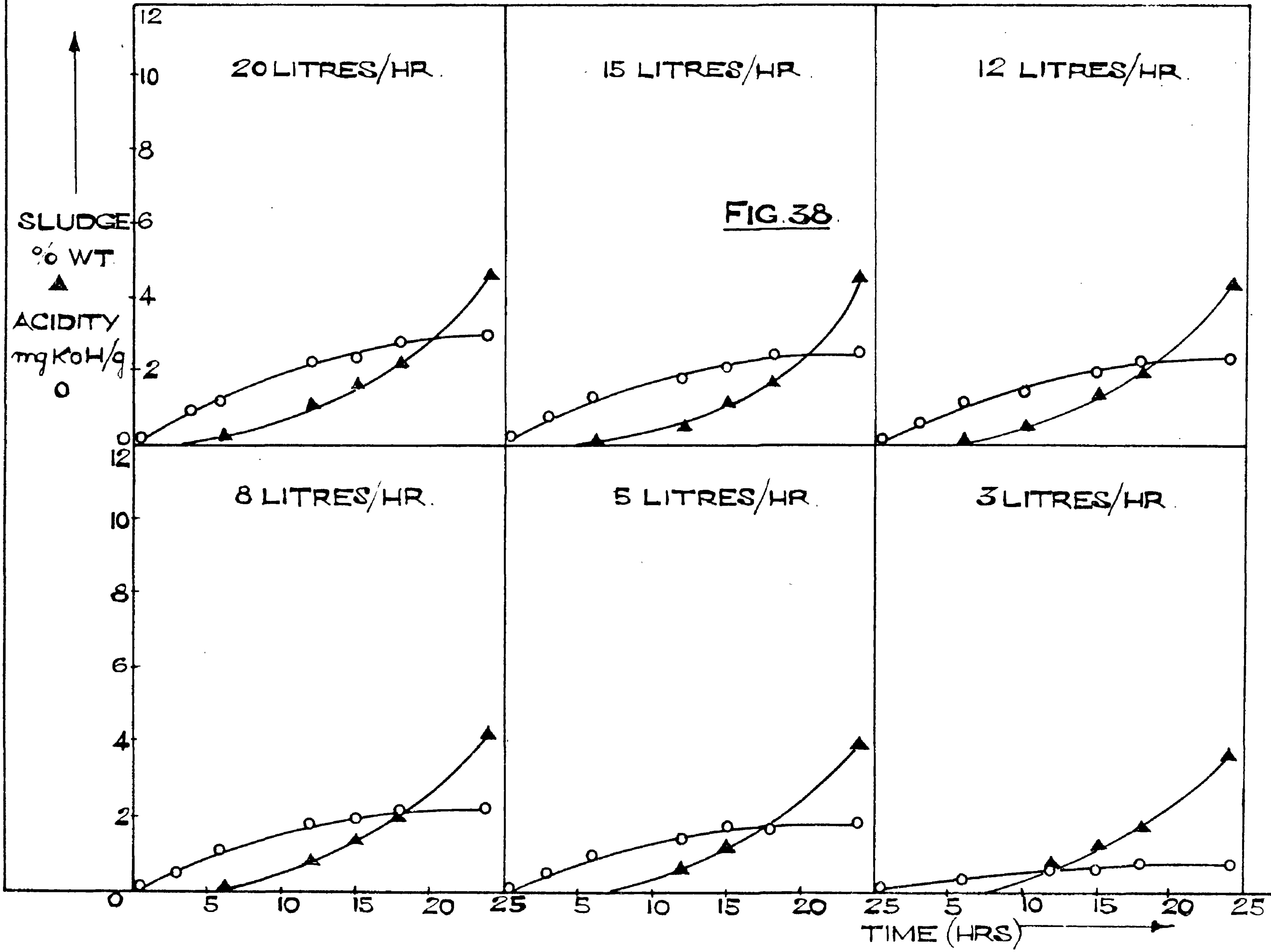


FIG. 38.

ACID & SLUDGE WITH VARYING AIR RATE - OIL 3.

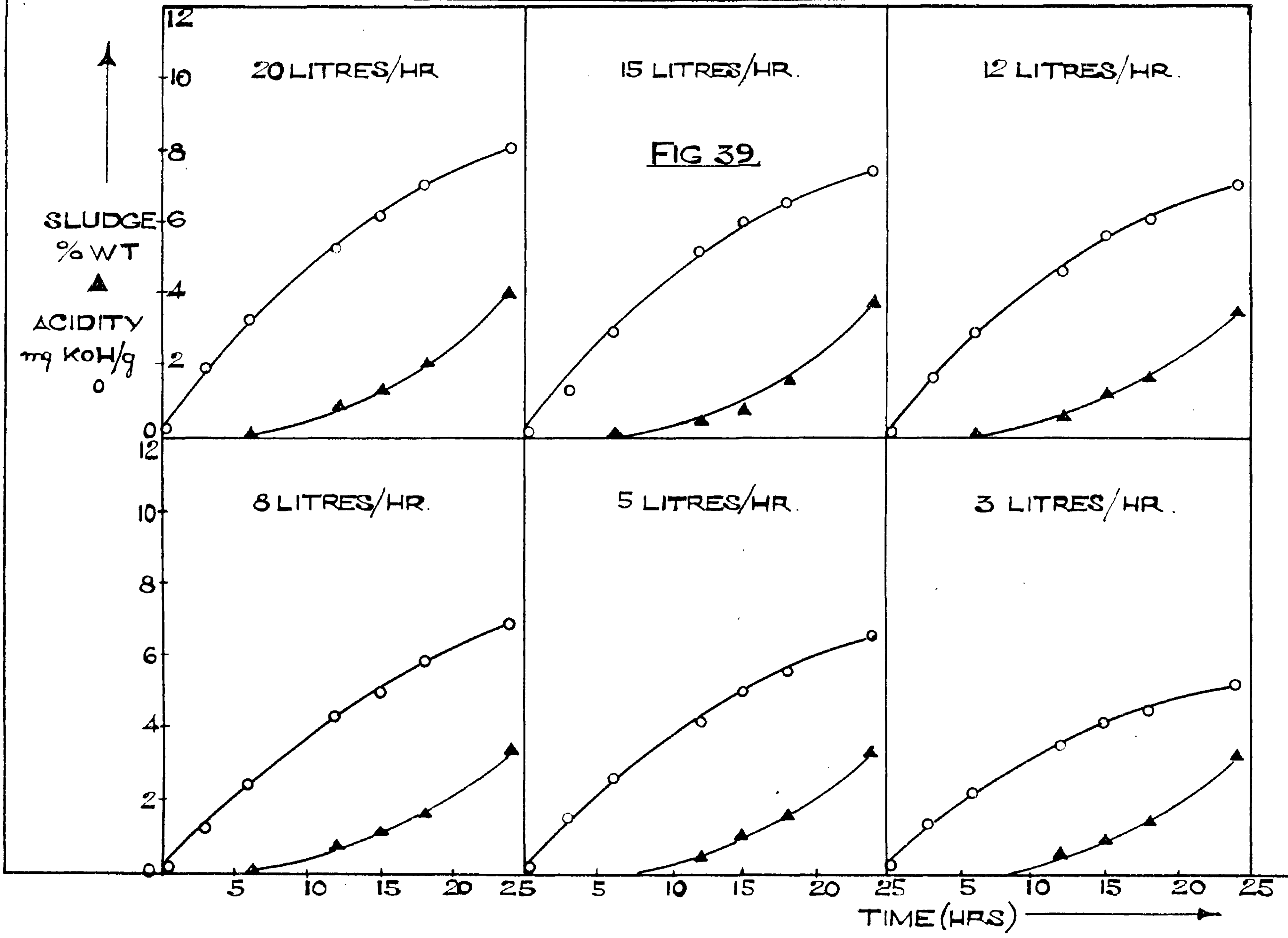


FIG 39.

ACID & SLUDGE WITH VARYING AIR RATE - OIL 4

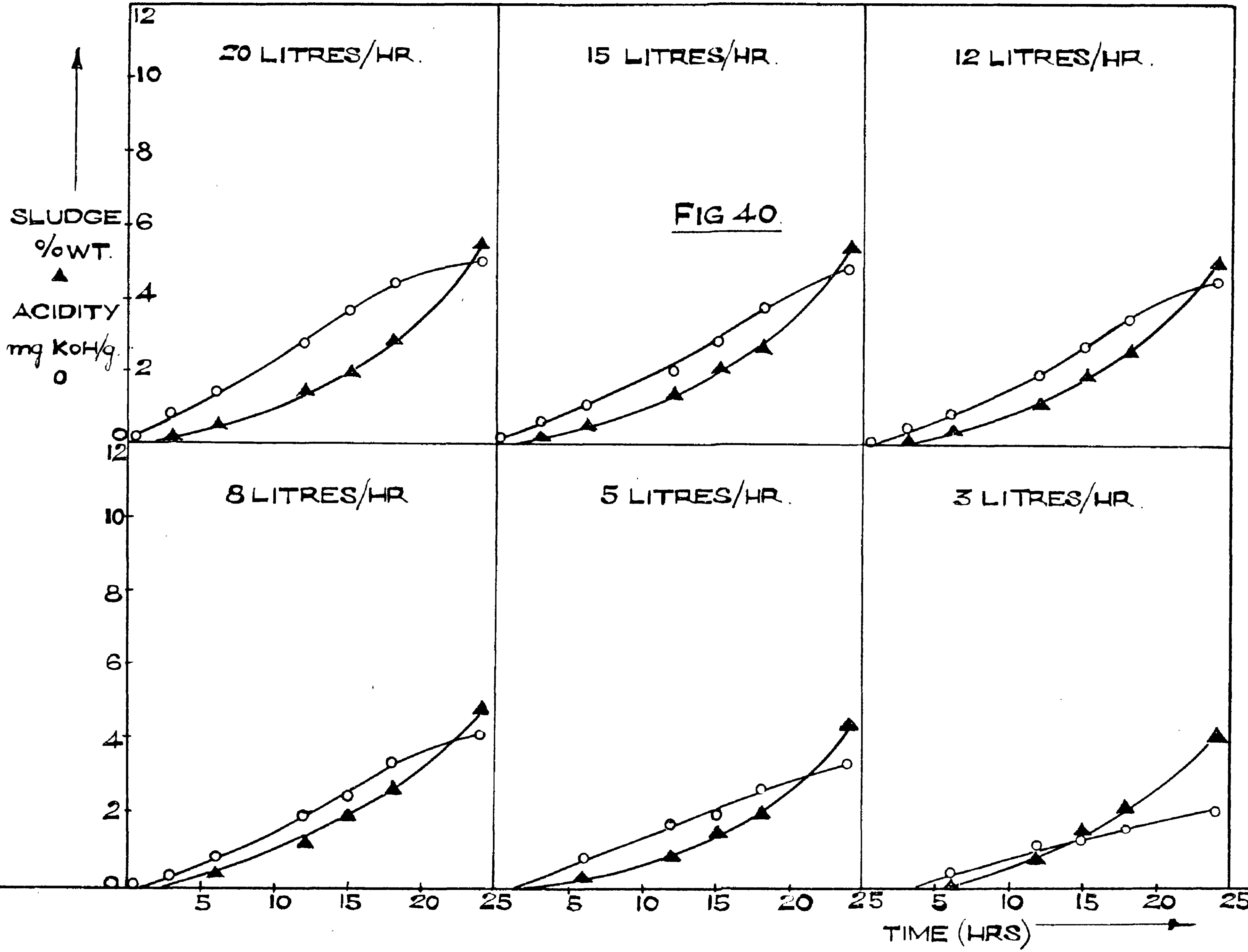


FIG 40

ACID & SLUDGE WITH VARYING AIR RATE - OIL 5

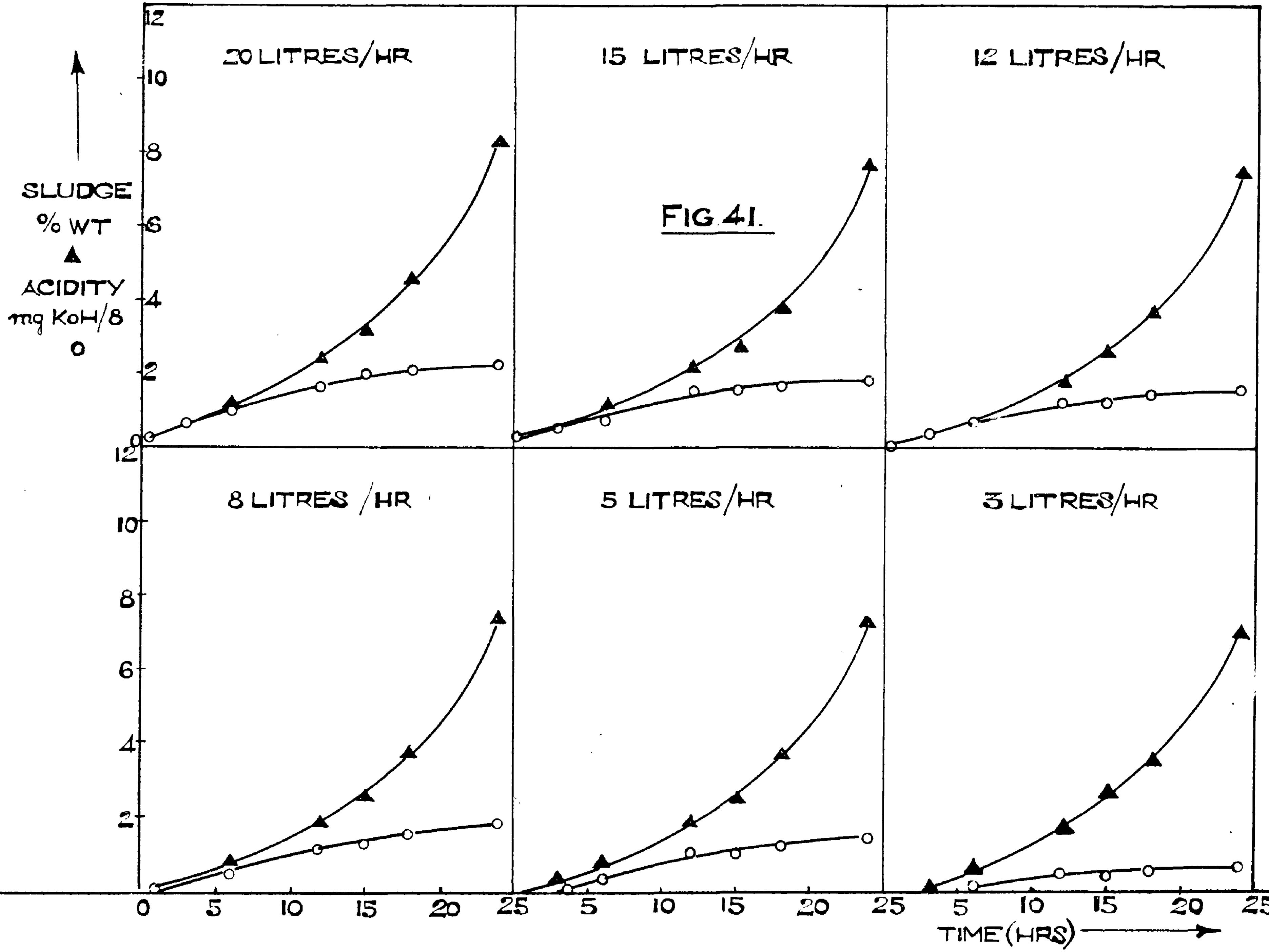


FIG. 41.

was measured and acid values were determined on the completely desludged oils.

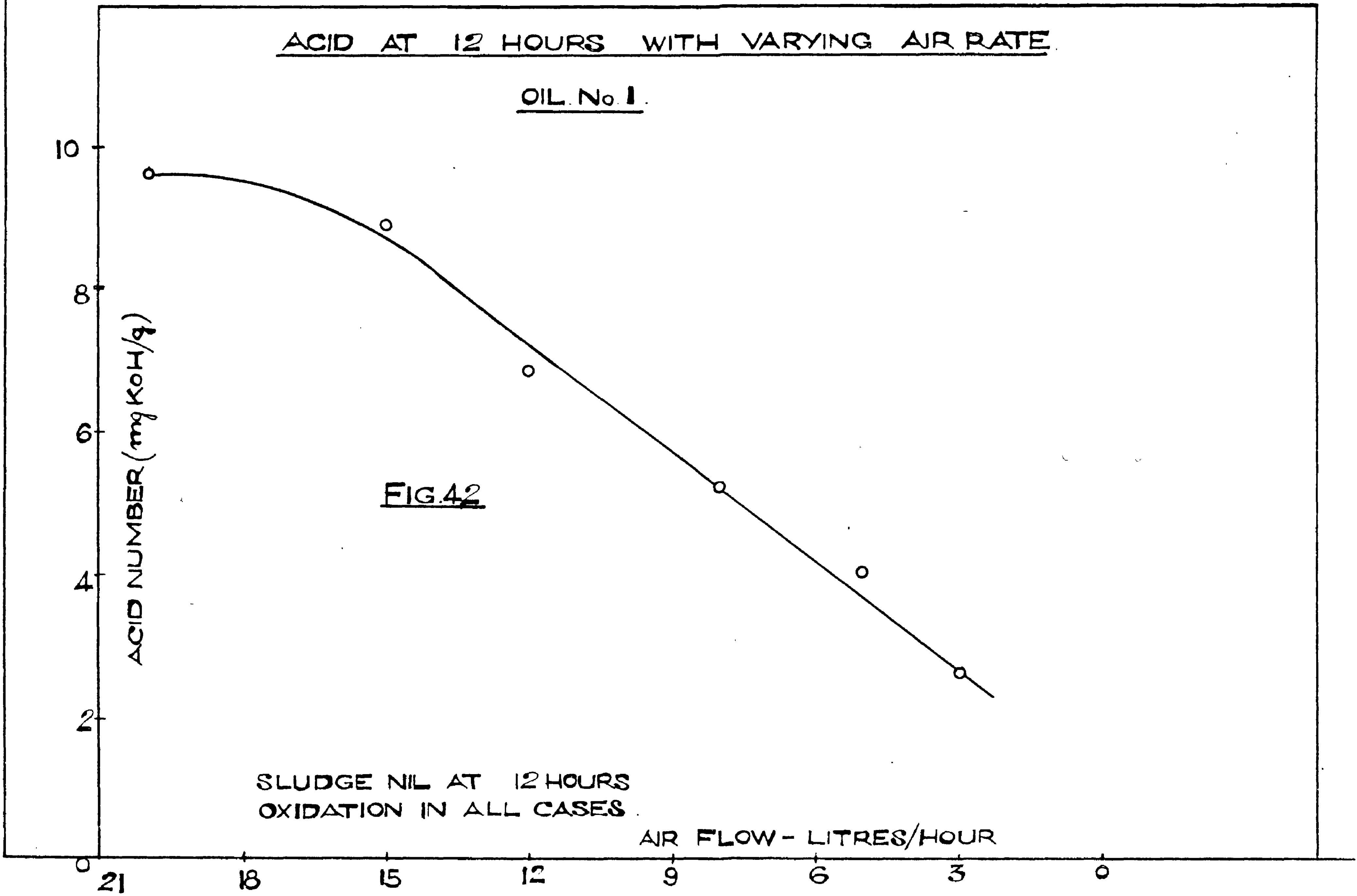
Preliminary determinations suggested that if the oxidation times were extended to 24 hours then a rather clearer picture of the acid and sludge produced would be obtained. The results obtained are shown in Figs.37 to 41.

It is seen that in all cases the overall acid plus sludge decreases with reduced air flow. At the same time acid and sludge do not fall at the same rate, i.e. the acid : sludge ratio has altered, acid values falling more rapidly than sludge as the rate of air flow is lowered.

Figs.42 to 46 show the sludge and acid produced at 12 hours oxidation plotted against air rate. These graphs show that total sludge changes only slightly as the air rate is decreased, although it does show a reduction, particularly with oil No.5 which was one of the two oils having considerable decrease in oxygen absorption. The other, oil 1, produced no sludge at 12 hours.

Acid values, on the other hand, show a much greater reduction with decreasing air flow, particularly with oil 1. In most cases linear or almost linear relationships between acid value and air flow rate are indicated.

No direct connection appears to exist between decrease



ACID AT 12 HOURS WITH VARYING AIR RATE

OIL. No. 1.

FIG.42

ACID & SLUDGE AT 12 HOURS WITH VARYING AIR RATE

OIL No. 2

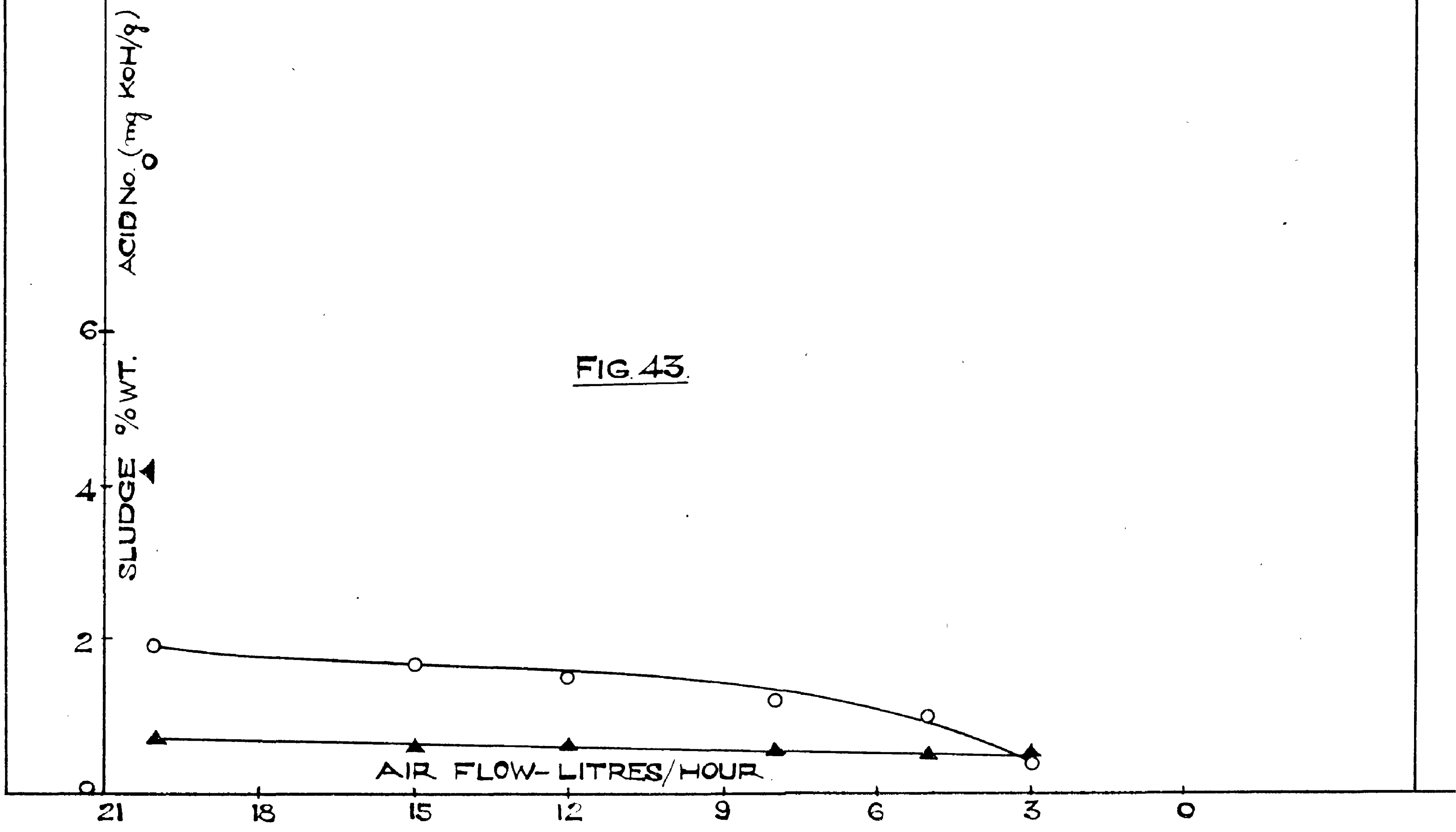
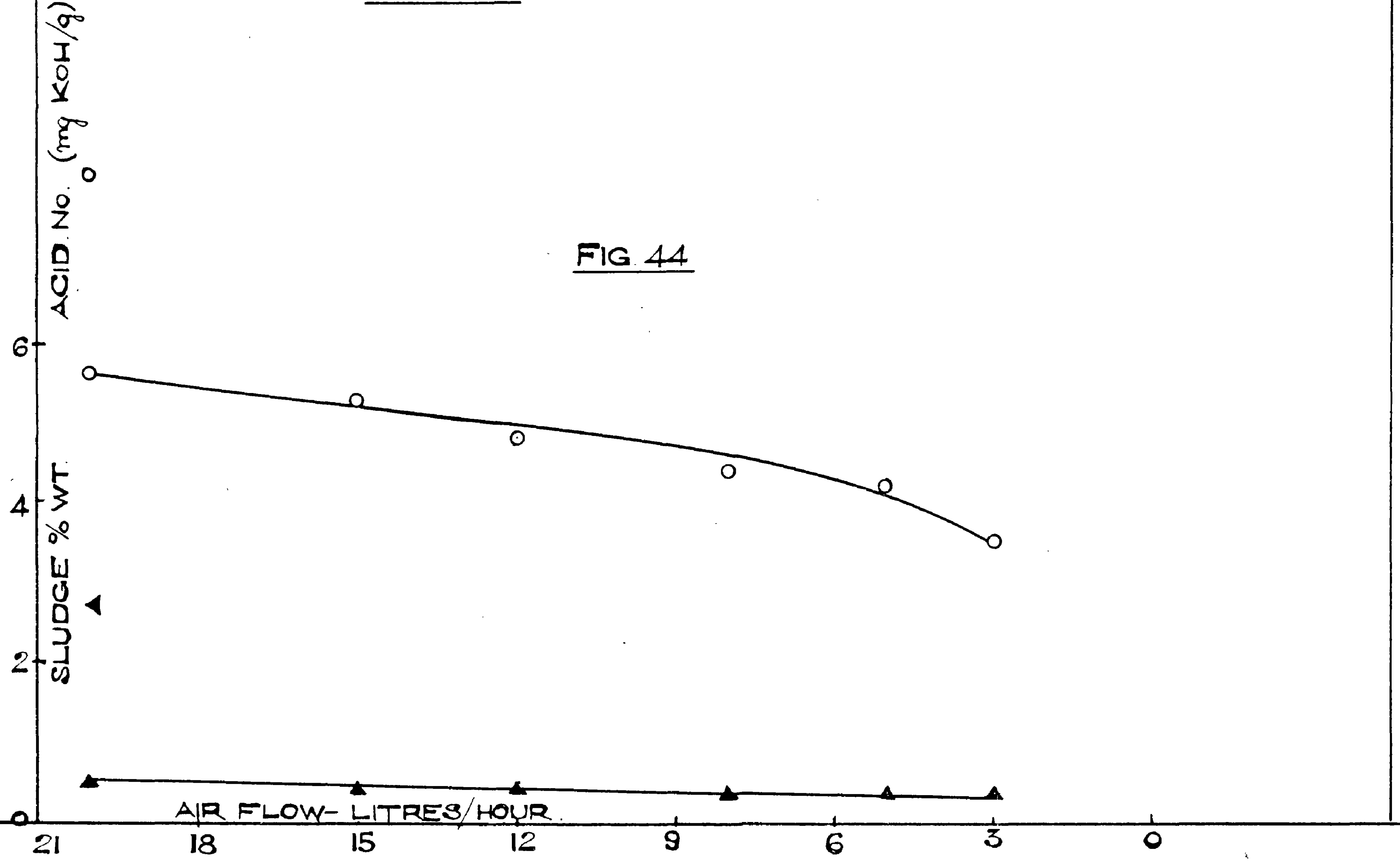


FIG. 43.

ACID & SLUDGE AT 12 HOURS WITH VARYING AIR RATE

OIL No. 3.

FIG. 44



ACID & SLUDGE AT 12 HOURS WITH VARYING AIR RATE

OIL No. 4.

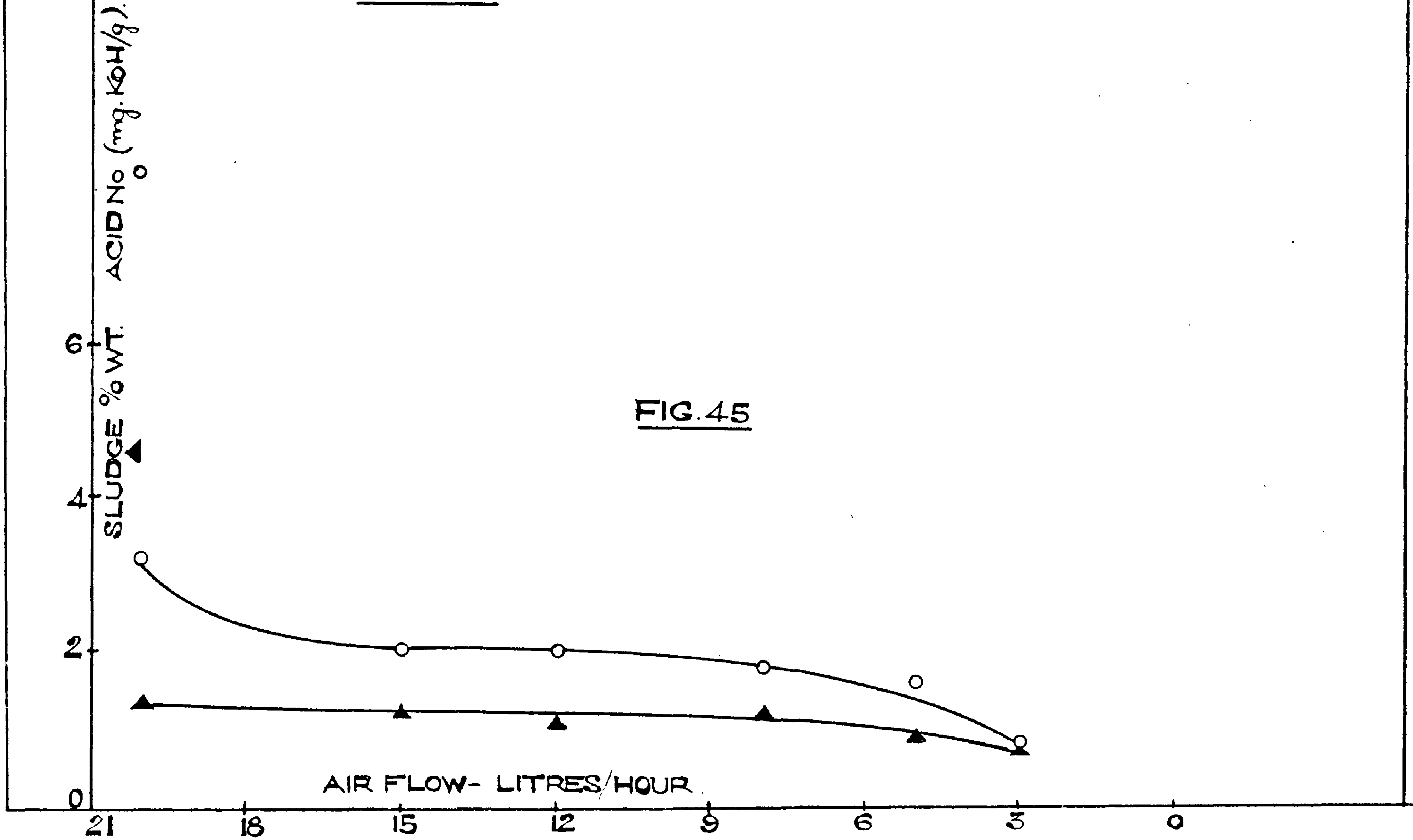


FIG. 45

ACID SLUDGE AT 12 HOURS WITH VARYING AIR RATE

OIL No 5.

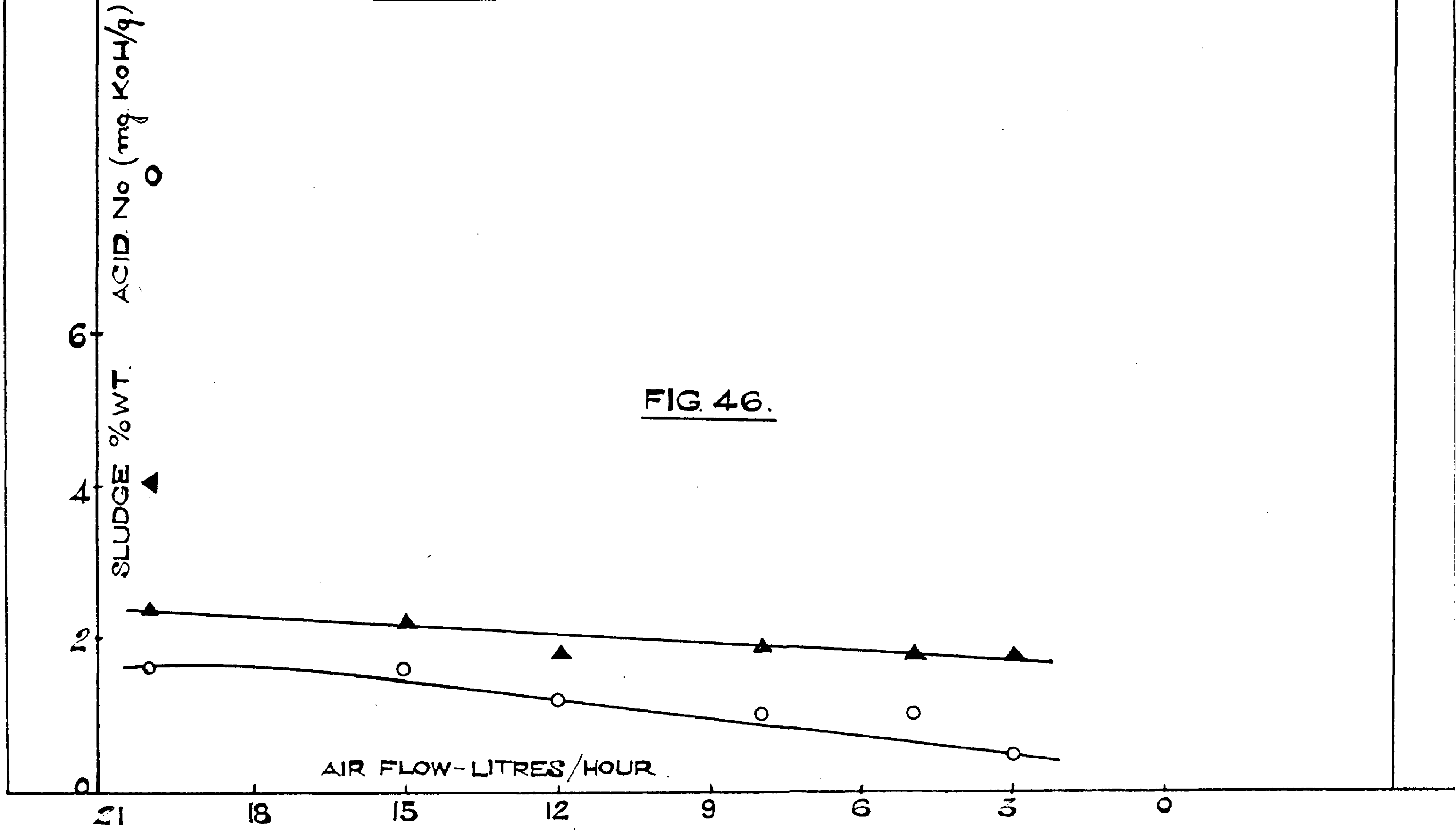


FIG. 46.

in sludge or acid and composition of the oil. The criterion seems to be the oxygen absorption. Oils whose absorption rates are considerably decreased by diminished air flow show correspondingly large decreases in sludge and acid values.

X.4. The Effect of Air Rate on Viscosity Ratio and Carbon Residue Increase.

Values of viscosity ratio and increase of carbon residue on oxidation were not measured in this case. Garner and co-workers[2], however, studied the effect of reduced air rate on these two quantities and obtained a nearly linear relationship in both cases.

CHAPTER XI

THE EFFECT OF TEMPERATURE ON THE OXYGEN ABSORBED AND ON THE PRODUCTS OBTAINED ON OXIDATION OF LUBRICATING OILS UNDER THE CONDITIONS OF THE STANDARD INSTITUTE OF PETROLEUM TEST

Oxygen Absorption with Varying Oxidation Temperature.

Acidity with Varying Oxidation Temperature.

Sludge with Varying Oxidation Temperature.

CHAPTER XI

THE EFFECT OF TEMPERATURE ON THE OXYGEN ABSORBED AND ON THE PRODUCTS OBTAINED ON OXIDATION OF LUBRICATING OILS UNDER THE CONDITIONS OF THE STANDARD INSTITUTE OF PETROLEUM TEST.

XI.1. Work has been done by Fenske and co-workers[48] on the effect of temperature on the oxidation of oils, but it was felt that a similar study could profitably be made in this present work. Fenske did not oxidise above 180°C and, in addition, the apparatus he used had many differences from that used in this work. One example of this difference is that Fenske used pure oxygen at 15 litres/hour with an oil sample of 250 g.

The temperatures used in this present investigation ranged from 140°C to 220°C by steps of 20°. Oils 1 to 5 were oxidised at these five temperatures for 12 hours and sludge and acid values were determined on all oxidised sample. Oxygen absorption was also measured.

XI.2. Oxygen Absorption with Varying Oxidation Temperature.

(a) It has been shown in Chapter VIII that at 200°C all the oils oxidised produced linear or nearly linear absorption/time relationships. As the oxidation temperature was lowered, however, certain differences in the absorption characteristics were noted. The results obtained are shown in Table 25.

TABLE 25.

Oxygen Absorbed with varying Temperature

Sample	mls. Oxygen Absorbed in 12 hours at different temperatures (°C)					% C_A
	140	160	180	200	220	
Oil 1	210	290	362	1520	6240	3.3
Oil 2	50	75	142	600	2510	8.7
Oil 3	46	68	125	520	2150	8.9
Oil 4	8	21	94	400	1680	13.0
Oil 5	14	41	196	820	3410	25.2

Oils of low aromatic content (Oil 1 in particular and oils 2 and 3 to a lesser extent) give an inhibited type of absorption curve with an obvious induction period. With the other two oils of higher aromatic content this effect does not occur and an approximately linear relationship is apparent at all temperatures. These two oils show an approximate doubling of absorption rate for every 10°C rise in temperature. Absorption curves for oil 5 ane shown in Fig.47.

The results obtained with oils 4 and 5 agree with those quoted by Fenske et al.[48] for oils containing aromatics. It is shown in this work, however, that the effect continues at least as far as 220°C.

Oils 1, 2 and 3 which show inhibition at lower temperatures of oxidation have their induction periods approximately halved for each 10°C rise in temperature, but beyond the induction period behaviour of these oils can not be predicted by a temperature/absorption relationship. Again this is in accordance with the findings of Fenske. It was found, however, that at higher temperatures, when the induction period disappears, that the absorption/time curve for these oils approaches linearity. This is shown for oil 1 in Fig.48. Fenske and co-workers did not obtain this effect, probably because they did not oxidise at sufficiently high temperatures.

It can be seen from Table 25 that at higher oxidation temperatures, when the low aromatic oils lose their induction

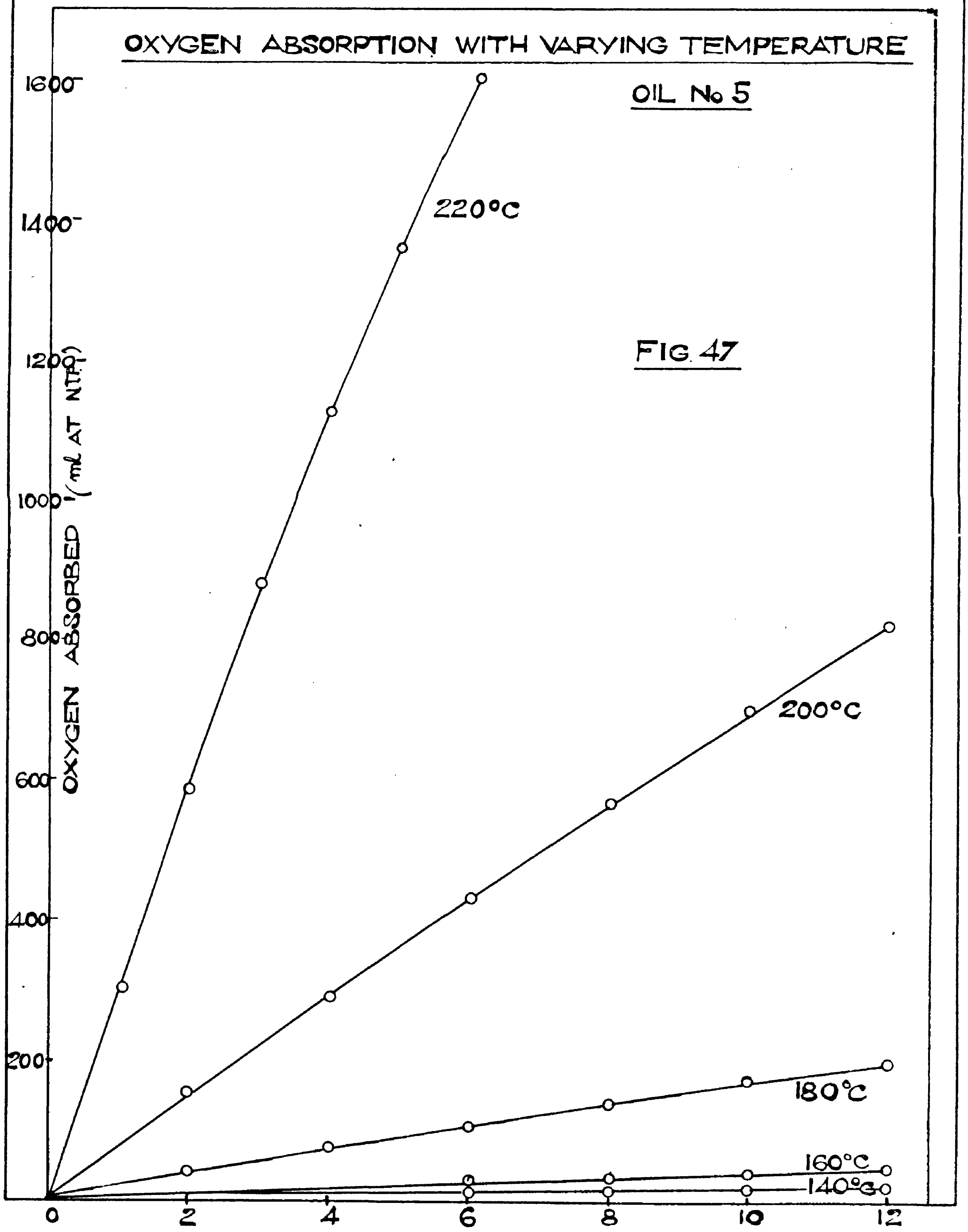
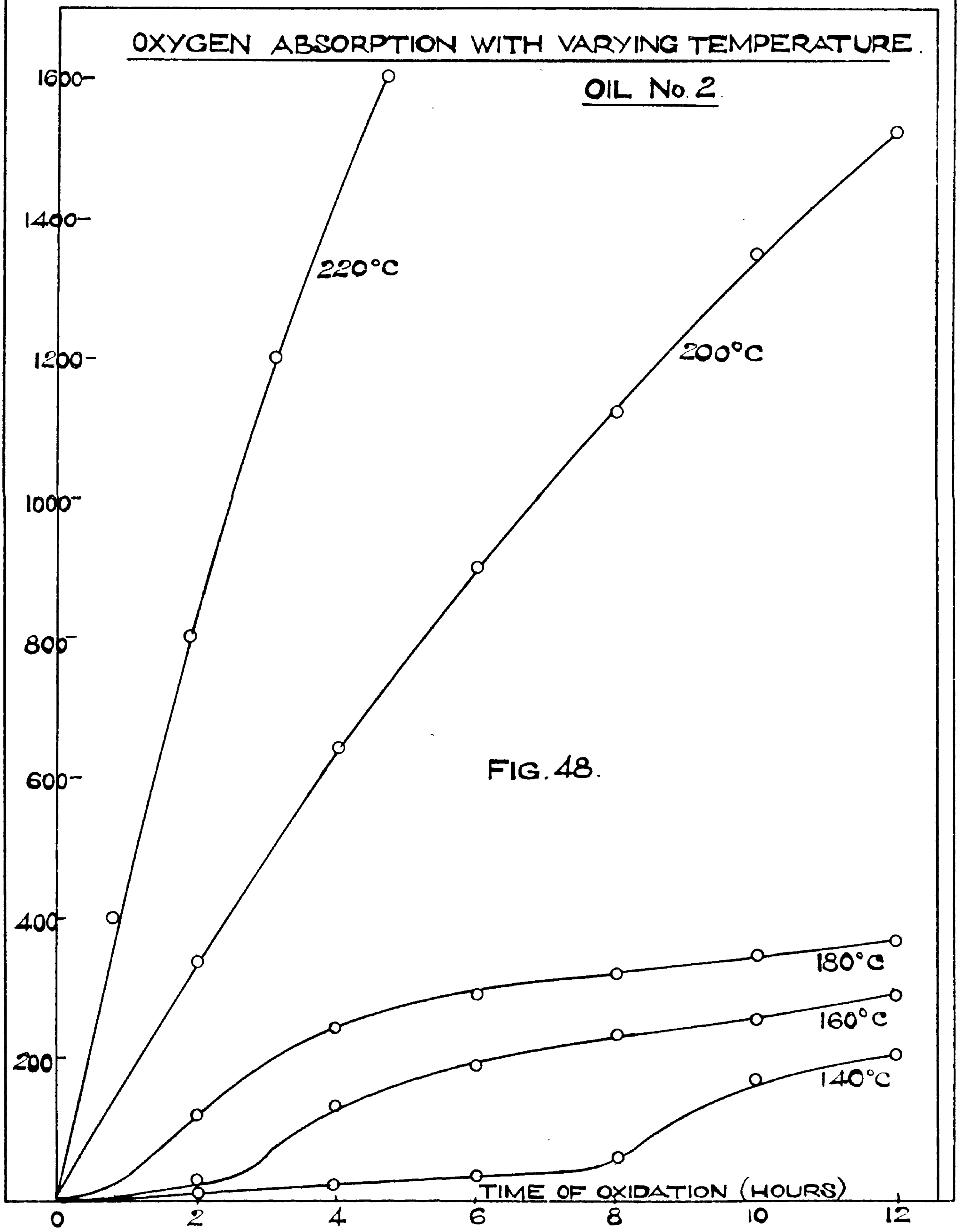

OXYGEN ABSORPTION WITH VARYING TEMPERATURE
OIL No 5
OXYGEN ABSORBED (ml AT N.T.P.)
1600
1400
1200
1000
800
600
400
200
0
2
4
6
8
10
12
220°C
200°C
180°C
160°C
140°C

FIG. 47



OXYGEN ABSORPTION WITH VARYING TEMPERATURE.

OIL No. 2.

FIG. 48.

period they become similar to the higher aromatic oils and absorption is approximately doubled for a 10°C rise.

(b) The results obtained in this absorption work lend some support to the hypothesis presented in Chapter IX (IX.6.) that oxidation of low aromatic oils is influenced by an inhibition effect. In IX.6. it was stated that inhibition of oxidation is probably caused by oxidation products of aromatic hydrocarbons. The fact that only oils 1, 2 and 3 show induction periods suggests that the 'critical aromatic content' of about 10% is again operative. The results suggest that at low oxidation temperatures the inhibition effect is enhanced and so a definite induction period due to oxidised aromatic compounds is produced.

It was suggested in IX.6. that above about 10% C_A sufficient aromatic material is present to control the oxidation rate. This would explain why no induction period was found in the lower temperature oxidation of oils 4, and 5; i.e. a certain inhibition of saturated material still persists but the criterion for rate of oxidation rests with the greater amount of aromatics.

XI.3. Acidity with Varying Oxidation Temperature.

As well as absorption being approximately doubled for each 10°C rise it was found that acid value was similarly affected. At the same time it was seen that only the acidity of <u>totally desludged oil</u> conformed to a simple log function, acidities of oils containing soluble or insoluble sludge showing deviations.

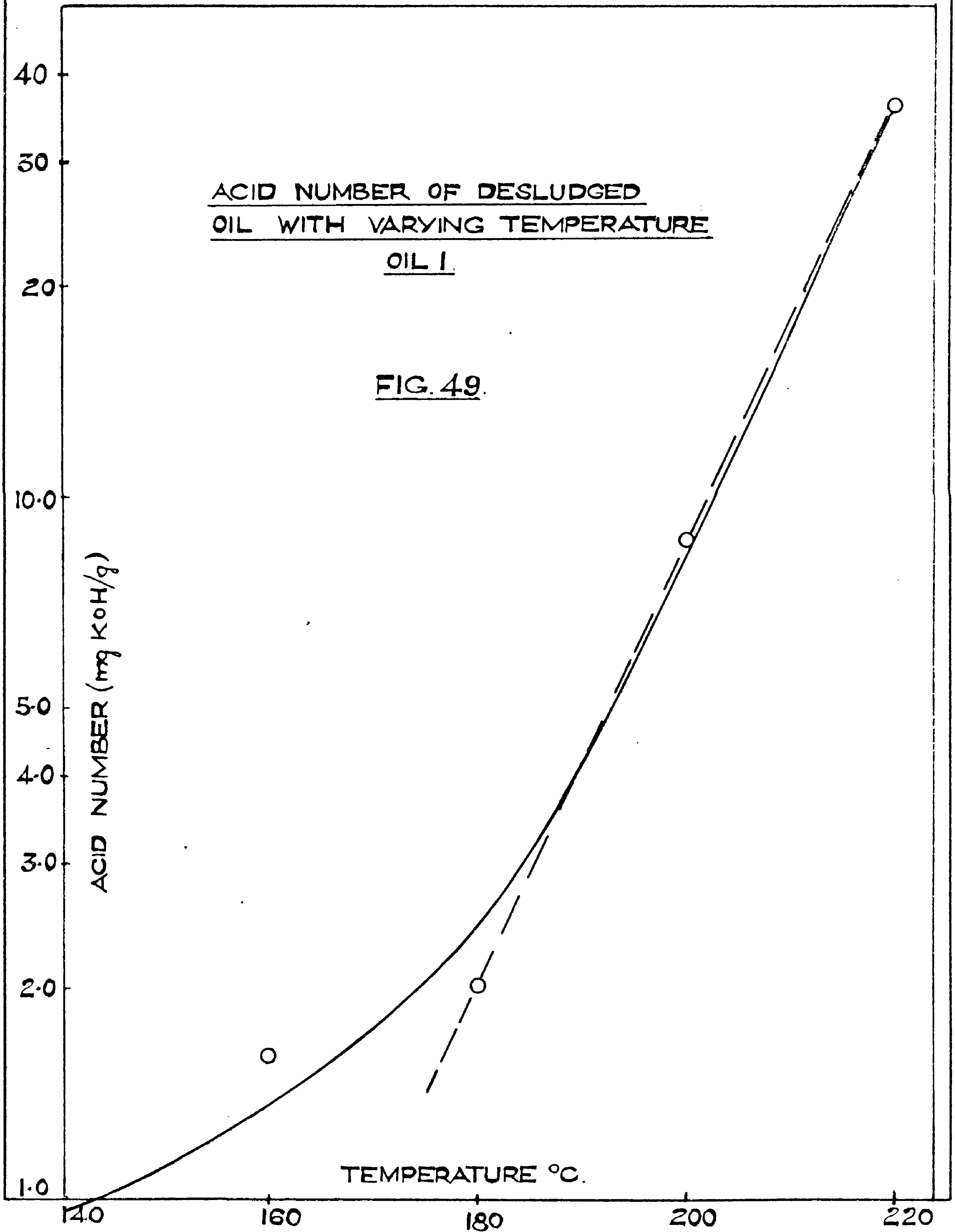
Table 26 gives acid numbers for desludged oils at 12 hours oxidation and Figs.49 and 50 show the log acid / temperature relationships for oils 1 and 5 respectively. It is seen that while oil 5 produces a straight line, oil 1 (which shows inhibition effects at low temperatures) gives rather irregular acid values at these low temperatures.

TABLE 26.

Acid Number (mg.KOH/gm.) of Desludged Oils at varying temperatures

Sample	Acid Number of Desludged Oil (12 Hours oxidation) at Different Temperatures(°C)				
	140	160	180	200	220
Oil 1	1.0	1.6	2.0	8.6	36.0
Oil 2	0.4	0.4	0.6	1.8	8.0
Oil 3	0.8	1.2	1.7	5.2	22.5
Oil 4	0.1	0.2	0.6	2.0	8.8
Oil 5	0.1	0.15	0.4	1.5	6.2

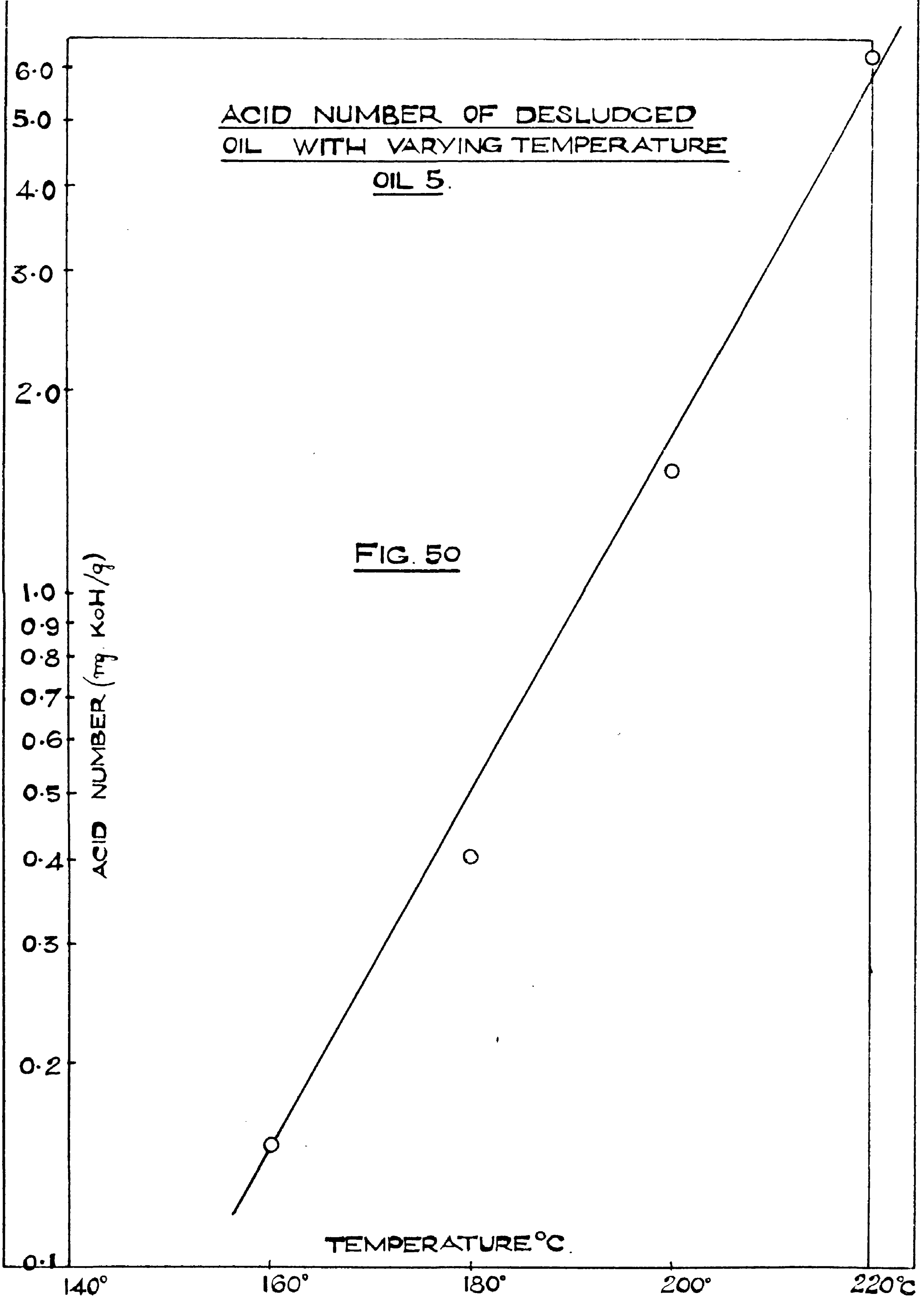
From this data it can be concluded that, where no induction period is evident, acid values of desludged oils



ACID NUMBER OF DESLUDGED OIL WITH VARYING TEMPERATURE

OIL I.

FIG. 49.



ACID NUMBER OF DESLUDGED OIL WITH VARYING TEMPERATURE

OIL 5.

FIG. 50

are related to the amount of oxygen absorbed. In other words almost the same percentage of oxygen goes towards acid production in the oil regardless of temperature.

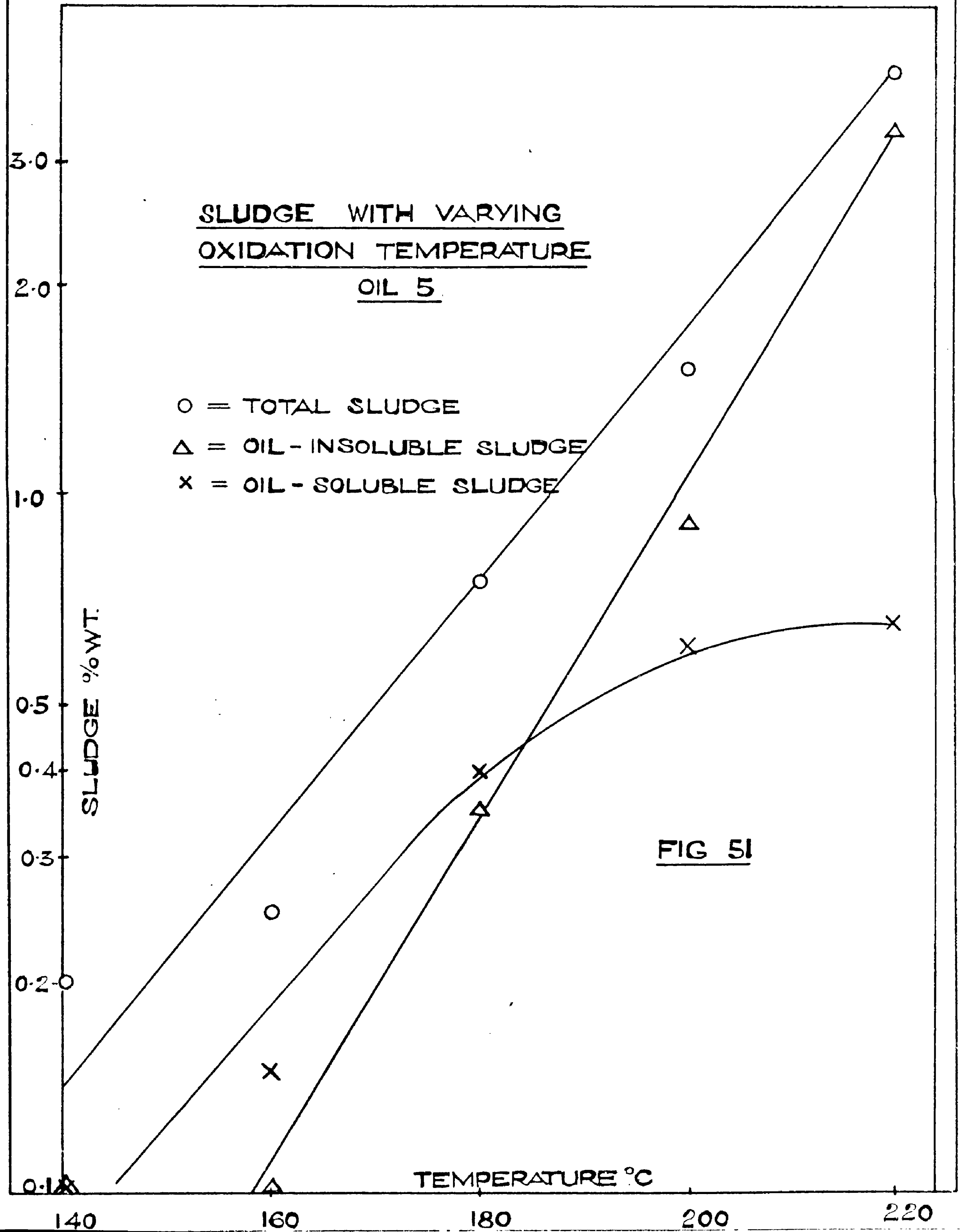
XI.4. Sludge with Varying Oxidation Temperature.

Sludge values are shown in Table 27 and it is seen that oil 5 is the only sample producing oil-soluble and oil-insoluble sludge at all temperatures. The sludge values for this oil are shown in Fig.51 plotted on a logarithmic scale against a linear temperature scale. Significant deviations from a simple log function are indicated. This accounts for the fact that acidity of the original oxidised oils and of the clarified oils showed no relationship with temperature.

TABLE 27.

Sludge values (% wt.) at varying oxidation temperature.

Sample	Type of Sludge	% wt. Sludge at 12 Hours Oxidation and Different Temperatures (°C.)				
		140	160	180	200	220
Oil 1	Soluble	-	-	-	0.1	0.2
	Insoluble	-	-	-	-	0.1
Oil 2	Soluble	trace	0.1	0.2	0.35	0.8
	Insoluble	-	-	trace	0.25	0.2
Oil 3	Soluble	-	0.1	0.1	0.3	0.4
	Insoluble	-	-	-	0.1	0.1
Oil 4	Soluble	0.1	0.1	0.2	0.6	0.9
	Insoluble	-	trace	0.15	0.8	1.7
Oil 5	Soluble	0.1	0.15	0.4	0.6	0.65
	Insoluble	0.1	0.1	0.35	0.9	3.3



SLUDGE WITH VARYING OXIDATION TEMPERATURE
OIL 5

FIG 51

CHAPTER XII

SUMMARY

CHAPTER XII

SUMMARY

This investigation has involved primarily, from the experimental viewpoint, determination of the oxygen absorbed on oxidation of lubricating oil under conditions of the Institute of Petroleum test; determination of both oil-soluble and oil-insoluble sludge and the measurement of acidity in dark-coloured oil.

Oxygen absorption has been measured by circulating air in a closed system and, on absorption of oxygen by the oil, adding measured amounts of oxygen. Volatile and gaseous oxidation products are removed by condensation and absorption.

Modification of a previously published method for estimating oil-insoluble sludge[76], has enabled both insoluble and soluble sludge to be determined by a simple experimental technique using one solvent. Methods for estimating oil-soluble sludge are empirical, and often of doubtful value, in that choice of solvent greatly influences the amount of sludge precipitated. Evidence suggests, however, that the commercial pentane used in this work gives soluble sludge values which are useful as an indication of potential oil-insoluble sludge.

Standard methods for estimating the acidity of lubricating oil fractions are recommended by the Institute of Petroleum and the American Society for Testing Materials. These methods involve either potentiometric titration or the use of coloured indicators. It has been shown in this work that use of a combination of fluorescein and methyl red provides a rapid method which is considered to be very useful for dark oils. This method has had brief mention in the literature[85,86], but appears to have been little used. Comparison of the method with the standard potentiometric (A.S.T.M. D 664) and colour-indicator (I P 139) methods has proved it to be reliable, particularly with very dark oxidised oil where the fluorescent end-point is easier to observe. Other combinations of fluorescent material and dye indicator have also been found useful.

Studies have shown, in general, that the acid and sludge formed and the oxygen absorbed by lubricating oil during oxidation under standard test conditions (I P 48), are not readily predictable from measurement of viscosity ratio and carbon residue increase as specified in that test. These two measured quantities in the I P test bear some relationship to the sludge formed and to the oxygen absorbed, in so far as all show a general tendency to increase with increase of percentage carbon in aromatic structure of the oil (C_A).

There are, however, important differences in all these quantities, especially for oils of low aromatic content. Of the four quantities only sludge appears to increase with C_A throughout the complete range of oils used; the other three measurements of deterioration show deviations from this trend for oils lower in C_A than about 10%. Oxygen absorption shows a distinct minimum at 10% C_A; carbon residue increase for low aromatic oils is proportional to carbon in naphthenic structure of the oil (C_N) and viscosity ratio assumes a constant value for oils of less than 10% C_A.

Acid number does not show any relationship to aromatic structure throughout the complete range of composition of the oils used, but log acid number increases linearly with percentage carbon in paraffinic structure (C_P), in the case of desludged oils.

These results suggest that a change in the oxidation mechanism takes place at about 10% C_A, and this is perhaps shown most clearly by the absorption <u>vs</u>. C_A curve plotted for 22 oil fractions (Fig.23). This 'optimum aromaticity' could well be the result of inhibition brought about by aromatic hydroxyl compounds produced on oxidation. Aromatic compounds, on oxidation, are known to use much of the oxygen absorbed in forming hydroxyl compounds, and moreover the stability of naphthalene aromatics etc. has been attributed to the naphthols produced on oxidation.[43,55,92,93] As oils nearing 10% C_A are oxidised, increased aromatic content would produce more aromatic hydroxyl compounds and hence the minimum at about 10% C_A could be explained as an increased inhibition effect.

Oils of still higher aromatic content show increased oxidation which may well be due to stimulated oxidation of aromatics by the presence of other hydrocarbons. These effects have previously been discussed[64]. Along with stimulation there is possibly a natural increase due to the increased number of α-carbon atoms in substituted aromatics. This effect has been shown to give increased reactivity.[45,56,64]

Carbon residue increase on oxidation also gives some indication of a change of oxidation pattern at about 10% C_A. Above this aromatic content a linear relationship between carbon residue increase and C_A is evident, and is probably related to the fact that sludge generally increases with C_A. For low aromatic oils (below about 10% C_A) carbon residue increase bears a relationship to C_N, but there is no obvious reason for this on the basis of inhibition by hydroxyl compounds.

Viscosity ratio measurements, also, tend to confirm that a different oxidation pattern exists between high and low aromatic oils. The increase of viscosity ratio with C_A

(above 10% C_A) is reasonable since soluble sludge shows a general increase with aromatic content, and increase in viscosity has been attributed to dissolved sludge[49]. Oils of lower aromatic content give almost constant values for viscosity ratio but the relationships here may be more complicated; the effect of reduction in soluble sludge could well be counteracted by increased acids which have been said to cause higher viscosity[49].

Oxidation of several oils at lower oxidation temperatures (down to 140°C) again suggests that an inhibition effect operates with low aromatic oils. It is seen that only such oils have an induction period and this could be due to the fact that at lower temperatures the inhibition effect is enhanced and a definite induction period produced.

Oxidation of original oils and raffinate fractions at 200°C indicate that, in general, the sludge produced increases with the amount of carbon in aromatic structure (C_A). Since paraffins and naphthenes do not form sludge it is reasonable that aromatic content should be the criterion. Oils low in aromatic content produce more oil-soluble than oil-insoluble sludge, whereas oils of higher aromatic content give almost equal amounts of each until 12-15 hours oxidation when the insoluble sludge content increases rapidly, soluble sludge remaining at an almost constant level.

It has often been expressed in the literature that sludge formation is caused by condensation and/or oxidation of acids. This is scarcely tenable since paraffins which produce much acid often form no sludge. Aromatic compounds absorb a large proportion of oxygen to form hydroxyl compounds and it is considered here that these hydroxyl compounds may be necessary for production of insoluble sludge. If oil-soluble sludge is a precursor of oil-insoluble sludge then the reaction can probably be represented as: soluble sludge + aromatic hydroxyl material ——→ insoluble sludge. Oil low in aromatic content would probably suffer from a time lag in this reaction in that fewer oxidised aromatic compounds would be available. Higher aromatic oil has much more aromatic material available and there would be little or no time lag under the oxidation conditions.

This hypothesis would explain the differences between sludge formation in low and high aromatic oils and would also give a reason for the constant amount of soluble sludge on prolonged oxidation of high aromatic oil. The constant sludge value suggests that enough aromatic material is available for reaction and implies an equilibrium between the reactions: oil ——→ soluble sludge and: soluble sludge ——→ insoluble sludge.

Oxidation of oil at air rates less than the standard

15 litres/hour produces variation in the acid : sludge ratio; acidity falling more rapidly than sludge on reduction of air flow. These experimental results can be interpreted if it is assumed that hydroxyl compounds do take part in the sludge reaction and must be taken as offering some indirect evidence that such is the case.

There is some evidence that sludge is produced by the condensation of aromatic hydroxyl compounds with carbonyl compounds. This view has also been offered recently by Taat[97] but has not been verified experimentally. If this mechanism is correct then it explains the change in proportions of acid and sludge with reduced air rates. If rapid, oxygen-consuming radical reactions take place during oil oxidation limitation of the oxygen supply means a reduction in the amount of oxygen available for the slower tertiary reactions. As a result, secondary oxidation products like carbonyl compounds would have a longer life and would be more able to condense with hydroxyl compounds. This means that less acid but more sludge would be formed. Under the experimental conditions where reaction rates have decreased this would be seen as a reduction in both acid and sludge with the sludge:acid ratio increasing as air flow is decreased.

Reduction in air flow was shown also to affect oxygen absorption at 200°C. Oil which has a low oxygen absorption at 15 litres/hour was shown not to suffer from a diminished rate of oxygen supply until a fairly low air rate is reached. Oil with a higher chemical oxidation rate is soon affected by diminished oxygen access. This is considered to be due to oxygen diffusion effects having a rate-controlling influence, particularly where the chemical rate of oxidation is high. Irving and Thompson[96] showed this to be the case in a series of static oxidation tests with air present over an oil surface. Here similar results are obtained with bubbles of air emerging from a tube immersed in the oil.

Oxidation of lubricating oil at temperatures lower than 200°C (down to 140°C) has been mentioned as adding support to the hypothesis of inhibition of low aromatic oils. Oils high in aromatic content (which give linear absorption curves) give an approximate doubling in absorption for every 10°C rise in oxidation temperature. Low aromatic oils have their induction periods approximately halved for each 10°C rise, but beyond the induction period the behaviour of the oil is not predictable by a temperature/absorption relationship. At higher temperatures, when the induction period is no longer produced, the absorption/time curve approaches linearity and absorption is shown to double for each 10°C rise in oxidation temperature. As suggested above, at low levels of aromatic content an enhanced inhibition is probably produced, leading to definite induction periods. Above about 10% C_A enough aromatic material would be present to control the oxidation rate.

Acidity of oxidised oil is affected by temperature of oxidation in a similar fashion to absorption, i.e. an approximate doubling for every 10°C rise, but only totally desludged oil conforms to a simple log function. This indicates that the same amount of oxygen goes towards acid production in the oil regardless of temperature.

Sludge formation appears to show deviations from a simple log function with temperature.

It can be concluded from this investigation that, due to the complexity of the oxidation reactions in a mixture of different hydrocarbon types, it would be difficult to assess from a simple laboratory oxidation test how an oil would behave during use in an engine. This is especially true where engine running conditions and temperatures vary widely.

Even making due allowance for the empirical nature of laboratory oxidation tests, the author feels that the I P test does not make full use of the information available. The standard measurements in the test are carbon residue increase and viscosify ratio, both of which have been shown to increase generally with % C_A of the oil. These two measurements, then, would correspond roughly to the sludge-forming potential of the oil which shows a similar relationship to C_A. Acidity on oxidation is not proportional to the aromatic carbon content of the oil and it is considered that acid value would be a valuable measurement. Since it was shown that sludge itself often has a high acid number a necessary acid determination would appear to be that of desludged oil. Estimation of total acid alone is misleading in that oils of very different acid forming characteristics can give similar values for total acid.

A serious disadvantage in assessing stability of an oxidised oil by the two measurements of the I P test is that the change in oxidation pattern seen below about 10% C_A may be very misleading. For example, oils can be chosen which, on oxidation, give similar values for viscosity ratio and carbon residue increase, and yet possess very different sludge and acid forming properties.

For the above reasons it is suggested that the I P test would furnish more valuable information on the behaviour of a lubricating oil in use if the following measurements were made:

(a) viscosity ratio

(b) total acid number

(c) acid number of desludged oil

(d) oil-insoluble sludge

(e) oil-soluble sludge.

Further work of interest would be the examination of the sludge-forming reaction on oxidation of lubricating oil. Work of this nature could clarify the position regarding reaction between aromatic hydroxyl compounds and carbonyl compounds. Estimation of the former by potentiometric titration was attempted in this investigation but proved unsuccessful.

Of interest, also, would be a study of the type of molecules undergoing oxidation. This might be possible by repeated oxidation of an oil and removal of oxygen-containing material by absorption on a clay or earth after each oxidation. The progress of oxidation could then be followed by the use of the n-d-M method of analysis.

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