

TIGHT BINGING BOOK

UNIVERSAL
LIBRARY

OU_168696

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 660.28/.W32C

Accession No. 40105

Author Waterman, H. I.

Title Correlation between physical constants and
chemical structure. 1958.

This book should be returned on or before the date last marked below

CORRELATION BETWEEN PHYSICAL CONSTANTS AND CHEMICAL STRUCTURE

SOLE DISTRIBUTORS FOR THE UNITED STATES OF NORTH AMERICA

D. VAN NOSTRAND COMPANY, INC.

120 Alexander Street, Princeton, N J (Principal office)

24 West 40th Street, New York 18, N Y

SOLE DISTRIBUTORS FOR CANADA

D. VAN NOSTRAND COMPANY (CANADA), LTD.

25 Hollinger Road, Toronto 16

SOLE DISTRIBUTORS

FOR THE BRITISH COMMONWEALTH EXCLUDING CANADA.

D VAN NOSTRAND COMPANY, LTD

358 Kensington High Street, London, W 14

CORRELATION BETWEEN PHYSICAL CONSTANTS AND CHEMICAL STRUCTURE

GRAPHICAL STATISTICAL METHODS OF IDENTIFICATION
OF MINERAL AND FATTY OILS, GLASS, SILICONES, AND CATALYSTS

by

H. I. WATERMAN

Professor of Chemical Technology

Technical University, Delft (The Netherlands)

in collaboration with

C. BOELHOUWER and J. CORNELISSEN

Research Associates, Delft, Technical University



ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK PRINCETON

1958

ALL RIGHTS RESERVED. THIS BOOK OR ANY PART
THEREOF MAY NOT BE REPRODUCED IN ANY FORM
(INCLUDING PHOTOSTATIC OR MICROFILM FORM)
WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS

Library of Congress Catalog Card Number. 58-10629

With 100 figures and 17 tables

Checked 1965

Checked 1965

First edition 1958

First reprint 1959

Second reprint with minor additions July 1960

Pages 1-116 of this book appeared as issue No. 5 of *Analytica Chimica Acta*, Vol. 18 (1958)

PRINTED IN THE NETHERLANDS BY
KRIPS REPRINT COMPANY

PREFACE

This monograph originated from an investigation of one particular subject, namely the ring analysis of mineral oils, which work was carried out by the author in collaboration with Dr. J. C. VLUGTER, Dr. H. A. VAN WESTEN and Dr. J. J. LEENDERTSE. This work has been developed into a complete new system of investigation methods which have a specific character and are suitable for general application. Therefore, the research field has become a very extensive one, and comes into contact with many branches of chemical industry

This is the reason why, in recent years, the author has, at the request of the research departments of various big chemical concerns in the U.S.A., Great Britain and other countries in Western Europe, delivered lectures with the purpose of achieving possible applications in the different fields. In the past years the author has also discussed these subjects at Delft Technical University in special courses of optional lectures. Some of the students or graduates, who attended these lectures, have contributed to the further development of the methods and thus have developed new fields of application.

From the examples chosen the reader will see how the discussed methods may assist in gaining more insight into many natural products handled in industry and products prepared in factories. The applications of these methods are numerous, it is the purpose of this monograph to enable everybody to become acquainted with the methods described, so that they can apply them to their problems of investigation. It is already known that the relation between temperature and kinematic viscosity of liquids, represented by the exponential formula $\log \nu = A/T^* + B$, is generally applicable and the same formula holds also for the relationship of vapour pressure and temperature, which fact opens many new perspectives. The past years have taught us that a two-months practical course in our institute is sufficient for experienced chemists and physicists to become familiar with the methods and the experimental procedures.

Attention has been given to the characterization of catalysts by parameters, as discussed in the last chapter, in which field Dr. A. B. R. WEBER *et al* have worked in this institute. This application may open up immediate possibilities of reducing the expenses of semi-industrial process development work.

My thanks are due to my son Dr. J. A. WATERMAN who has given us valuable help in correcting the manuscript

Delft, March 1958

H. I. WATERMAN

CONTENTS

Preface	v
I. Introduction	i
II. Mineral oils and related hydrocarbon mixtures	3
1. Introduction and definitions	3
2. Ring analysis and carbon-type analysis of mineral oil fractions	4
a. Analytical hydrogenation of mineral oils	4
b. Ring analysis and carbon-type analysis of saturated mineral oil fractions	9
(i) Original ring analysis of saturated mineral oil fractions	9
(ii) Carbon-type analysis of saturated mineral oil fractions	16
c. Ring analysis and carbon-type analysis of natural mineral oil fractions by means of the Direct Method	21
(i) Determination of $\%C_A$	21
(ii) Determination of the total ring-number R_T	21
(iii) Determination of $\%C_R$	22
(iv) Determination of the number of aromatic rings R_A	22
(v) Determination of the number of naphthenic rings R_N	24
(vi) Determination of $\%C_N$	24
d. Ring analysis and carbon-type analysis of mineral oil fractions by means of the $n-d-M$ method	24
e. Kinematic viscosity and structure of mineral oil fractions	26
(i) Structure of saturated mineral oil fractions $\nu-M$ diagrams and $\nu-n$ diagram	26
(ii) Structure of straight-run mineral oil fractions	28
(a) The $\nu-n-d$ method	28
(b) The $\nu-n-d$ space model and its cross-sections	29
(c) The application of nomograms of the cross-sections of the $\nu-n-d$ space model	33
(d) The applications of $\log \nu-f(n,d)$ graphs	36
3. Correlation of physical constants of mineral oil fractions	38
a. Correlation of the viscosity, the refractive index, the density and the ultrasonic sound velocity of mineral oil fractions	39
(i) Application of cross-sections of the $\log \nu-n-d$ space model	39
(ii) Application of nomograms of the cross-sections	42
(iii) Application of a $\log \nu-(n-1/d)$ graph	42
(iv) Application of a nomogram of the $\log \nu-(n-1/d)$ graph	44
b. Correlation of the viscosity, the refractive index, the density and the surface tension of mineral oil fractions	45
(i) Application of cross-sections of the $\nu-n-d$ space model	45
(ii) Application of a $\log \nu-d$ graph	48

c. Correlation of the ultrasonic sound velocity, the density and the surface tension of mineral oil fractions	48
d. Correlation of physical constants of saturated mineral oil fractions	50
e. Temperature dependence of the viscosity	50
4. Analysis of branched hydrocarbon mixtures	57
a. Introduction	57
b. The Faraday effect	57
c. The magneto-optical rotation	59
d. The parachor	61
e. Applications	67
(i) Mineral oil fractions	67
(ii) Saturated liquid polymers	68
(iii) Isomerization phenomena	68
5. Determination of mono- and di-aromatics in mineral oils	68
a. Introduction	68
b. Applications	71
(i) Analysis of aromatic mineral oil fractions	71
(ii) Hydrogenation of aromatic mineral oil fractions	72
6. Sulphur compounds in mineral oils	72
III. Application of graphical statistical methods in the determination of the composition of glasses and silicones	75
1. Introduction	75
a. Determination of the density of glass	75
b. Determination of the refractive index of glass	76
2. The thermal behaviour of potassium and sodium silicates	77
3. Temperature dependence of the kinematic viscosity of glasses	82
4. The structure of silicones	83
5. Temperature dependence of the kinematic viscosity of silicones	83
IV. Analyses in the field of fatty oils	87
1. Introduction	87
2. Transformation of fatty acid esters into saturated hydrocarbon mixtures	89
3. Direct graphical tracing of transformations of fatty oils	90
a. Hydrogenation of fatty oils	93
b. Polymerization of drying oils	93
c. Cis-trans isomerism of fatty oils	97
4. Graphical analysis of styrenated oils	98
V. Composition of coal	99
1. Demethanation	99

2. Dehydration	100
3. Decarboxylation	101
VI. Graphical statistical methods for studying catalytic processes. Characterization of catalysts by parameters	103
1. Introduction	103
2. Characterization of catalysts	104
3. Applications	105
a. Catalytic hydrogenation of linoleic esters	105
b. The hydro-isomerization of paraffin wax	108
c. The chlorination of benzene	109
d. Selective hydrotreating of shale gasoline	110
4. Selection of catalysts	110
References	114
Subject Index	117
Addendum	118

I INTRODUCTION

In modern chemical technology we often have to deal with complicated mixtures. In these cases the application of chemical analytical methods is not sufficient to obtain the necessary information for satisfactory scientific research, process development and process management. Reliable chemical methods for a detailed analysis of complicated mixtures are not available. Therefore their chemical structure will remain unknown if we restrict ourselves to the application of chemical methods only.

The ultimate analysis of a mixture of organic compounds, however important it may be, is not decisive for its structural identification; likewise, knowledge of the elementary composition of an alloy is not sufficient to describe its physical and mechanical behaviour, because the nature and phase composition of the alloy are left undetermined. The properties of silicates, *e.g.* glass, may be greatly influenced by thermal treatment while the chemical composition of the products remains unaltered.

Therefore *physical* methods of analysis have been introduced into nearly every field of scientific research, especially those methods that can be applied with accuracy. Relationships exist not only between the physical constants (and functions thereof) and the chemical structure and elementary composition, but also mutually between a wide variety of physical (and mechanical) constants. This is of value for the knowledge of several important technical properties.

The various physical constants and functions are used for the identification of complex mixtures such as mineral oils, fatty oils, plastics, resins and silicates. Separation of these products into individual components is generally impossible, and methods had to be developed in which certain structural groupings of the mixtures are considered instead of individual molecules or atoms. To identify such complicated mixtures physical constants could be applied successfully for their "structural group" analysis and for the prediction of various important technical properties.

The methods discussed have been called "Graphical Statistical Methods" since:

1. *Graphs* are generally used, for example for the correlation of physical constants of mixtures, for the structural analysis of mixtures and for graphic recording of hydrogenation, polymerization and isomerization processes.

2. For the construction of these graphs use has to be made of data of many mixtures. Therefore the data have to be treated *statistically*.

3. The mixtures investigated contain many different structural units (for example molecules), which represent a *statistical* distribution.

The development of reliable methods for structural analysis of mixtures is very laborious. Physical data of pure compounds may serve as a base for the investigations. It has, however, been proved that not in all cases can these data be simply correlated with those of the mixtures. Thus correlations of physical data of pure, individual hydrocarbons often prove not to be valid in the analysis of mineral oils. In this case physical constants of mineral oil fractions of widely different origin form a more reliable basis for the structural analysis, provided that their structure has been determined by absolute methods.

When determining the composition of mixtures it is advisable to start with the most simple case. Thus the development of methods for the structural analysis of mineral oil fractions was greatly facilitated by analytical hydrogenation, the aromatic rings being quantitatively transformed into the corresponding naphthenes. The problem is then limited to the determination of only naphthenic and alkyl carbon atoms in these saturated mixtures by means of physical constants. After this problem had been solved the analysis of *non-hydrogenated* aromatic fractions could be carried out by considering the influence of aromatics on the correlations found for the *hydrogenated* fractions; along these lines it was possible to extend the analysis step by step to more complex mixtures.

In the analysis of fatty oils complete expelling of the oxygen by a catalytic high pressure hydrogenation process reduces the problem to the analysis of saturated hydrocarbon mixtures. Such drastic chemical transformations should be executed under strongly controlled conditions only.

In principle any physical constant may be useful for structural analysis of mixtures. For practical reasons those constants should be applied that can be easily determined. High demands should be made upon the accuracy of the determinations. For example the physical constants density, refractive index, kinematic viscosity, ultrasonic sound velocity and surface tension may be chosen. Combination of constants, *e.g.* in certain "additive" functions, is useful only when the constants in question have been determined with comparable accuracy. In this respect density and refractive index may be combined, whereas molecular weight, the determination of which is not so precise, cannot always be combined with refractive index and density.

In general more independent physical constants that are sensitive to structure are needed when it is necessary to know more structural elements of a mixture. It will be clear that, dependent on the collected basic data, statistical methods for the analysis of mixtures in general only give a certain approach to their structures, but should never be considered as the ultimate purpose. Improvement of existing methods is imperative when new and more accurate data become available, the development of various physical separation methods (distillation, chromatography, thermodiffusion, etc.) and of independent physical identification methods (ultraviolet and infrared spectra, mass spectrometry) may also contribute considerably to their perfection.

It is to be expected that complete knowledge of the structure of mixtures of complicated nature will remain illusory. Nevertheless, it will be proved that it is already

possible in such a case to predict physical constants from other physical constants, or functions thereof, with the same accuracy as the experimental accuracy.

There is another group of mixtures, which are too complicated to be described by a restricted number of physical constants. To this group belong many *catalysts*, namely the heterogeneous ones. Although several methods of measuring physical properties have been proposed (determination of internal surface, pore volume and pore size, X-ray diagrams), these are not sufficient to characterize their catalytic properties, *viz.* their activity in influencing chemical transformations, even in more simple reactions. It has been proved, however, that also for these complex mixtures characterization is possible by means of a certain limited number of *parameters* that can be determined by a simple method of graphic tracing. This principle has been applied to a large number of complex catalytic reactions and offers the possibility of a direct comparison of catalysts in all kinds of chemical transformations under different reaction conditions.

This shows the many-sidedness of the principles that are developed in the following pages.

II MINERAL OILS AND RELATED HYDROCARBON MIXTURES

1. INTRODUCTION AND DEFINITIONS

Mineral oils consist chiefly of mixtures of hydrocarbons, besides sulphur-, nitrogen- and oxygen-containing compounds in varying quantities. The number of constituents is generally too large to make possible the separation of the individual compounds from the oils or oil fractions. Thus it is not possible to analyse mineral oils according to quantity and character of the separate hydrocarbons, or S-, O-, and N-containing compounds.

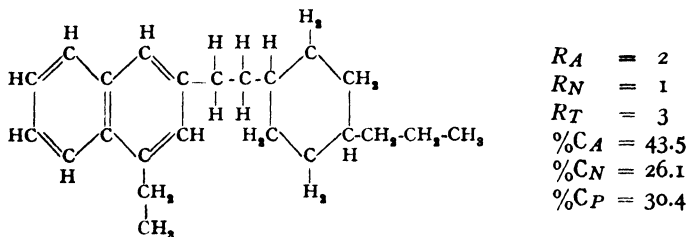
A solution to the problem of determining the composition of mineral oil fractions, especially those of high molecular weight, is provided by dealing with the oil fractions in a statistical way, *i.e.* some characteristic structural elements in the mixture are defined and determined by appropriate means.

In this monograph only those mineral oils are discussed that have a molecular weight higher than 200, that do not contain compounds with olefinic double bonds (as is the case, for instance, with several cracked products), and that do not contain compounds with oxygen or nitrogen in the molecules. Olefins are generally present in only very small amounts in mineral oils. It should be mentioned here that the hydrogen value, introduced by VAN WESTEN for the determination of the olefinic non-saturation, has recently been improved and simplified by SIE AND WATERMAN¹. Ozonization techniques also have been brought to perfection, in this connection the work of BOER AND KOOYMAN² should be consulted.

The following structural elements will be determined: ring-number per average molecule* in naphthenic structure ($= R_N$), ring-number per average molecule in aromatic structure ($= R_A$), total ring-number per average molecule ($= R_T$ being equal

* A hypothetical molecule which represents the average nature of the molecules present in the mixture.

to $R_A + R_N$, the percentage of carbon atoms (of the total number of carbon atoms) present in naphthenic structure ($= \%C_N$), the percentage of carbon atoms present in aromatic structure ($= \%C_A$), the percentage of carbon atoms present in ring structure ($= \%C_R$ being equal to $\%C_A + \%C_N$) and the percentage of carbon atoms present in paraffinic structure ($= \%C_P$), while $\%C_A + \%C_N + \%C_P = 100$. Thus in the compound



Another important structural element is the degree of branching of the mixture. The definition and a description of its determination will be given in section II 4 (p. 57).

More detailed knowledge of the composition of mineral oils can be obtained by splitting the oils into as narrow fractions as possible by means of fractionation, thermodiffusion, chromatography, extraction and other means. On the opposite page a scheme is given as an illustration of the application of distillation techniques in the investigation of mineral oils and polymerized fatty oils.

Spectrographic data are gradually becoming more important for the analysis of hydrocarbon mixtures. These methods will not be discussed as they fall outside the scope of this monograph.

2. RING ANALYSIS AND CARBON-TYPE ANALYSIS OF MINERAL OIL FRACTIONS

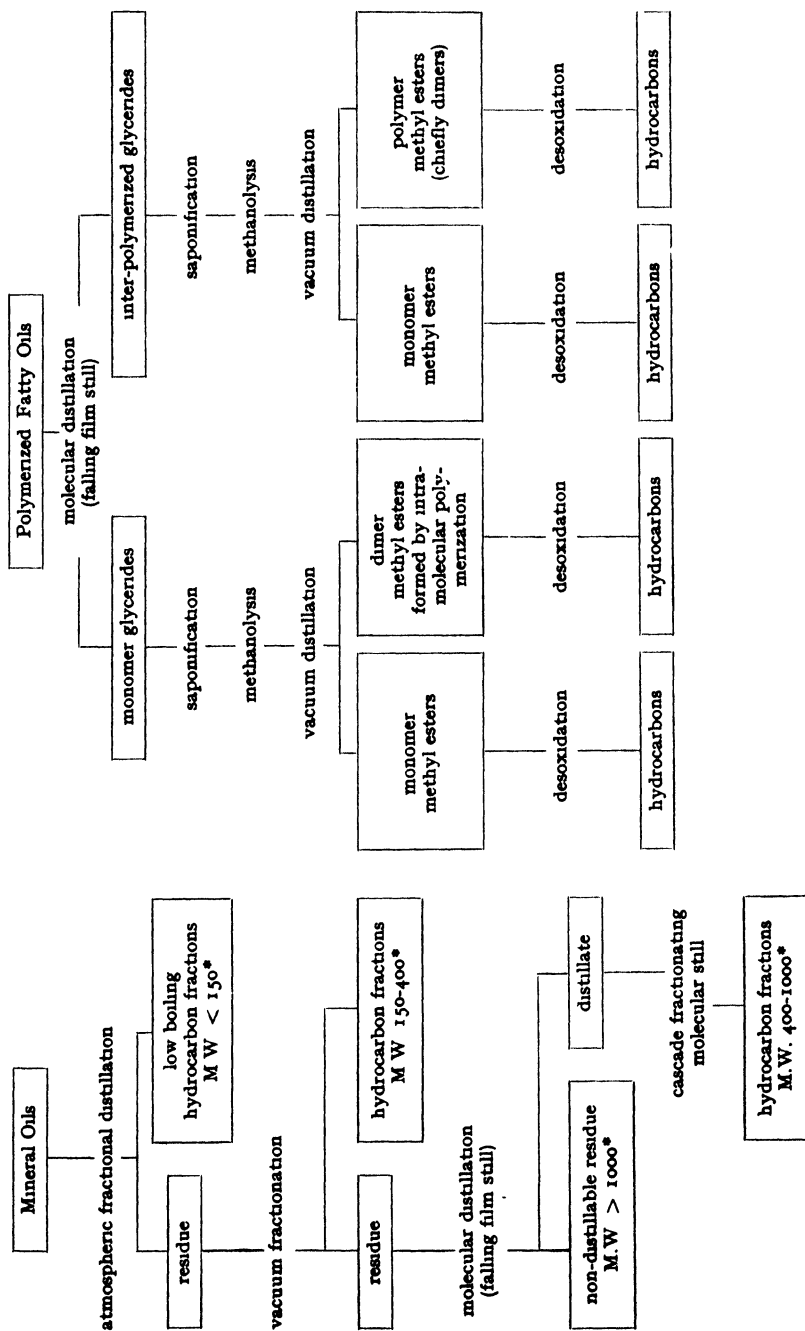
a. Analytical hydrogenation of mineral oils

When determining the composition of mixtures it is advisable to start with the most simple case. In the field of hydrocarbon mixtures this means the investigation of saturated fractions, obtained by careful hydrogenation of aromatic-containing fractions. Hydrogenation is carried out by means of a selective, catalytic hydrogenation process, which consists of treating the fraction with hydrogen at high pressure (up to 200 atmospheres) and high temperature (up to 300°C) in the presence of nickel on kieselguhr for a period that is dependent on the structure of the oil.

Especially when larger amounts of foreign elements (sulphur, nitrogen, oxygen) are present, precautions are necessary to avoid undesired side reactions, such as cracking, ring opening or ring formation, during the hydrogenation process. VAN NES AND VAN WESTEN³ described a stepwise hydrogenation technique in a prehydrogenation procedure mainly the elimination of the foreign elements was achieved, the actual saturation of the aromatics followed in a second step. Details are given in their book³.

When highly aromatic fractions are hydrogenated prolonged heating of the completely hydrogenated material in the presence of nickel catalyst and high pressure

APPLICATION OF DISTILLATION TECHNIQUES IN THE INVESTIGATION OF MINERAL OILS AND POLYMERIZED FATTY OILS



* The indicated molecular weights are approximate values and serve only to illustrate the scheme

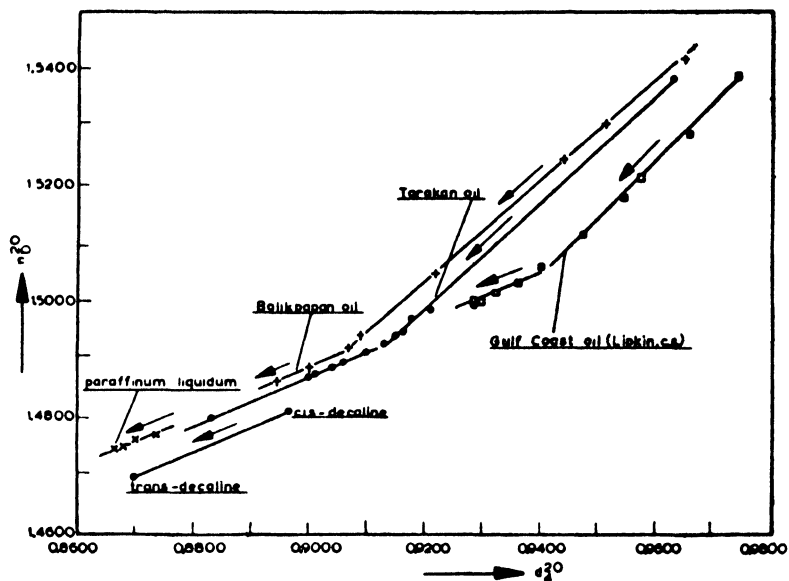


Fig. 1a.

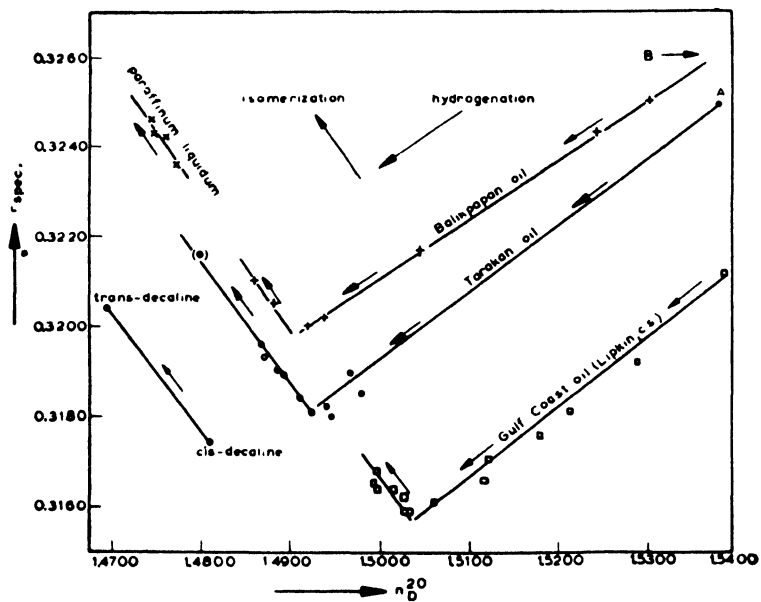


Fig. 1b.

Fig. 1. Treatment of aromatic mineral oil fractions with nickel on kieselguhr catalysts and high pressure hydrogen

hydrogen may cause distinct changes in certain physical constants (refractive index, density, specific refraction, viscosity) of the saturated fractions, which changes show remarkable resemblance to those occurring in the *cis-trans* conversion of decalin under comparable conditions (*cf.* Fig. 1).

In all probability isomerizations of the same type take place during the prolonged, hydrogenation. As follows from Fig. 1 these reactions bring about a small but obvious

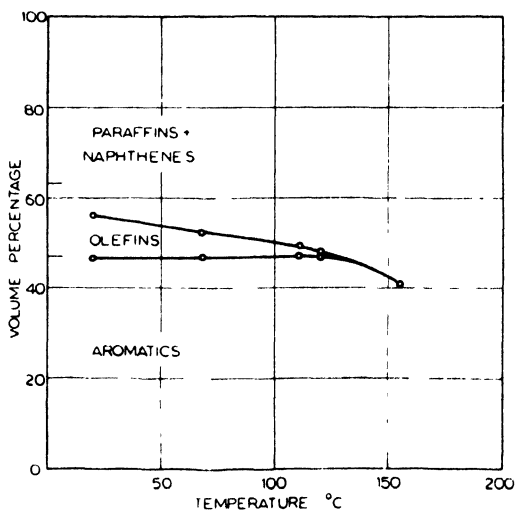
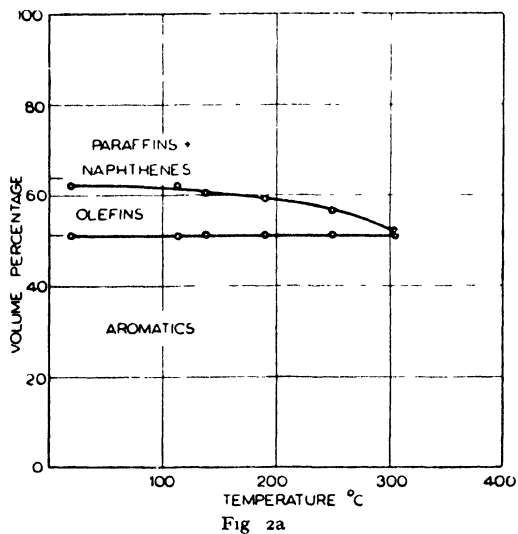


Fig. 2b

Fig. 2a, b Selective analytical hydrogenation of olefinic distillates

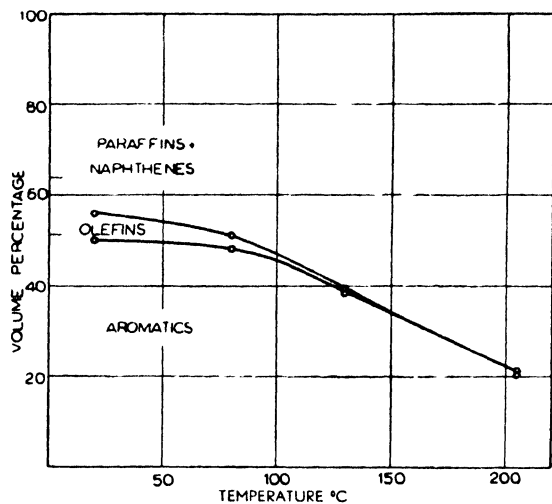


Fig 2c.

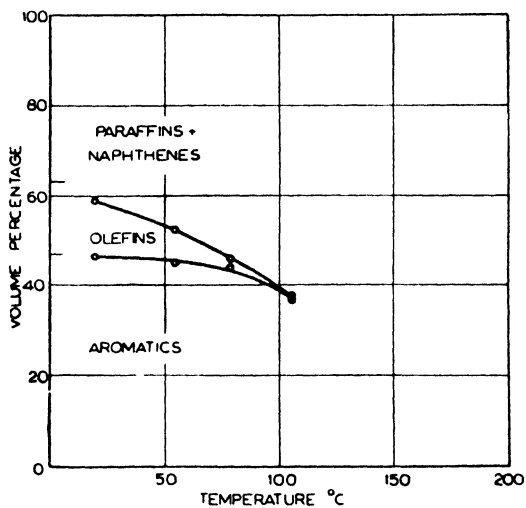


Fig 2d.

Fig 2c, d. Selective analytical hydrogenation of olefinic distillates.

increase of the specific refraction, and this is especially of importance with regard to the applicability of methods for ring analysis and carbon-type analysis based upon this function. Fortunately the isomerization process takes place very slowly. Only extremely prolonged reaction times (25-100 h) and relatively high temperatures (300-350°C) result in a pronounced isomerization of the oil, which might influence the results of graphical statistical analytical methods to some extent.

In normal cases the hydrogenation of mineral oil fractions can be used as an analytical tool for a quantitative transformation of aromatic rings into the corresponding naphthenes.

When *olefins* are present in the fractions to be investigated (this might be the case in, for instance, cracked products) it is sometimes useful to saturate the olefinic double bonds by a *selective* hydrogenation process, *viz.* without saturation of the aromatics. According to WATERMAN, WEBER AND ZWEEKHORST⁴ especially molybdenum oxide on active carbon (100 atm hydrogen, 300°C, Fig. 2a) and platinum on silica-alumina (10 atm hydrogen, 120°C, Fig. 2b) are suitable for a selective hydrogenation of kerosine fractions, in contrast to other catalysts (*e.g.* Ni on kieselguhr, Fig. 2c, and Pd on active carbon, Fig. 2d) that are not strictly selective. This analytical hydrogenation of olefinic double bonds is especially useful for the evaluation of the constitution of cracked distillates

When the problem of establishing the structure of hydrogenated products has been solved, more complicated mixtures, *e.g.* aromatic-containing fractions, can be considered. The existing methods of determining the composition of mineral oil fractions have been developed according to this scheme. The methods presented below are treated in principle in chronological order.

b. Ring analysis and carbon-type analysis of saturated mineral oil fractions

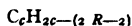
(1) Original ring analysis of saturated mineral oil fractions

The only unambiguous way of establishing the number of naphthenic rings R_N ($= R_T$) in saturated mineral oil fractions is by applying the Direct Method. This method involves the determination of the molecular weight M and the percentage hydrogen, %H. The number of rings in the saturated mixtures can then be calculated by means of the equation

$$R = 1 + (8.326 - 0.5793\%H) \cdot \frac{M}{100} \quad (1)$$

A consequence of the presence of each ring in the average molecule of the fraction is that there are two hydrogen atoms lacking compared to the corresponding fraction with no ring, *independent of the type of the ring* (five-membered, six-membered ring, etc.) and of the way in which the various rings are linked

If it is assumed that the number of carbon atoms in the average molecule of the oil fraction is c and the number of hydrogen atoms h then the molecular formula is C_cH_h . If the number of rings in the average molecule is R , this formula can also be represented by



For the molecular weight M it follows from the given molecular formula that

$$M = 12.010c + 1.008h \quad \dots \quad (2)$$

and

$$M = 12.010c + 1.008 \{2c - (2R - 2)\} \quad \dots \quad (3)$$

The percentage of hydrogen %H is given by

$$\%H = \frac{1.008h}{M} \cdot 100 \quad \dots \quad (4)$$

or, on replacing h by $\frac{(M - 12.010c)}{1.008}$ according to equation (2)

$$\%H = \frac{(M - 12.010c)}{M} \cdot 100 \quad \dots \quad (5)$$

From equation (5) it follows for the value of c that

$$c = \frac{100M - \%H M}{12.010} \quad \dots \quad (6)$$

Substitution of this value of c in equation (3) gives

$$M = 12.010c + 2.016c - 2.016R + 2.016$$

$$R = \frac{-M}{2.016} + \frac{14.026(100M - \%H M)}{12.010 \times 2.016} + 1$$

or

$$R = 1 + (8.326 - 0.5793 \%H) \frac{M}{100} \quad \dots \quad (1)$$

By means of equation (1) the number of rings in saturated mineral oil fractions can be calculated if %H and M are known

The number of rings in saturated mixtures of hydrocarbons can also be read from the graph in Fig. 3, which represents equation (1) in the form

$$\%H = 14.37 + \frac{172.6(1-R)}{M} \quad \dots \quad (7)$$

In this diagram lines of equal ring-number have been constructed, R increasing with 1 unit from top to bottom starting from a ring-number zero (paraffins). The diagram clearly shows the fact that with constant molecular weight the number of rings increases with a decreasing amount of hydrogen in the fractions considered. Special

mention must be made of the fact that if $R = 1$, it follows that $\%H = \frac{8.326}{0.5793} = 14.37$.

Though the method described is the only unambiguous one for ring determination in saturated hydrocarbon mixtures, it is rather laborious. Only experts can carry out the ultimate analysis to determine the hydrogen content with sufficient accuracy and it always takes much time. A method described by VLUGTER, WATERMAN AND VAN WESTEN⁵ makes it possible to replace the hydrogen content by the specific refraction, defined according to LORENTZ-LORENZ⁶, as

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

where n = refractive index and d = density in g/ml.

Both the refractive index and the density are measured at the same temperature, e.g. 20°C. The refractive index is generally measured for the sodium D-line. In the fol-

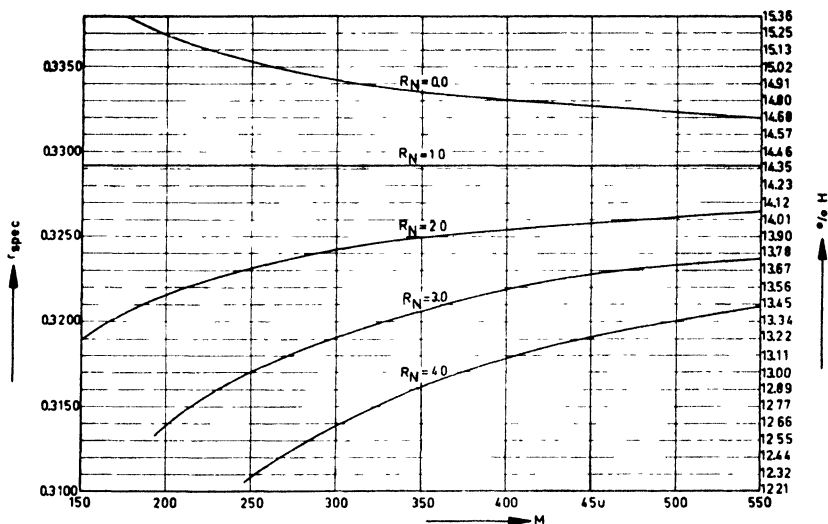


Fig. 3 Ring analysis diagram according to VLUGTER, WATERMAN AND VAN WESTEN

lowing for reasons of conciseness, the specific refraction at 20°C will be indicated as r_{spec}^{20} , omitting the symbol D sometimes used for indicating the sodium D-line*

A diagram has been constructed from which it is possible to determine the number of rings of saturated mineral oil fractions if the specific refraction and the molecular weight are known (Fig. 3). The diagram is called the ring analysis diagram.

The possibility of using the specific refraction instead of the hydrogen content in the analysis of saturated mineral oil fractions is due to the fact that there exists a linear relationship between the specific refraction r_{spec}^{20} and the hydrogen content %H.

This can be elucidated by the following consideration:

If the molecular formula of the "average" molecule, which represents the mineral oil fraction under examination, is again taken as C_cH_h then

$$\text{and} \quad M = 12.010c + 1.008h \quad \dots \quad (2)$$

$$\%H = \frac{1.008h}{M} \cdot 100 \quad \dots \quad (4)$$

The specific refraction is equal to the molecular refraction $\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}\right)$ divided by the molecular weight M .

The molecular refraction r_{mol} is an additive function, i.e. it is a function which is equal to the sum of the atomic refraction of carbon, r_c , and that of hydrogen, r_h , each multiplied by its number of atoms in the "average" molecule.

$$\text{The molecular refraction } r_{\text{mol}} = M r_{\text{spec}}^{20} = c r_c + h r_h \quad \dots \quad (8)$$

and

$$r_{\text{spec}}^{20} = \frac{c r_c + h r_h}{M} \quad \dots \quad (9)$$

* The omission of D cannot give rise to confusion as in this monograph the wavelength of the sodium D-line is the principle wavelength at which refractions have been measured. If other wavelengths are used this is specially indicated.

From equation (4) it follows that

$$h = \frac{M \%H}{100.8} \quad \dots \dots \dots (10)$$

and from equation (2) and equation (10)

$$M = 12.010c + \frac{1.008M \%H}{100.8}$$

or

$$c = \left(M - \frac{M \%H}{100.8}\right) \frac{1}{12.010} = \frac{100 - \%H}{12010} M \quad \dots \dots \dots (11)$$

Substitution of the values of c and h , according to equations (10) and (11), in equation (9) gives

$$\begin{aligned} r_{\text{spec}}^{20} &= \frac{(100 - \%H) \frac{M}{12010} r_c + \frac{\%H}{100.8} M r_h}{M} \\ r_{\text{spec}}^{20} &= (100 - \%H) \frac{r_c}{12010} + \frac{\%H}{100.8} r_h \\ r_{\text{spec}}^{20} &= \frac{r_c}{12010} + \left(\frac{r_h}{100.8} - \frac{r_c}{12010}\right) \%H \quad \dots \dots \dots (12) \end{aligned}$$

Since r_c and r_h can be considered as constants for the majority of the hydrocarbons present in saturated natural mineral oils (the influence of the presence of naphthenic rings, of branches, and of *cis-trans* isomers can be neglected in a first approximation), it follows from equation (12) that there is a linear relationship between r_{spec}^{20} and $\%H$

The values of r_c and r_h have been calculated by EISENLOHR from "pure" substances⁷. This author gave the values $r_c = 2.478$ and $r_h = 1.100$. Substitution of these values in equation (12) gives

$$r_{\text{spec}}^{20} = 0.20133 + 0.00890 \%H \quad \dots \dots \dots (13)$$

and

$$\%H = 112.36 r_{\text{spec}}^{20} - 22.620 \quad \dots \dots \dots (14)$$

If this value of $\%H$ is substituted in equation (1) the following relationship between r_{spec}^{20} , M and R_N is obtained

$$R_N = 1 + \{8.326 - 0.5793 (112.36 r_{\text{spec}}^{20} - 22.620)\} \frac{M}{100}$$

or

$$R_N = 1 + (21.430 - 65.090 r_{\text{spec}}^{20}) \frac{M}{100} \quad \dots \dots \dots (15)$$

Thus it is possible to calculate the number of naphthenic rings of saturated oil fractions from the specific refraction and molecular weight by means of equation (15). The number of rings can also be determined from Fig. 4, in which the relationship between r_{spec}^{20} , M and R_N (besides that between $\%H$, M and R_N) has been constructed by means of equation (15), which has been transformed into

$$r_{\text{spec}}^{20} = 0.3292 - \frac{(R_N - 1) 1.536}{M} \quad \dots \dots \dots (16)$$

From equations (7) and (16) it follows that the curves representing fractions of equal ring-numbers in the $\%H$ - M and r_{spec}^{20} - M diagram (Fig. 3) are hyperbolas. These curves become straight lines if $\%H - \frac{1}{M}$ and $r_{\text{spec}}^{20} - \frac{1}{M}$ plots are made instead. This is shown in Fig. 4.

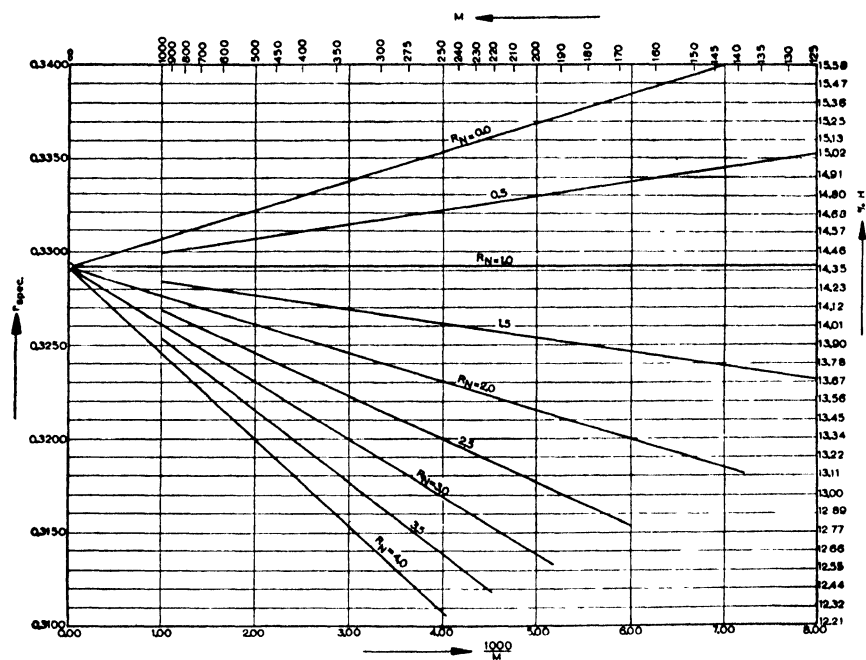


Fig 4 $\%H - \frac{I}{M}$ and $r_{spec}^{20} - \frac{I}{M}$ plots in connection with the ring-number of saturated mineral oil fractions

The distances Δr_{spec}^{20} between the lines of equal ring-number for a definite value of the molecular weight are equal. This holds for both Fig. 3 and Fig. 4. This follows from equation (15)

$$R_N = 1 + (21.430 - 65.090 r_{spec}^{20}) \frac{M}{100} \quad \dots \quad (15)$$

by writing

$$\Delta R_N = -65.090 \cdot \frac{M}{100} \cdot \Delta r_{spec}^{20}$$

If $\Delta R_N = 1$ then

$$\Delta r_{spec}^{20} = -\frac{1.5363}{M} \quad \dots \quad (17)$$

From this equation it follows that linear interpolation is permissible for the calculation of R_N from r_{spec}^{20} and M .

Recently another ring analysis diagram (Fig. 5) has been introduced by GEELEN, WATERMAN AND WESTERDIJK⁸. It has been constructed by means of the equation

$$r_{spec}^{20} = 0.3310 + \frac{1.419 - 1.654 R_N}{M} \quad \dots \quad (18)$$

taking $\frac{I}{M}$ as abscissa.

This equation has been obtained by applying the method of least squares to 81 saturated mineral oil fractions, of which the number of rings had been determined by the $n-d-M$ method (*cf.* p. 24).

Equation (16) has been obtained by means of data of the substances available to EISENLOHR at that time. It differs somewhat from equation (18), which has been obtained by means of data from $n-d-M$ analysis. The most notable difference is that the one-ring line in Fig. 5 does not run parallel to the horizontal axis, contrary to the one-ring line in Fig. 4.

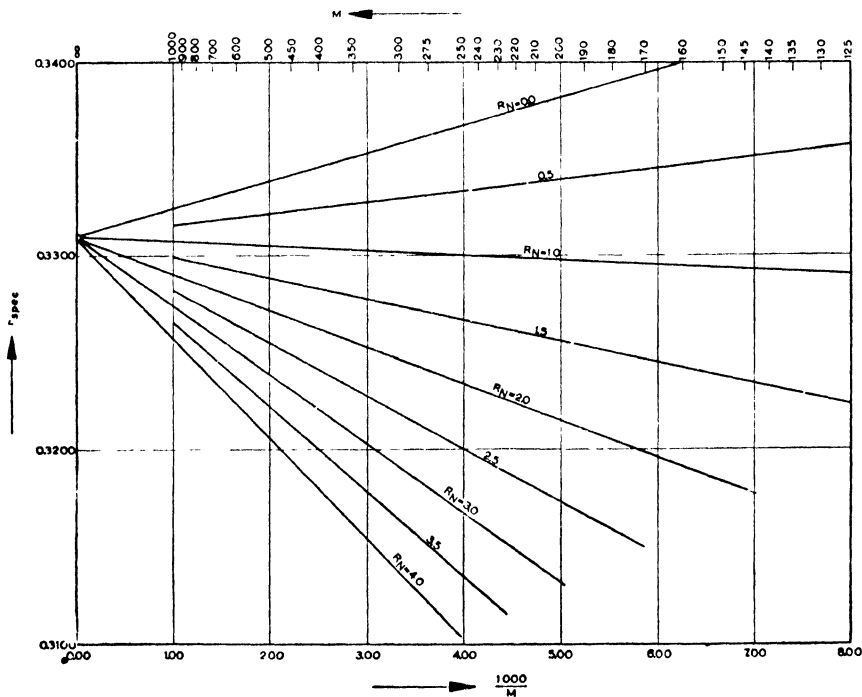


Fig. 5 Diagram representing the relationship between $\gamma_{\text{spec}}^{20}$, $\frac{1}{M}$ and R_N for saturated mineral oil fractions, based on $n-d-M$ data

The slope of the lines, *e.g.* in Fig. 5, can be determined by calculating the coefficient of $\frac{1}{M}$ in equation (18), the value being equal to $1.419 - 1.654 R_N$. *E.g.* for $R_N = 1$ the slope is equal to -0.235 .

It is also possible, as BOELHOUWER AND WATERMAN⁹ have shown, to base a ring analysis diagram on physical constants of pure hydrocarbons belonging to homologous series (*n*-paraffins, *n*-alkyl-cyclopentanes, *n*-alkyl-cyclohexanes), in combination with the specific parachor this method permits a reliable determination of R_N in branched and non-branched saturated hydrocarbon mixtures of different origin: saturated mineral oil fractions, hydrogenated polymers, etc. (*cf.* Figs. 59 and 60 and p. 64).

Other methods have in the course of time been proposed for the determination of the number of rings in saturated mineral oil fractions.

BOOY AND WATERMAN¹⁰ developed a diagram by plotting the specific refraction $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ against the dispersion $n_{G'} - n_C$ in connection with R_N of saturated mineral oil fractions (Fig. 6) ($n_{G'}$ and n_C are the refractive indices measured for the G' and C lines of the hydrogen spectrum). A drawback of this method is that four physical constants have been used whilst in this case two are sufficient. In principle it must, however, be possible to replace n_D in the formula $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ by either n_C or $n_{G'}$, which reduces the number of physical constants to three

STIJNTJES, WATERMAN AND WESTERDIJK^{10a} introduced a diagram in which density was plotted against refractive index in connection with R_N (Fig. 7).

This was the first time that only *two* physical constants were used (the minimum number) to determine the ring-number of saturated mineral oil fractions

A few other methods of determining the ring content of saturated mineral oil fractions will be discussed further on in connection with the application of the viscosity in the field of graphical statistical methods.

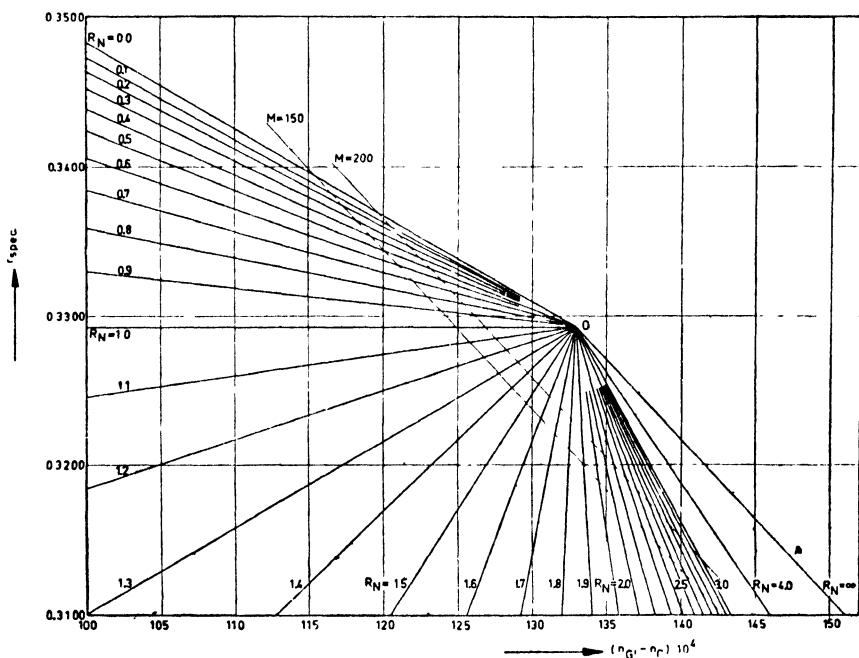


Fig. 6 $\left[\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \right] - (n_{G'} - n_C)$ diagram for the determination of R_N of saturated mineral oil fractions

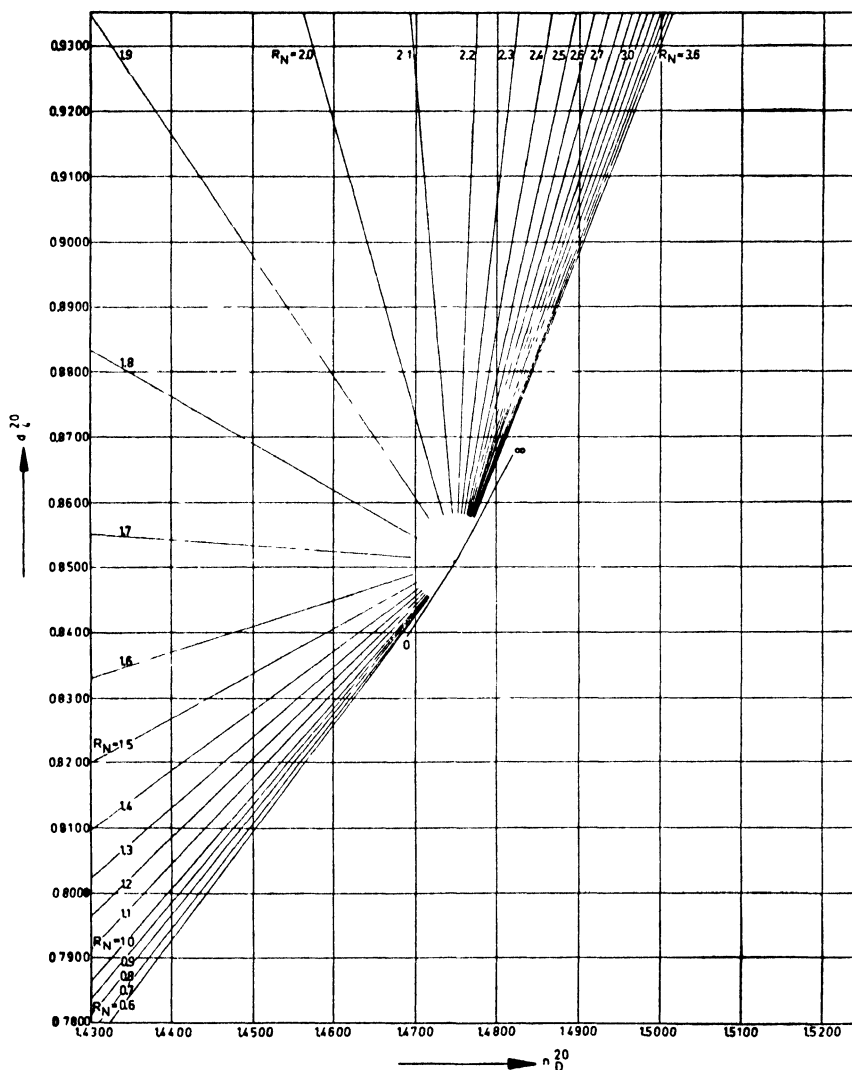


Fig 7 $n-d$ diagram for the determination of R_N of saturated mineral oil fractions

(ii) *Carbon-type analysis of saturated mineral oil fractions*

The carbon-type analysis of saturated mineral oil fractions involves the determination of the percentage of carbon in naphthenic structure, $\%C_N$, which equals the percentage of carbon in ring structure, $\%C_R$. This can be done as follows.

If it is assumed that the ring-number of the saturated fraction is equal to R_N , the

molecular weight equal to M and the molecular formula of the "average" molecule representing the oil fraction is $C_cH_{2c-(2R_N-2)}$ then

$$M = 12.010c + 1.008 [2c - (2R_N - 2)] \quad \dots \quad (3)$$

Now $\%C_R$ is defined as follows

$$\%C_R = \frac{\text{number of C atoms in ring structure per molecule}}{\text{total number of carbon atoms per molecule}} \cdot 100$$

To determine the number of C atoms in ring structure from R_N , an assumption must be made concerning the type of the rings and the manner of fusion of the rings. Type and manner of fusion of the naphthenic rings may vary from one oil to another and because it is difficult as yet to obtain full information about this matter the determination of $\%C_N (= \%C_R)$ cannot be exact. However, in order to gain an approximate insight into the amount of carbon present in cyclic or non-cyclic structure the following assumptions are made

(α) The rings only contain six carbon atoms

(β) The molecules only contain kata-condensed molecules, i.e. molecules with the rings fused together in the same way as in naphthalene, anthracene, phenanthrene and the corresponding saturated compounds such as decalin. The consequences of deviations from these assumptions will be discussed later.

On the basis of these assumptions it can be said that the first ring present in the molecule contains six carbon atoms and each following ring adds four carbon atoms to this number

Therefore two cases must be distinguished 1. The ring-number of the fraction $\leq r$, 2. The ring-number of the fraction $\geq r$

1. If the ring-number of the fraction $\leq r$ then the total number of carbon atoms present in ring structure is equal to $6R_N$.

Consequently

$$\%C_R = \frac{6R_N}{c} \cdot 100$$

From equation (3) it follows for the value of c that

$$c = \frac{M + 1.008 (2R_N - 2)}{14.026} \quad \dots \quad (3a)$$

Combination of these two equations gives

$$\%C_R = \frac{3R_N \cdot 2805.2}{M + 2.016 (R_N - 1)} \quad \dots \quad (19)$$

2. If the ring-number of the fraction under examination $\geq r$ then the total number of carbon atoms present in ring structure is equal to $6 + (R_N - 1) \cdot 4$. In this case

$$\%C_R = \frac{6 + 4R_N - 4}{c} \cdot 100 = \frac{2(2R_N + 1)}{c} \cdot 100$$

Insertion of the value of c from equation (3a) gives

$$\%C_R = \frac{(2R_N + 1) 2805.2}{M + 2.016(R_N - 1)} \quad \dots \quad (20)$$

On combining equation (15) with equation (19) and (20), respectively, r_{spec}^{30} can be expressed as follows:

$$1. \text{ if } R_N \leq 1 \quad r_{\text{spec}}^{30} = \frac{\frac{8415.6}{M} + 1803.5 - 1.432 \%C_R}{5477.7 - 1.3122 \%C_R} \quad (21)$$

$$2. \text{ if } R_N \geq 1 \quad r_{\text{spec}}^{30} = \frac{\frac{8415.6}{M} + 1202.3 - 1.432 \%C_R}{3651.8 - 1.3122 \%C_R} \quad \dots (22)$$

For a particular value of $\%C_R$ there exists a linear relationship between r_{spec}^{30} and $\frac{1}{M}$, which follows from equations (21) and (22). This makes it possible to construct the lines of equal values of $\%C_R$ in a $r_{\text{spec}}^{30} - \frac{1}{M}$ diagram in a simple manner (Fig. 8).

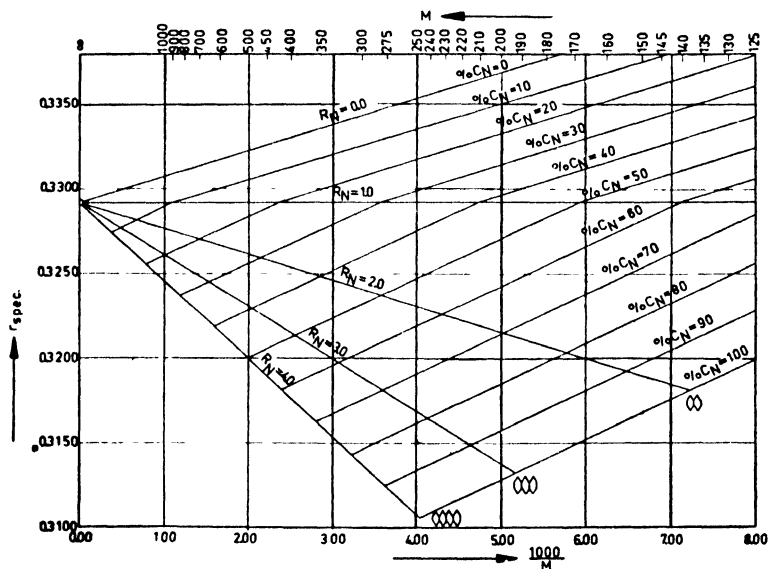


Fig 8 Diagram representing the $r_{\text{spec}}^{30} - \frac{1}{M}$ relationship of saturated mineral oil fractions in connection with R_N and $\%C_R (= \%C_N)$

The fact that two regions have to be used to calculate the value of $\%C_R$, viz one in which $R_N \leq 1$ and one in which $R_N \geq 1$, gives rise to another reason why $\%C_R$ is no exact measure for the percentage of carbon atoms present in ring structure. This is also illustrated by the fact that in Fig 8 the lines for equal $\%C_R$ show a discontinuity at $R_N = 1$.

To show the influence of possible wrong assumptions on the value of $\%C_R$ the following example may be given

Example The average molecule of a saturated mineral oil fraction contains 0.9 rings. This fraction is composed of molecules containing 20 carbon atoms. The following 6 cases I, II, III, IV, V and VI will be considered. In cases I, II, III and IV it is supposed that 70% of the molecules in the oil contain one ring per molecule, 20% of the molecules contain no rings and 10% of the molecules contain two rings per molecule, whilst molecules with three rings or more do not occur in appreciable amount. This supposition seems to be in agreement with the real situation in many mineral oil fractions. In cases V and VI it is supposed that 90% of the molecules of the fraction contain one ring per molecule and 10% of the molecules contain no ring.

- I In the molecules with two rings the rings are kata-condensed and the different rings contain six carbon atoms per ring. In this case

$$\%C_R = 70 \frac{6}{20} + 20 \frac{0}{20} + 10 \frac{10}{20} = 21 + 0 + 5 = 26\%$$

- II In the molecules with two rings the rings are kata-condensed and the different rings contain five carbon atoms per ring. Then

$$\%C_R = 70 \frac{5}{20} + 20 \frac{0}{20} + 10 \frac{8}{20} = 17.5 + 0 + 4 = 21.5\%$$

- III The molecules with two rings contain two separate rings and the different rings contain six carbon atoms per ring. In this case

$$\%C_R = 70 \frac{6}{20} + 20 \frac{0}{20} + 10 \frac{12}{20} = 21 + 0 + 6 = 27\%$$

- IV The molecules with two rings contain two separate rings and the various rings contain five carbon atoms per ring. Then

$$\%C_R = 70 \frac{5}{20} + 20 \frac{0}{20} + 10 \frac{10}{20} = 17.5 + 0 + 5 = 22.5\%$$

- V Molecules with two rings do not occur and the rings contain six carbon atoms per ring. The $\%C_R$ amounts to

$$\%C_R = 90 \frac{6}{20} + 10 \frac{0}{20} = 27 + 0 = 27\%$$

- VI Molecules with two rings do not occur and the rings contain five carbon atoms per ring. Then

$$\%C_R = 90 \frac{5}{20} + 10 \frac{0}{20} = 22.5 + 0 = 22.5\%$$

From these examples it can be concluded that if $R_N \leq 1$ the greatest influence on $\%C_R$ is exerted by the replacement of six-membered rings by five-membered rings (cf. I and II, III and IV, V and VI).

The influence of the replacement of kata-condensed by non-condensed rings (cf. I and III, III and V) and the two-ring systems by one-ring systems (cf. I and III with V, II and IV with VI) (if $R \leq 1$) is much smaller.

If $R \geq 1$ then the influence of the way in which the molecules are linked (kata-condensed or non-kata-condensed) becomes greater as the ring-number increases.

Besides constructing lines for equal ring-number or equal $\%C_R$ values in the ring analysis diagram, it is also possible to construct lines of equal values of the aniline point³ and the density³. This is shown in Figs. 9 and 10 respectively.

Thus it is possible to determine the value of the aniline point (A.P.) of a saturated mineral oil fraction by means of Fig. 9 if the specific refraction and the molecular weight are known.

From Fig. 10 it is possible to determine the value of the specific refraction if M and d are known. From the value of the specific refraction thus determined and the experimental value of the density the refractive index can be determined.

An example has been given here of the correlation existing between physical constants of saturated mineral oil fractions. Other examples will be given when the viscosity is discussed.

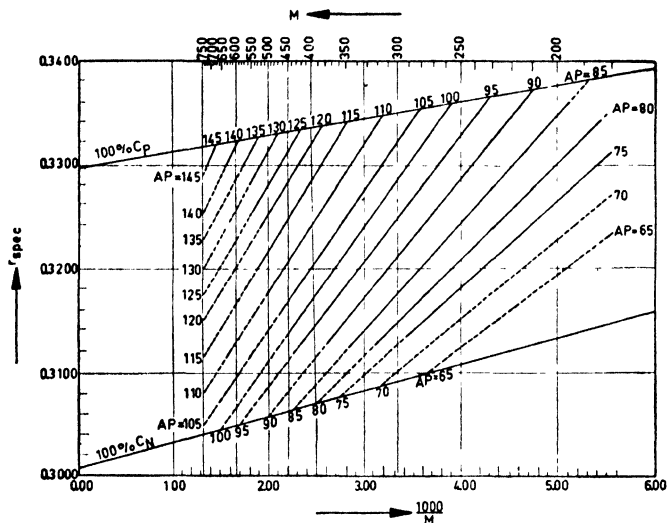


Fig 9 Diagram representing the $r_{\text{spec}}^{20} - \frac{1}{M}$ relationship in connection with R_N and the aniline point
(Saturated mineral oil fractions)

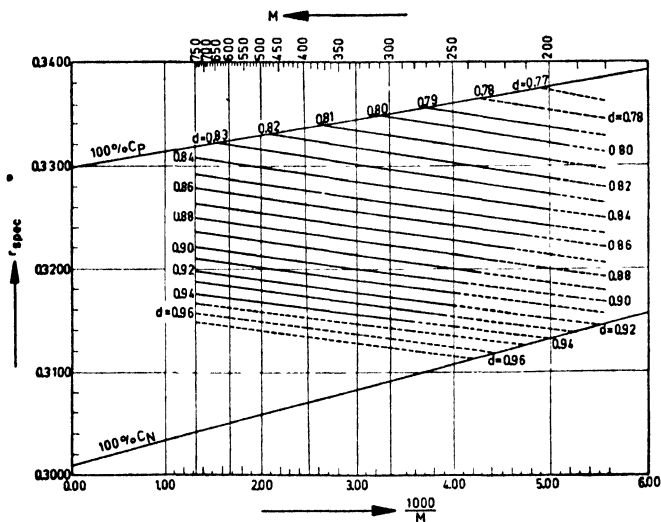


Fig 10 Diagram representing the $r_{\text{spec}}^{20} - \frac{1}{M}$ relationship in connection with R_N and density
(Saturated mineral oil fractions)

c. Ring analysis and carbon-type analysis of natural mineral oil fractions by means of the Direct Method

(i) *Determination of %CA*

If no cracking, ring opening or ring closure takes place during the hydrogenation and no "foreign" elements (elements other than carbon and hydrogen) are present in the mineral oil fraction, the equation for determining the %CA can be derived as follows.

Defining the hydrogen content before and after complete hydrogenation as %H_o and %H, respectively, the molecular weight before and after hydrogenation as M_o and M, respectively, and the molecular formulae before and after hydrogenation as C_cH_{h_o} and C_cH_h, respectively (the number of carbon atoms remaining constant during the hydrogenation), the following relation holds

$$\%CA = \frac{\text{number of carbon atoms per molecule in aromatic structure}}{\text{total number of carbon atoms present in the average molecule}} \cdot 100$$

or

$$\%CA = \frac{h - h_o}{c} \cdot 100 \quad (23)$$

From equation (4) it follows that

$$h = \frac{\%H \cdot M}{1.008 \cdot 100} \text{ and } h_o = \frac{\%H_o \cdot M_o}{1.008 \cdot 100}$$

and from equation (6)

$$c = \frac{100M - \%H \cdot M}{1201.0} \quad (6)$$

Substitution of h , h_o and c in equation (23) gives

$$\%CA = \frac{\frac{\%H \cdot M}{1.008} - \frac{\%H_o \cdot M_o}{1.008}}{100M - \%H \cdot M} \cdot 1201.0$$

or

$$\%CA = 1191 \cdot \frac{\%H - \%H_o \cdot \frac{M_o}{M}}{100 - \%H} \quad (24)$$

By means of equation (24) it is possible to calculate the value of %CA of mineral oil fractions if molecular weight and hydrogen content of both the original and the saturated fraction are known. Olefinic compounds should be absent.

The value of %CA calculated in this way is exact, however, the method requires much practical experience (*cf* p. 10). Since M and M_o are almost equal, certainly within the experimental error, %CA is practically independent of the molecular weight.

(ii) *Determination of the total ring-number R_T*

After complete hydrogenation of the mineral oil fraction the total ring content can be determined in the same way as has been described for the saturated fractions, *viz.* by applying equation (1) (p. 9):

$$R_T = 1 + (8.326 - 0.5793 \%H) \cdot \frac{M}{100} \quad (1a)$$

where %H = hydrogen content of the saturated oil fraction
and M = molecular weight of the saturated oil fraction.

No assumptions regarding the ring type or the extent to which the rings are condensed need be made, R_T is an exact value, inasmuch as M can be considered to be determinable in practice.

(iii) *Determination of %C_R*

After the complete hydrogenation of the mineral oil fractions use can once again be made of the equations that have been derived for saturated mineral oil fractions on the assumption that six-membered rings are present and that the rings in the multiple ring systems are kata-condensed. The equations are

if $R_T \leq 1$

$$\%C_R = \frac{3 R_T \cdot 2805.2}{M + 2.016(R_T - 1)} \quad \dots \quad (19a)$$

if $R_T \geq 1$

$$\%C_R = \frac{(2 R_T + 1)2805.2}{M + 2.016(R_T - 1)} \quad \dots \quad (20a)$$

(iv) *Determination of the number of aromatic rings R_A*

The number of aromatic rings R_A in mineral oil fractions can be calculated from %C_A (eqn. 24):

$$\%C_A = 1191 \cdot \frac{\%H - \%H_0 \cdot \frac{M_0}{M}}{100 - \%H} \quad \dots \quad (24)$$

and the molecular weight. The value of R_A cannot be determined with exactitude. Nevertheless, a reasonable approximation may be obtained by assuming that multiple aromatic ring systems are kata-condensed. It is almost certain that only six-membered aromatic rings occur.

Two cases must be distinguished: (α) the ring-number of the fraction ≤ 1 , (β) the ring-number of the fraction ≥ 1 .

(α) If the ring-number of the fraction ≤ 1 and there are no molecules present that contain more than one ring, then the total number of carbon atoms present in aromatic structure is equal to $6 R_A$. According to the definition of %C_A the following equation holds true:

$$\%C_A = \frac{6 R_A}{c} \cdot 100 \quad \dots \quad (25)$$

The number of hydrogen atoms in the average molecule amounts to

$$h_0 = 2c - (8 R_A - 2) \quad \dots \quad (26)$$

if $R_A \leq 1$

One aromatic ring causes a deficiency of 8 hydrogen atoms compared to an alkane with the same number of carbon atoms. This explains the term $8 R_A$ in equation (26).

From equation (26) it follows for the molecular weight that

$$M = 12.010 c + 1.008 \{2c - (8 R_A - 2)\} \quad \dots \quad (27)$$

Equation (27) gives for the value of c

$$c = \frac{M + 1.008 (8 R_A - 2)}{14.026} \quad \dots \dots \dots (28)$$

Introducing this value of c into equation (25) gives

$$\%C_A = \frac{6 R_A \cdot 14.026}{M + 1.008(8 R_A - 2)} \cdot 100 \quad \dots \dots \dots (29)$$

$$\%C_A \cdot M + 8.064 R_A \cdot \%C_A - 2.016 \%C_A = 84.156 R_A \cdot 100$$

or

$$R_A = \frac{(M - 2.016) \%C_A}{8415.6 - 8.064 \%C_A} \quad \dots \dots \dots (30)$$

(β) If the number of aromatic rings present in mineral oil fractions ≥ 1 , the number of aromatic carbon atoms present in the average molecule is equal to

$$6 + (R_A - 1) 4 = 2 + 4 R_A.$$

From the definition of $\%C_A$ the following equation is obtained

$$\%C_A = \frac{2 + 4 R_A}{c} \cdot 100 \quad \dots \dots \dots (31)$$

The number of hydrogen atoms present in the average molecule can be put equal to

$$h_o = 2c - 6 R_A \quad \dots \dots \dots (32)$$

This can be explained as follows.

The number of hydrogen atoms present in an alkane with the same number of carbon atoms is $2c + 2$. The presence of the first aromatic ring results in a decrease of eight hydrogen atoms, each further aromatic ring causes a decrease of a further six hydrogen atoms if the rings are kata-condensed (two for the ring closure, four for the replacement of CH_2 groups by CH groups). The overall result is the presence of $(2c + 2) - 8 - (R_A - 1) 6 = 2c - 6 R_A$ hydrogen atoms in the average molecule representing the mineral oil fraction.

The molecular weight of the fraction is

$$M = 12.010 c + 1.008 (2c - 6 R_A) \quad \dots \dots \dots (33)$$

From this equation it follows for the value of c

$$c = \frac{M + 1.008 \cdot 6 R_A}{14.026} \quad \dots \dots \dots (34)$$

Introducing this value of c into equation (31) gives

$$\%C_A = \frac{(2 + 4 R_A) 14.026}{M + 1.008 \cdot 6 R_A} \cdot 100 \quad \dots \dots \dots (35)$$

$$\%C_A \cdot M + 6 R_A \cdot 1.008 \cdot \%C_A = 5610.4 R_A + 2805.2$$

$$R_A = \frac{\%C_A \cdot M - 2805.2}{5610.4 - 6.048 \%C_A} \quad \dots \dots \dots (36)$$

By means of equations (30) and (36) it is possible to calculate the number of aromatic rings per average molecule of mineral oil fractions with $R_A \leq 1$ and $R_A \geq 1$, respectively, from the molecular weights and the percentages of carbon atoms in aromatic structure. The calculated values are not exact values since it is assumed that the multiple ring systems are kata-condensed, however, this often seems to be the case.

VAN WESTEN AND VAN NES^{3,12}. It is based on the fact that there is a linear relationship between the percentage of carbon, %C (in either naphthenic, aromatic or paraffinic structure) and the refractive index, the density and the reciprocal molecular weight, according to the equation:

$$\%C = \frac{a}{M} + b\Delta d + c\Delta n \quad \dots \dots \dots (39)$$

where a , b and c are constants,

$$\Delta d = d - d_{\infty}$$

$$\Delta n = n - n_{\infty}$$

d_{∞} and n_{∞} are the values of the refractive index and density, respectively, of the hypothetical normal hydrocarbon with infinite chain length. For the number of rings (either naphthenic or aromatic rings or total number of rings) an analogous equation is valid

$$R = a' + b'M \Delta d + c'M \Delta n \quad \dots \dots \dots (39a)$$

a' , b' and c' are constants different from a , b and c . The determination of the constants mentioned in equations (39) and (39a) have been described by VAN NES AND VAN WESTEN^{3,12} and will not be repeated here. The results are reported in Table I.

TABLE I
FORMULAE OF THE n - d - M METHOD

Measurements at 20°C		Measurements at 70°C	
$v = 2.51(n-1.4750) - (d-0.8510)$ $w = (d-0.8510) - 1.11(n-1.4750)$		$x = 2.42(n-1.4600) - (d-0.8280)$ $y = (d-0.8280) - 1.11(n-1.4600)$	
%C _A	If v is positive $\%C_A = 430v + \frac{3660}{M}$ If v is negative $\%C_A = 670v + \frac{3660}{M}$	%C _A	If x is positive $\%C_A = 410x + \frac{3660}{M}$ If x is negative $\%C_A = 720x + \frac{3660}{M}$
%C _R	If w is positive $\%C_R = 820w - 3S + \frac{10000}{M}$ If w is negative $\%C_R = 1440w - 3S + \frac{10600}{M}$	%C _R	If y is positive $\%C_R = 775y - 3S + \frac{11500}{M}$ If y is negative $\%C_R = 1400y - 3S + \frac{12100}{M}$
%C _N	$\%C_N = \%C_R - \%C_A$	%C _N	$\%C_N = \%C_R - \%C_A$
%C _P	$\%C_P = 100 - \%C_R$	%C _P	$\%C_P = 100 - \%C_R$
R _A	If v is positive $R_A = 0.44 + 0.055Mv$ If v is negative $R_A = 0.44 + 0.080Mv$	R _A	If x is positive $R_A = 0.41 + 0.055Mx$ If x is negative $R_A = 0.41 + 0.080Mx$
R _T	If w is positive $R_T = 1.33 + 0.146M(w-0.005S)$ If w is negative $R_T = 1.33 + 0.180M(w-0.005S)$	R _T	If y is positive $R_T = 1.55 + 0.146M(y-0.005S)$ If y is negative $R_T = 1.55 + 0.180M(y-0.005S)$
R _N	$R_N = R_T - R_A$	R _N	$R_N = R_T - R_A$

S is weight percentage of sulphur

By means of the equations given in Table I the various values of $\%R$ can be calculated if n , d and M are known.

If sulphur is present a correction must be made in the case of $\%C_R$ and R_T . This correction is given in the equation for $\%C_R$ and R_T , where the weight% of sulphur is denoted as S . No correction has to be applied to $\%C_A$ and R_A for the presence of sulphur.

Should data at some other temperature, say 40°C , be available, then similar equations as listed in Table I are valid. The numerical values of the constants of these equations can be obtained by linear interpolation of the values of the constants given in the table for 20°C and 70°C .

The n - d - M method for determining the composition of olefin-free mineral oil fractions has proved to be reliable if $\%C_R \leq 75$ with the further limitation that $\%C_A \leq 1\frac{1}{2} \%C_N$. For the number of rings the limitation is $R_T \leq 4$ with $R_A \leq \frac{1}{2} R_T$.

The method is also applicable to olefin-free paraffin waxes, residual oils and oils containing less than 2% sulphur, 0.5% oxygen and 0.5% nitrogen.

The method has the fundamental drawback that different numerical constants have to be used in the formulae, depending on the range considered. However, the practical application is not hampered by this fact.

e. Kinematic viscosity and structure of mineral oil fractions

(1) Structure of saturated mineral oil fractions v - M diagrams and v - n diagram

In the last few years the kinematic viscosity and its temperature dependence have been used for the determination of the composition of mineral oil fractions. The first steps in this field were made by BOELHOUWER, VAN STEENIS AND WATERMAN¹³, who

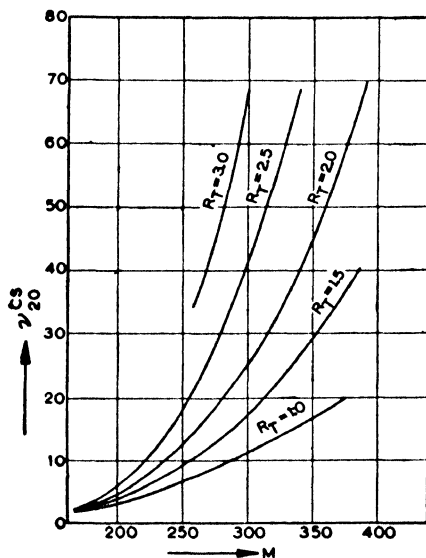


Fig 11 v - M diagram for determining the number of rings per molecule in saturated mineral oil fractions

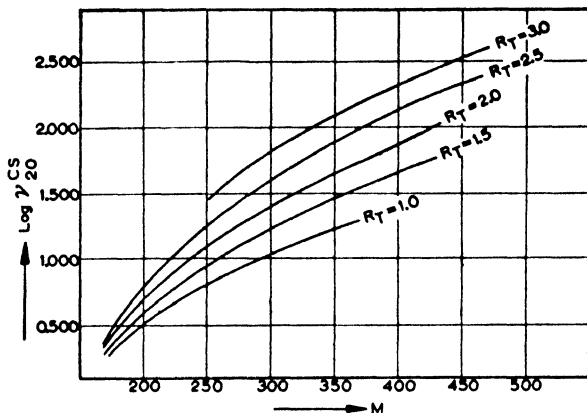


Fig. 12 Log ν - M diagram for determining the number of rings per molecule in saturated mineral oil fractions

constructed the diagrams represented in Figs. 11 and 12 for the ring analysis of saturated mineral oil fractions.

With these diagrams it is possible to find the number of (naphthenic) rings per molecule from the molecular weight and kinematic viscosity. However, the accuracy of this determination is in some regions rather small. This is one of the reasons why another diagram^{13,14} has been introduced, in which $\nu_{C_{10}}^{CS}$ has been plotted against the refractive index n_D^{20} , Fig. 13. Another reason is that the molecular weight is preferably not used because its determination is difficult and inaccurate.

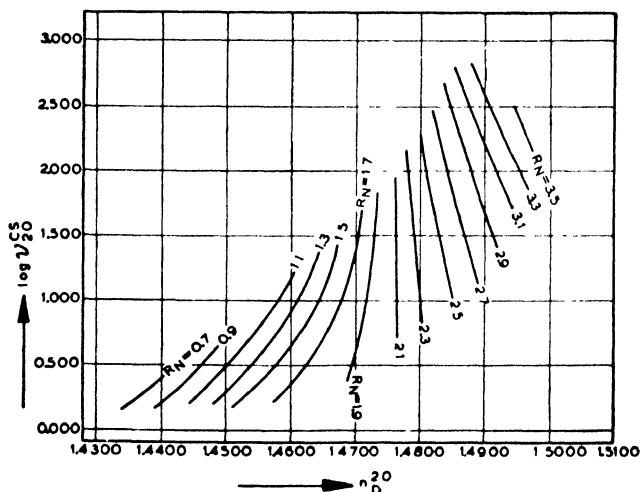


Fig. 13 Log ν - n diagram for determining the number of rings per molecule in saturated mineral oil fractions

In Fig. 13 the number of rings per molecule of a saturated mineral oil fraction can be read if the kinematic viscosity and the refractive index are known.

In Fig. 14 the correlation is shown between some physical constants of saturated mineral oil fractions, as well as the relation between physical constants and R_N and $\%C_R$. This diagram shows how the ring-number R_N and the percentage of carbon present in ring structure, $\%C_R$, as well as the molecular weight M and the density d_4^{20} , can be determined for saturated mineral oil fractions by means of their $\log \nu_{20}^{CS}$ and n_D^{20} values

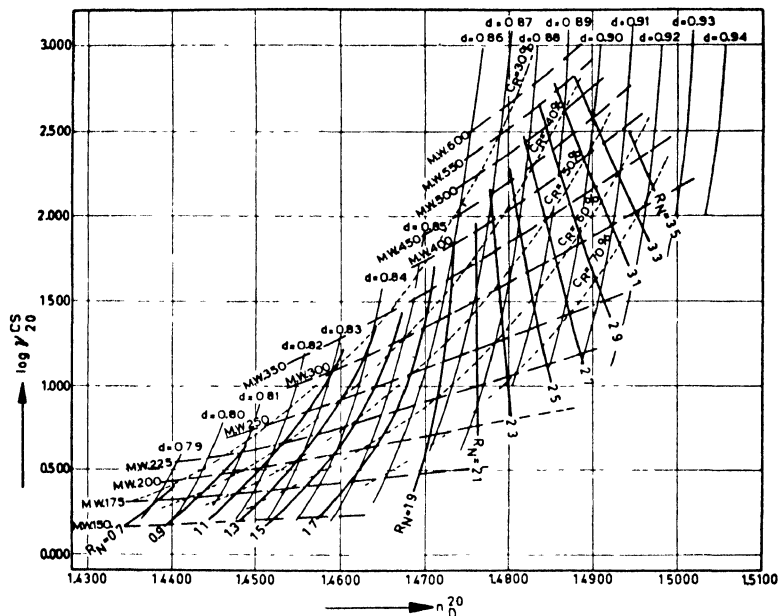


Fig. 14 Correlation of some physical constants of saturated mineral oil fractions, the relation between physical constants and structure

(11) Structure of straight-run mineral oil fractions

(a) *The ν - n - d method* As has just been discussed the density d_4^{20} of saturated mineral oil fractions can be determined by means of Fig. 14, if the values of $\log \nu_{20}^{CS}$ and n_D^{20} of the fractions are known. The value of d_4^{20} thus obtained appears to be in accordance with the experimental value up to the third decimal place. This is not so if the fractions under examination contain aromatics. In that case it will be observed that the value d' of the density obtained by means of Fig. 14 and the experimentally determined value d do not agree. The difference $d' - d = \Delta d$ appears to be a measure for the percentage of carbon in aromatic structure according to the experimentally established equation

$$\%C_A = 600 \Delta d - (40 \Delta d)^2 \quad \dots \quad (40)$$

The value of $\%C_A$ thus obtained is independent of the sulphur content. From Δd , the value of the density d^* and the logarithm of the viscosity $\log \nu^*$ of the saturated

oil fraction can be predicted by means of the experimentally established equations

$$d^* = d - 0.62 \Delta d - 0.008 \%S \quad \dots \dots \dots (41)$$

and

$$\log \nu^* = (1 - 3 \Delta d) \log \nu + \Delta d \quad \dots \dots \dots (42)$$

When determining d^* a correction for the sulphur content has to be applied, which correction is equal to $-0.008 \%S$

By means of the values of d^* and $\log \nu^*$ the following values can be read from Fig. 14, viz. the number of rings $R_N (= R_T)$, the percentage of carbon in ring structure, $\%C_R$ and the molecular weight, M . The values of R_T , $\%C_R$ and M are the same for the non-hydrogenated and the saturated oil fractions if it is assumed that the molecular weight does not change on hydrogenation. This is true if no cracking during hydrogenation has taken place within the limits of accuracy of the molecular weight determination.

The number of aromatic rings follows from the values of $\%C_A$ and M by applying the equations

if $R_A \geq 1$

$$(2 R_A + 1) = \frac{M \cdot \%C_A}{2800} \quad \dots \dots \dots (43)$$

if $R_A \leq 1$

$$3 R_A = \frac{M \%C_A}{2800} \quad \dots \dots \dots (44)$$

Equations (43) and (44) can be derived from equations (35) and (29) respectively, recognizing that, in view of the accuracy of the molecular weight determination ($\pm 5\%$), the denominators may be replaced by M , while the constant value 14 026 in the numerators may be replaced by 14 0 without unduly affecting the accuracy of $\%C_A$.

For the determination of $\%C_A$ no sulphur correction need be made.

The method described is known as the ν - n - d method. It has the advantage that the rather laborious, time-consuming and inaccurate determination of the molecular weight can be avoided, while the viscosity can easily be determined with a relatively high accuracy. Furthermore it is now possible to predict the molecular weight.

(β) *The ν - n - d space model and its cross-sections* It has recently been shown by CORNELISSEN AND WATERMAN¹⁵ that use can be made of a $\log \nu$ - n - d space model to determine the carbon-type composition of oil fractions. The space model consists of the mutually perpendicular coordinates $\log \nu_{20}^{CS}$, n_D^{20} and d_4^{20} (ν_{20}^{CS} is the kinematic viscosity in centistokes at 20°C, n_D^{20} is the refractive index for the sodium D-line at 20°C and d_4^{20} is the density in g/ml at 20°C), it is schematically represented in Fig. 15

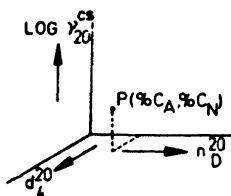


Fig. 15 Schematic representation of the $\log \nu$ - n - d space model for the determination of the carbon-type composition of mineral oil fractions

In Fig. 15 a fraction P with certain values for $\log \nu_{30}^c$, n_D^{20} and d_4^{20} is indicated. The fraction has the assumed composition $\%C_A$ and $\%C_N$. Other fractions with different values of $\log \nu_{30}^c$, n_D^{20} and d_4^{20} may have the same carbon-type composition (which is possible if the molecular weights are not the same) or different carbon-type compositions. Fractions with the same carbon type composition form space lines, which are the intersecting lines of surfaces of equal $\%C_A$ and $\%C_N$, respectively.

For practical use of the $\log \nu$ - n - d space model, cross-sections are made of these surfaces of equal $\%C_A$ and $\%C_N$ values parallel to the n_D^{20} - d_4^{20} coordinate plane or, in other words, for certain different viscosity values, namely $\log \nu_{30}^c = 0.300, 0.500, 1.000, 1.500, 2.000$ and 2.500 . The cross-sections are shown in the Figs. 16, 17, 18, 19, 20 and 21, respectively.

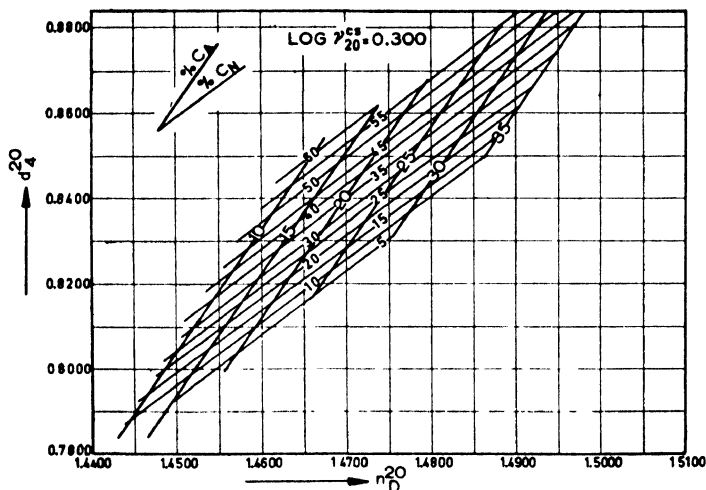


Fig. 16 Cross-section of the $\log \nu$ - n - d space model at $\log \nu_{30}^c = 0.300$, with the surfaces of equal values of $\%C_A$ and $\%C_N$

The cross-sections can be used for the determination of the carbon-type composition of mineral oil fractions in the following way.

Example: An oil fraction has the values

$$\begin{aligned}\log \nu_{30}^c &= 0.428 \\ n_D^{20} &= 1.4884 \\ d_4^{20} &= 0.8634\end{aligned}$$

As the value of $\log \nu_{30}^c$ is equal to 0.428 use must be made of the two cross-sections for $\log \nu_{30}^c = 0.300$ and $\log \nu_{30}^c = 0.500$, which are the adjacent values of the series of six cross-sections.

In both graphs values of $\%C_A$ and $\%C_N$ are read from the values of n_D^{20} and d_4^{20} , these values are

$$\begin{aligned}\text{from the } \log \nu_{30}^c = 0.300 \text{ diagram} \quad & \begin{aligned} \%C_A &= 32 \text{ and} \\ \%C_N &= 30 \end{aligned}\end{aligned}$$

$$\begin{aligned}\text{from the } \log \nu_{30}^c = 0.500 \text{ diagram} \quad & \begin{aligned} \%C_A &= 29 \text{ and} \\ \%C_N &= 22 \end{aligned}\end{aligned}$$

As the real value of $\log \nu_{30}^c$ of the fraction in question is equal to 0.428, the values of $\%C_A$ and $\%C_N$

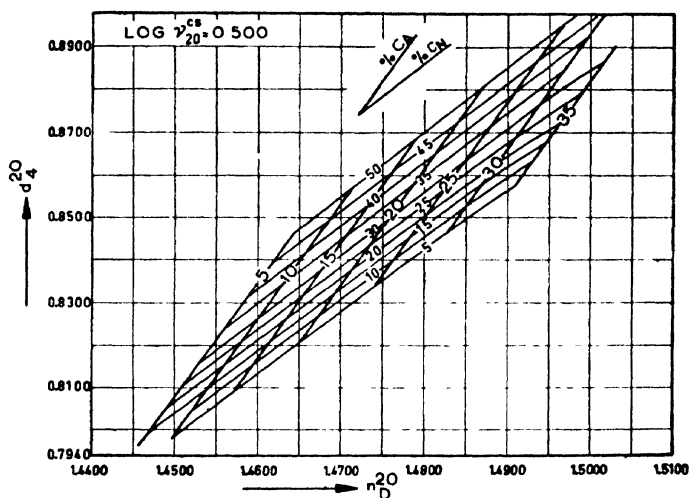


Fig 17 Cross-section of the log ν - n - d space model at $\log \nu_{20}^{CS} = 0.500$, with surfaces of equal values of $\%C_A$ and $\%C_N$

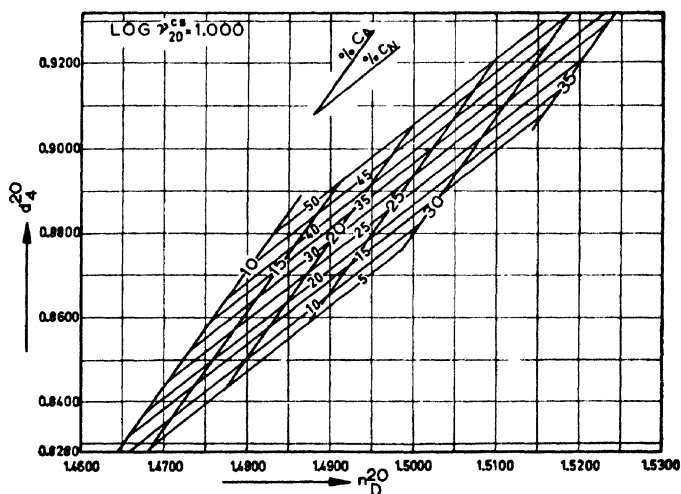


Fig 18 Cross-section of the log ν - n - d space model at $\log \nu_{20}^{CS} = 1.000$, with surfaces of equal values of $\%C_A$ and $\%C_N$

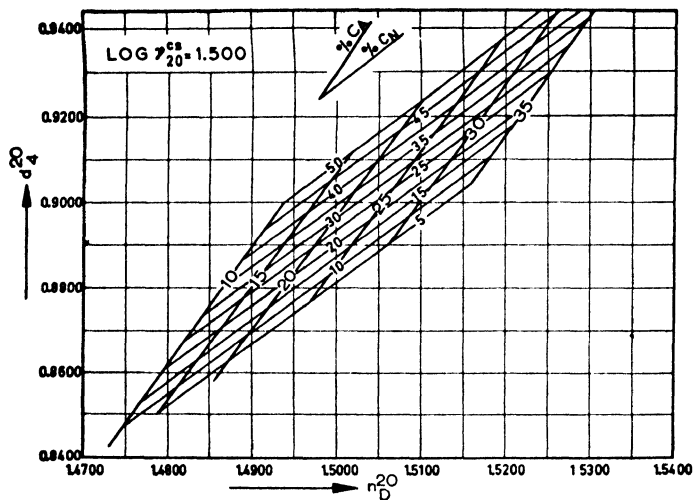


Fig 19 Cross-section of the log v - n - d space model at $\log v_{20}^{cs} = 1.500$, with surfaces of equal values of $\%C_A$ and $\%C_N$

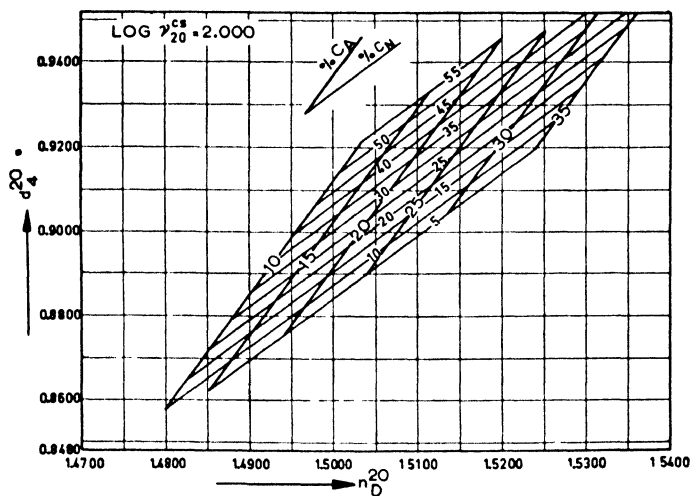


Fig 20 Cross-section of the log v - n - d space model at $\log v_{20}^{cs} = 2.000$, with surfaces of equal values of $\%C_A$ and $\%C_N$

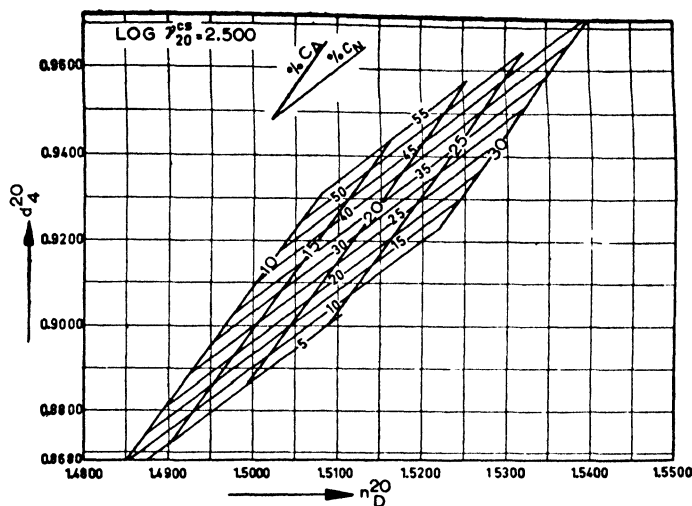


Fig. 21 Cross-section of the $\log \nu$ - n - d space model at $\log \nu_{20}^{cs} = 2.500$, with surfaces of equal values of $\%C_A$ and $\%C_N$

can be obtained by linear interpolation between the values read from the graphs. The results are

$$\%C_A = 32 - \frac{0.128}{0.200} \cdot 3 = 32 - 2 = 30$$

and

$$\%C_N = 30 - \frac{0.128}{0.200} \cdot 8 = 30 - 5 = 25$$

The carbon-type composition* of the oil appears to be

$$\begin{aligned}\%C_A &= 30 \\ \%C_N &= 25 \\ \%C_P &= 45\end{aligned}$$

As no auxiliary constants (like d^* and $\log \nu^*$, see preceding section) are used in the $\log \nu$ - n - d space model cross-section method it can be regarded as an improvement of the application of the viscosity in the field of graphical statistical methods.

(y) *The application of nomograms of the cross sections of the ν - n - d space model.* A further development of the ν - n - d method is the use of nomograms¹⁶ replacing the cross-sections of the space model, which have been discussed in the previous section. This replacement is possible because the intersecting lines of these cross-sections with the surfaces of equal values of $\%C_A$ and $\%C_N$ are practically straight. If a nomogram is used with the parallel coordinates n_D^{20} and d_4^{20} the straight lines from the cross-sections become single points in the nomogram. As we are dealing with straight *parallel* lines in the cross-sections, the points in the nomogram corresponding to these lines constitute a straight line in the nomogram, which is parallel to both the coordinates.

The nomograms replacing the cross-sections are given in the Figs. 22-27.

In the nomograms not only the lines for the determination of $\%C_A$ and $\%C_N$ are given, but also those for the determination of R_A and R_N as well as molecular weight M .

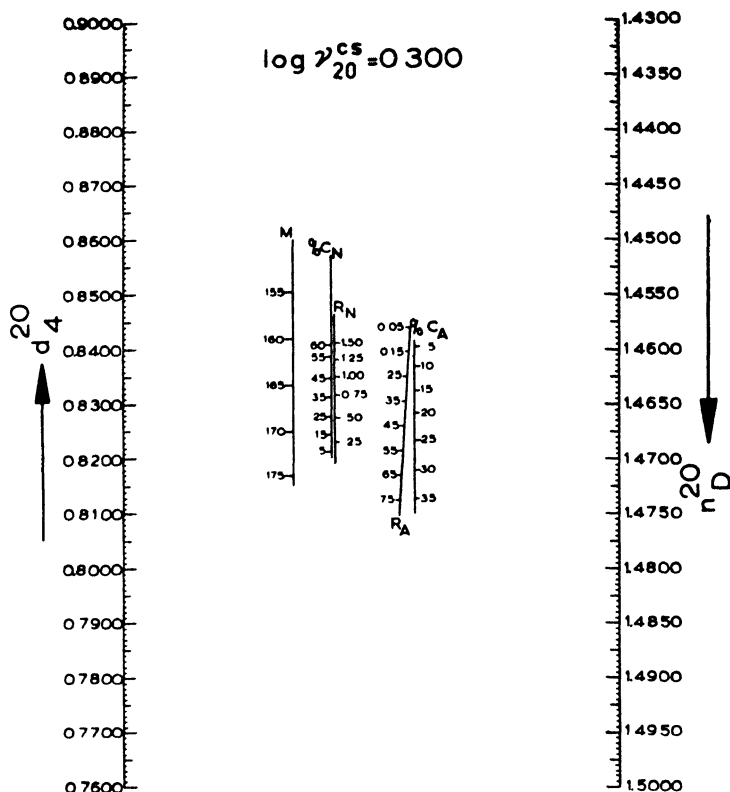


Fig. 22 Nomogram of the cross-section of the log ν - n - d space model at $\log \nu_{20}^{CS} = 0.300$

The use of the nomograms will be illustrated by an example

Example An oil fraction has the values

$$\begin{aligned}\log \nu_{20}^{CS} &= 0.828 \\ n_D^{20} &= 1.4695 \\ d_4^{20} &= 0.8390 \\ M &= 232\end{aligned}$$

As the value of $\log \nu_{20}^{CS}$ is equal to 0.828 use has to be made of the two nomograms for $\log \nu_{20}^{CS} = 0.500$ and $\log \nu_{20}^{CS} = 1.000$, these being the adjacent values of the six cross-sections. In these two nomograms the following values of $\%C_A$, $\%C_N$, R_A , R_N and M are read from the values of n_D^{20} and d_4^{20}

nomogram	$\%C_A$	$\%C_N$	R_A	R_N	M
$\log \nu_{20}^{CS} = 0.500$	17	29	0.39	0.71	191
$\log \nu_{20}^{CS} = 1.000$	12	18	0.40	0.74	262

As the value of $\log \nu_{20}^{CS}$ of the fraction in question is equal to 0.828 the values of $\%C_A$, $\%C_N$, R_A , R_N and M can be obtained by linear interpolation between the values read from the graph. The results are

$$\%C_A = 17 - \frac{0.328}{0.500} \cdot 5 = 17 - 3 = 14$$

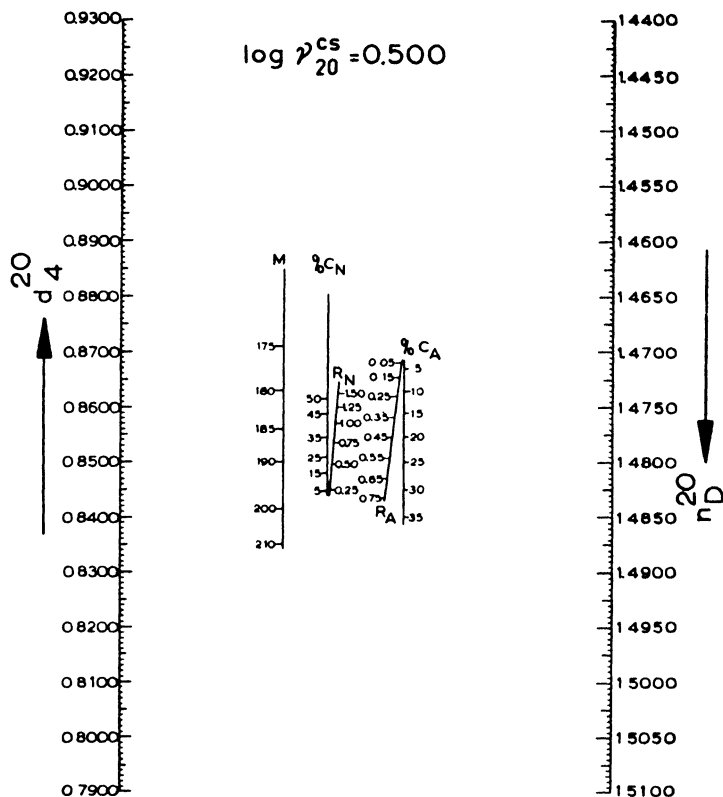


Fig 23 Nomogram of the cross-section of the log ν - n - d space model at $\log \nu_{20}^{cs} = 0.500$

$$\%C_N = 29 - \frac{0.328}{0.500} \cdot 11 = 29 - 7 = 22$$

$$R_A = 0.39 + \frac{0.328}{0.500} \cdot 0.01 = 0.39 + 0.01 = 0.40$$

$$R_N = 0.71 + \frac{0.328}{0.500} \cdot 0.03 = 0.71 + 0.02 = 0.73$$

$$\text{and } M = 191 + \frac{0.328}{0.500} \cdot 71 = 191 + 47 = 238$$

It appears that the different structural elements and molecular weight have the following values

$$\begin{aligned} \%C_A &= 14 \\ \%C_N &= 22 \\ \%C_R &= 36 \\ \%C_P &= 64 \end{aligned}$$

$$\begin{aligned} R_A &= 0.40 \\ R_N &= 0.73 \\ R_T &= 1.13 \\ M &= 238 \end{aligned}$$

It must be emphasized that the nomograms and cross-sections presented here are only applicable to the original mineral oil fractions and not to the hydrogenated fractions. The advantage of using the nomograms instead of the cross-sections lies in the

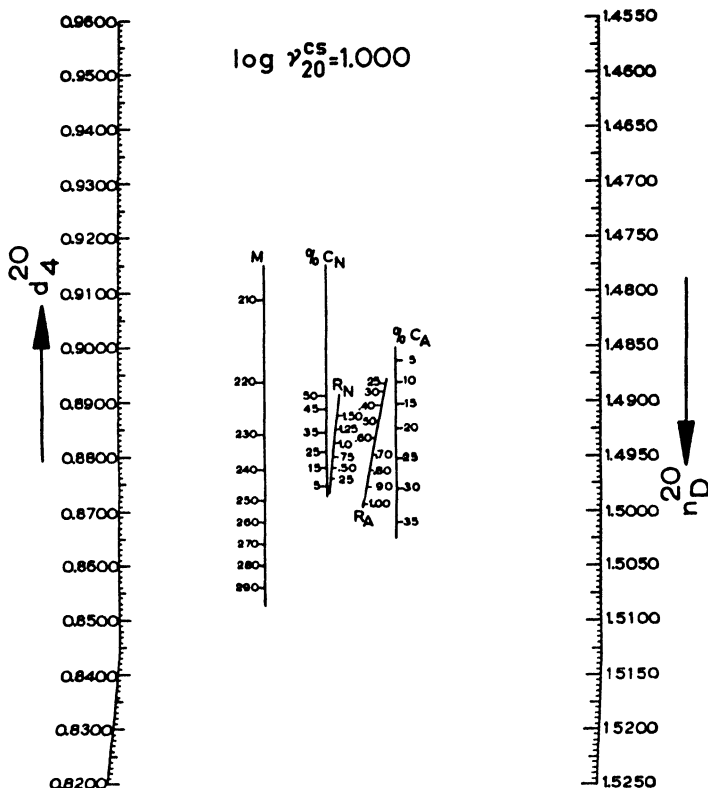


Fig 24 Nomogram of the cross-section of the $\log \nu$ - n - d space model at $\log \nu_{20}^{cs} = 1.000$

fact that in the nomograms values of several structural elements and physical constants can be represented simultaneously, whereas this is practically impossible in the cross-sections because they would become overburdened with lines. Moreover, the nomograms are easier to handle. Consequently they can be recommended for practical use for making the carbon-type analysis and ring analysis of mineral oil fractions. See Addendum 2, p 113

(δ) *The applications of $\log \nu$ - $f(n, d)$ graphs.* It may sometimes be felt as a drawback that the methods described under (β) and (γ) require the use of *two* different cross-sections or nomograms. If one wishes to know, for instance, the value of one structural element, say $\%C_A$, it proves to be possible to construct a graph from which $\%C_A$ can be read directly. The graph has as coordinates $\log \nu_{20}^{cs}$ and a simple function of the refractive index and the density. Two such graphs have been constructed by CORNELISSEN AND WATERMAN¹⁷, one for the determination of $\%C_A$ and one for the determination of $\%C_N$ (Figs. 28 and 29, respectively).

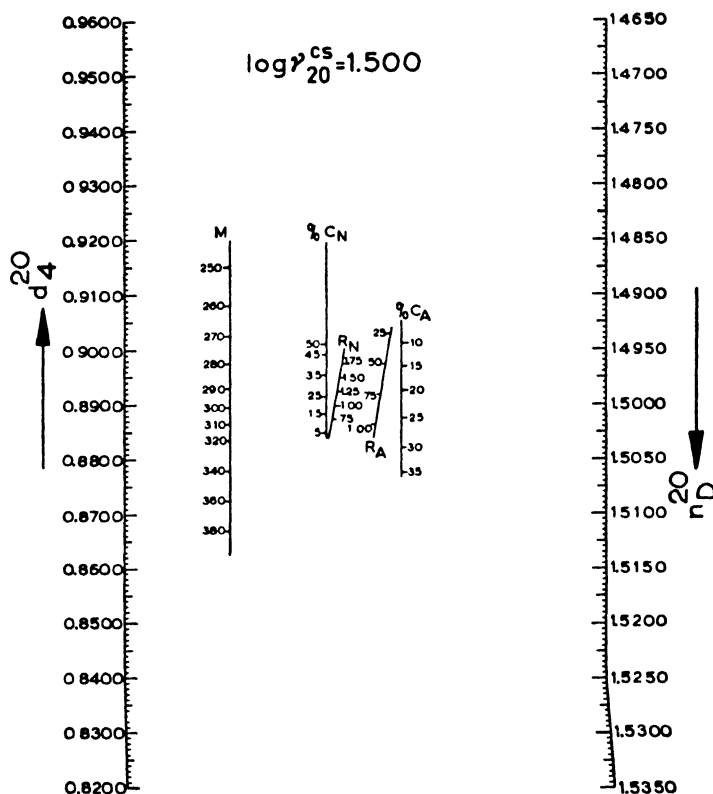


Fig 25 Nomogram of the cross-section of the log ν - n - d space model at $\log \nu_{20}^{cs} = 1.500$

These graphs can be derived from the cross-sections of the log ν - n - d space model. In these cross-sections the lines of equal values of $\%C_A$ and $\%C_N$ have a constant slope. Accordingly the general equation of these lines can be represented by

$$n_D^{30} = a \cdot d_4^{20} + b$$

in which a is a constant, whereas the value of b varies

Since

$$b = n_D^{30} - a \cdot d_4^{20}$$

it follows that b , or $n_D^{30} - a \cdot d_4^{20}$, represents a certain value of $\%C_A$ or $\%C_N$ for the constant value of $\log \nu$ of the considered cross-section

In the log ν - b ($= n - a \cdot d$) graphs the lines of equal values of $\%C_A$ and $\%C_N$ from the cross-sections for a certain viscosity, are represented by points lying on a line parallel to the $n - a \cdot d$ axis

When the points for the different $\log \nu$ values of the respective cross-sections are connected, lines are obtained as given in Figs 28 and 29

The value of a is equal to the cotangent of the slope of the lines of equal $\%C_A$ or $\%C_N$ in the cross-sections of the log ν - n - d space-model

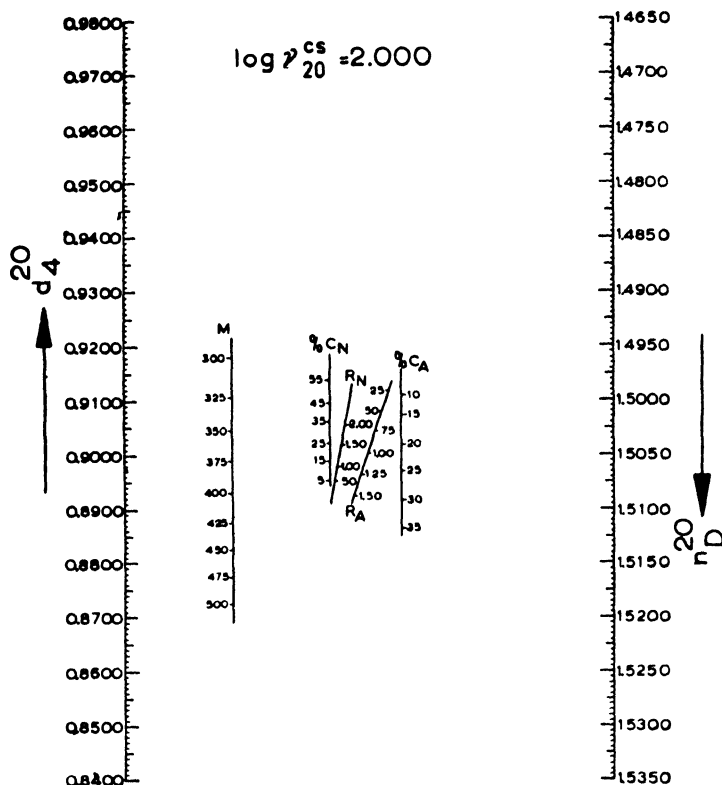


Fig. 26 Nomogram of the cross-section of the $\log \nu$ - n - d space model at $\log \nu_{20}^{cs} = 2.000$

The function of the refractive index and the density in the case of the determination of $\%C_A$ proves to be $(n - 0.35d)$ and in the case of the determination of $\%C_N$ $(n - \frac{2}{3}d)$.

The use of the graphs does not need further explanation. The value of the coefficients of d in the (n, d) functions have been derived from the constant slope of the lines of equal values of $\%C_A$ and $\%C_N$ in the cross-sections.

Though these graphs are convenient to use it is a drawback that for each structural element a different graph has to be employed. Therefore the nomogram method in general seems to be the most attractive method for determining the values of the various structural elements of mineral oil fractions.

3. CORRELATION OF PHYSICAL CONSTANTS OF MINERAL OIL FRACTIONS

In this section it will be shown that it is not only possible to determine the chemical structure of mineral oil fractions from physical constants, but also to predict the values of other physical constants. That it is possible to correlate the physical constants of

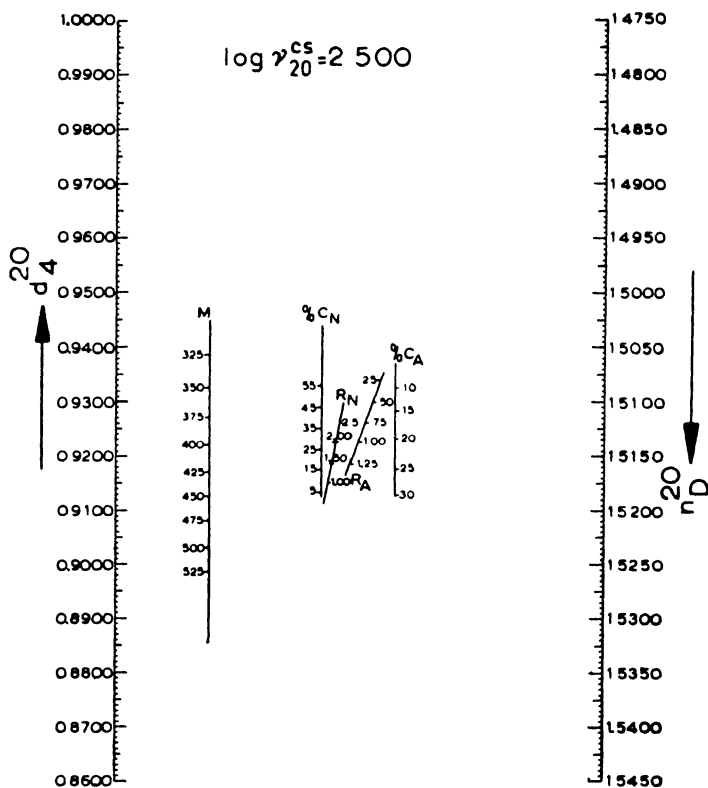


Fig. 27 Nomogram of the cross-section of the $\log \nu$ - n - d space model at $\log \nu_{20}^{cs} = 2.500$

saturated mineral oil fractions can be seen from a few particular examples, previously given in connection with the determination of $\%C_N$

These are

(a) The correlation between specific refraction, molecular weight and aniline point or density (p. 20, Figs. 9 and 10).

(b) The correlation between kinematic viscosity, refractive index and density (p. 28, Fig. 14)

New methods of finding correlations between physical constants of straight-run as well as of saturated mineral oil fractions will be discussed below.

a. Correlation of the viscosity, the refractive index, the density and the ultrasonic sound velocity of mineral oil fractions

(1) Application of cross-sections of the $\log \nu$ - n - d space model

It has been found by CORNELISSEN AND WATERMAN¹⁸ that it is possible to construct surfaces of equal values of the ultrasonic sound velocity in the $\log \nu$ - n - d space model.

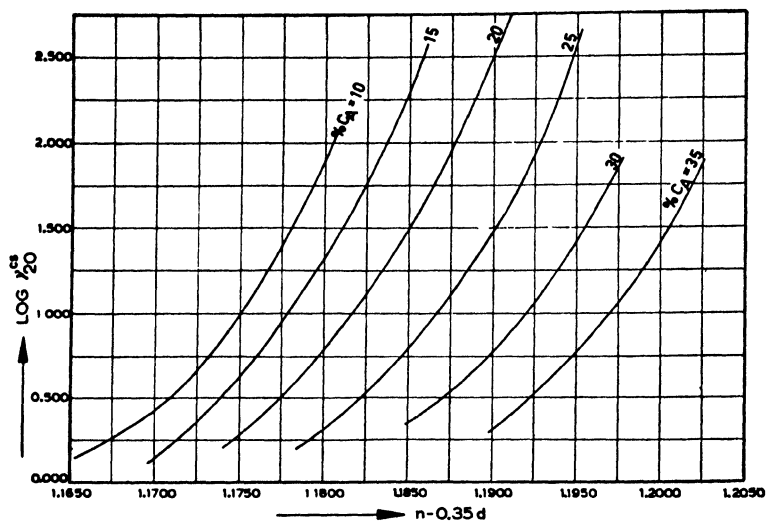


Fig. 28 $\text{Log } v_{80}^{cs} - (n - 0.35d)$ graph for the determination of $\%C_A$ in mineral oil fractions

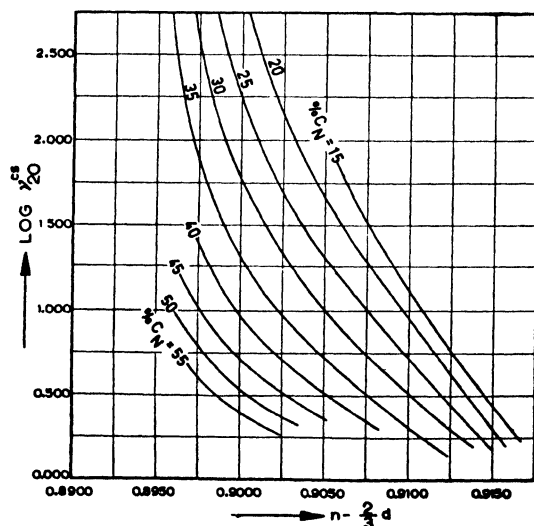


Fig. 29 $\text{Log } v_{80}^{cs} - (n - 2/3d)$ graph for the determination of $\%C_N$ in mineral oil fractions.

For practical purposes it is necessary to represent the connection between the ultrasonic sound velocity u (m/sec) and v , n and d by means of cross-sections for constant $\log v$ values of the $\log v - n - d$ space model. The sections contain the intersecting lines with the surfaces of equal u values, Figs. 30, 31, 32, 33 and 34.

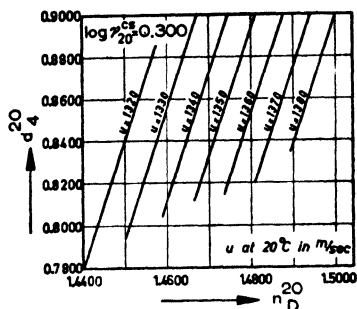


Fig. 30. Cross-section of the log ν - n - d space model at $\log \nu_{30}^{cs} = 0.300$

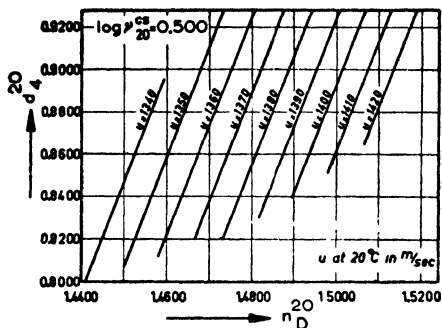


Fig. 31. Cross-section of the log ν - n - d space model at $\log \nu_{30}^{cs} = 0.500$

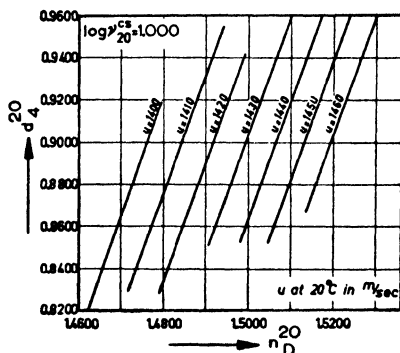


Fig. 32. Cross-section of the log ν - n - d space model at $\log \nu_{30}^{cs} = 1.000$

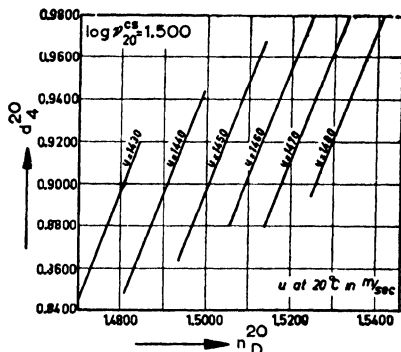


Fig. 33. Cross-section of the log ν - n - d space model at $\log \nu_{30}^{cs} = 1.500$

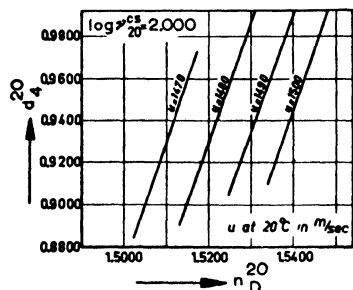


Fig. 34. Cross-section of the log ν - n - d space model at $\log \nu_{30}^{cs} = 2.000$

The figures 30-34 are related to mineral oil fractions.

The intersecting lines of equal u values are straight and mutually parallel. In order to determine the ultrasonic sound velocity at 20°C from $\log v_{20}^{cs}$, n_D^{20} and d_4^{20} , use has in general to be made of two cross-sections for the $\log v_{20}^{cs}$ values adjacent to the actual $\log v_{20}^{cs}$ value of the oil fraction in question. This will be made clear in the following example.

Example For an oil fraction the following values of the physical constants were found

$$\begin{aligned}\log v_{20}^{cs} &= 0.828 \\ n_D^{20} &= 1.4695 \\ d_4^{20} &= 0.8390 \\ u_{20} &= 1394 \text{ m/sec}\end{aligned}$$

From the cross-sections for constant $\log v_{20}^{cs} = 0.500$ and $\log v_{20}^{cs} = 1.000$ values, the u_{20} values are read by means of the values $n_D^{20} = 1.4695$ and $d_4^{20} = 0.8390$ $u_{20} = 1369 \text{ m/sec}$ and 1405 m/sec respectively

By linear interpolation the following value is obtained

$$u_{20} = 1369 + \frac{0.328}{0.500} 36 = 1369 + 24 = 1393.$$

$u_{20} = 1393 \text{ m/sec}$, while the experimental value amounted to 1394 m/sec , measured at a frequency of $2 \cdot 10^6$ Hertz

The u_{20} determined in the way just described is about as accurate as the experimentally determined value.

The method is applicable to the original mineral oil fractions.

(ii) Application of nomograms of the cross-sections

As has been discussed in the case of the determination of the values of certain structural elements, the sets of straight lines in a cross-section can be replaced by a single line in a nomogram consisting of the parallel coordinates n_D^{20} and d_4^{20} .

As the straight lines in the cross-sections are parallel, the single line in the nomograms is parallel to the coordinate axes n_D^{20} and d_4^{20} . The distance of the single line from the parallel coordinates will depend on the slope of the lines of equal u_{20} values in the cross-sections. Since the slope of the lines in the cross-sections amounts to about 3, the situation of the single line in the nomogram is as represented in Fig. 35, provided that the scales on both the cross-section and the nomogram are the same.

The way in which u_{20} can be determined from $\log v_{20}^{cs}$, n_D^{20} and d_4^{20} by means of the nomogram is the same as described for the cross-sections in the preceding section and will not further be discussed.

(iii) Application of a $\log v - (n - \frac{1}{3}d)$ graph

As has already been discussed, the slopes of the lines for equal u values in the cross-sections for constant $\log v$ values of the $\log v - n - d$ model, are all approximately the same, provided the same scales are chosen for both the refractive index and the density. Therefore it is possible to construct a graph with the coordinates $\log v_{20}^{cs}$ and $(n - \frac{1}{3}d)$, in which lines of equal values of the ultrasonic sound velocity can be indicated¹⁹. This has been done in Fig. 36.

By means of this graph it is possible to determine u_{20} from $\log v_{20}^{cs}$, n_D^{20} and d_4^{20} , if the value of the function $(n - \frac{1}{3}d)$ is calculated from n_D^{20} and d_4^{20} .

It appears that the lines of equal values of the ultrasonic sound velocity in the graph are straight. The slope of the lines changes steadily from one line to the next.

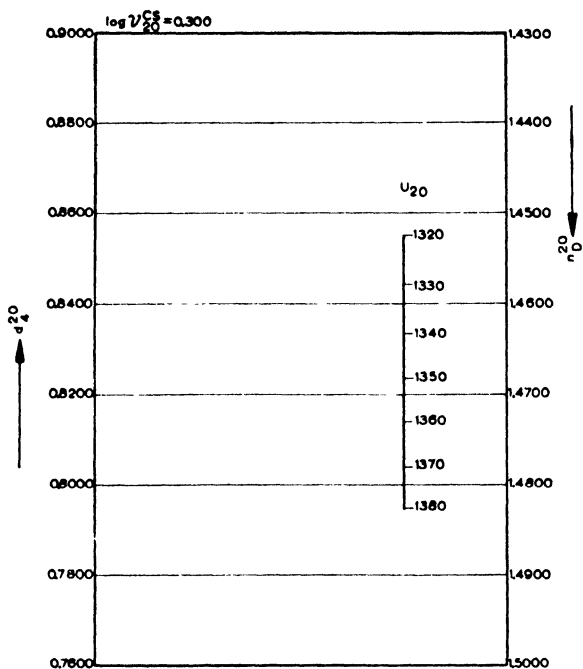


Fig. 35 Nomogram for the determination of u_{20} , replacing a cross-section of the $\log \nu - n - d$ space model at $\log \nu_{20}^{cs} = 0.300$

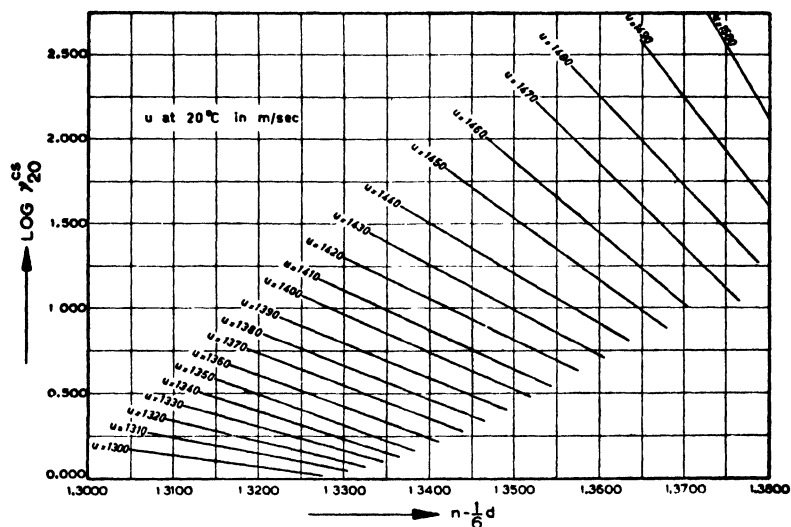


Fig. 36 $\log \nu - (n - \frac{1}{6}d)$ graph for the determination of u of mineral oil fractions

(iv) *Application of a nomogram of the $\log v - (n - \frac{1}{8}d)$ graph*

As has been stated above the lines for equal values of the ultrasonic sound velocity of mineral oil fractions in the $\log v - (n - \frac{1}{8}d)$ graph are straight. Therefore it is possible to construct a nomogram with the parallel coordinates $\log v_{20}^{cs}$ and $(n - 0.181 d)$, the value of 0.181 in the function $(n - 0.181 d)$ being somewhat more accurate than $\frac{1}{8}$ in the function $(n - \frac{1}{8}d)$.

It is also possible to determine the value of $(n - 0.181 d)$ by means of the nomogram given in Fig. 37. For this purpose parallel coordinates n_D^{20} and d_4^{20} parallel to the $\log v_{20}^{cs}$ and $(n - 0.181 d)$ coordinates have been constructed in the appropriate way.

In Fig. 37 an example has been given how to determine the value of u_{20} from $\log v_{20}^{cs}$.

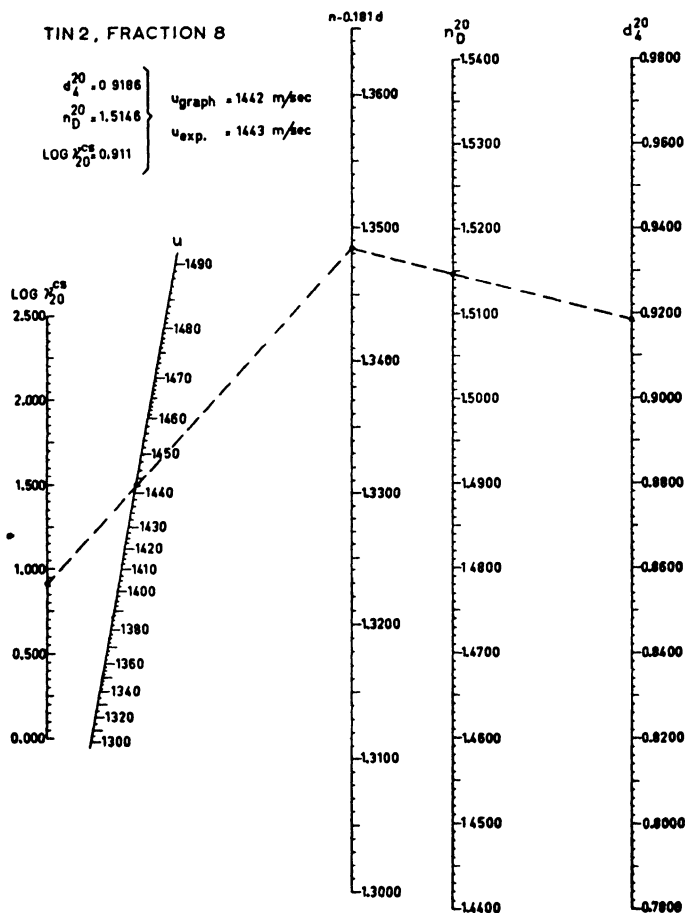


Fig 37 Nomogram of the $\log v - (n - \frac{1}{8}d)$ graph for the determination of u of mineral oil fractions.

d_A^{20} and n_D^{20} by means of the nomogram. The use of the nomogram is more attractive than the use of the graph (Fig. 36) since no calculations of the $(n-d)$ function have to be made.

b. Correlation of the viscosity, the refractive index, the density and the surface tension of mineral oil fractions

(1) Application of cross-sections of the ν - n - d space model

It is possible to construct surfaces of equal values of the surface tension σ in the log ν - n - d space model in the same way as surfaces of equal values of $\%C_A$ and $\%C_N$ and the ultrasonic sound velocity have been constructed before. For practical application use has to be made of five different cross-sections for constant log ν -values, as has been worked out by CORNELISSEN, HARVA AND WATERMAN²⁰. These are represented in Figs. 38, 39, 40, 41 and 42.

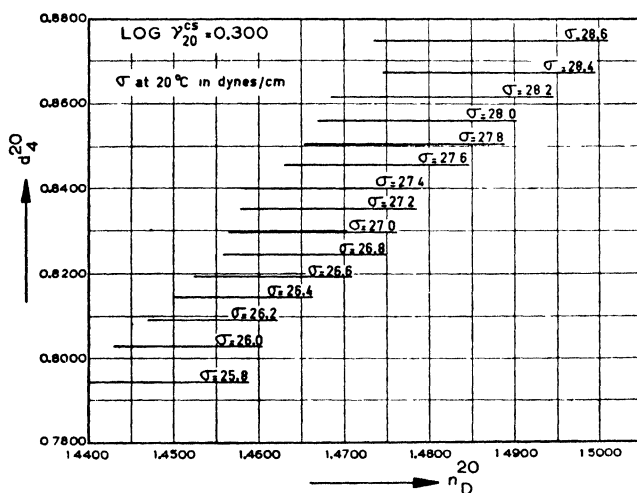


Fig. 38 Cross-section of the log ν - n - d space model at $\log \nu_{20}^{cs} = 0.300$, for the determination of σ_{20}

For the determination of the surface tension from the viscosity, the refractive index and the density of mineral oil fractions two cross-sections have, in general, to be used. The value of σ_{20} can be obtained by linear interpolation between values read from the two cross-sections.

The lines for equal values of σ in the different cross-sections are parallel to the n_D^{20} axis. This means that the surface tension at a constant value of the viscosity and the density is independent of the refractive index and in fact of any other physical constant, i.e. the viscosity and the density are the only two physical constants of mineral oil fractions that are necessary to determine the value of the surface tension of these fractions.

text continued on p. 48

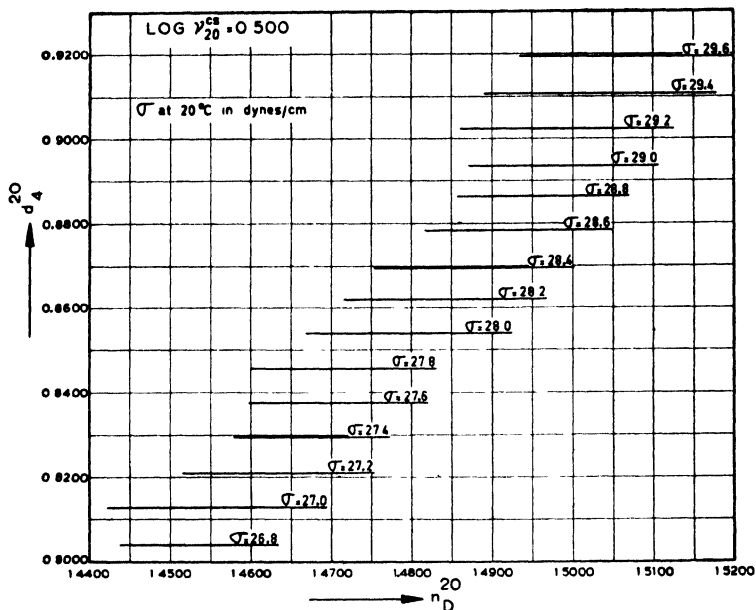


Fig. 39 Cross-section of the log ν - n - d space model at log $\nu_{20}^{cs} = 0.500$, for the determination of σ_{30} .

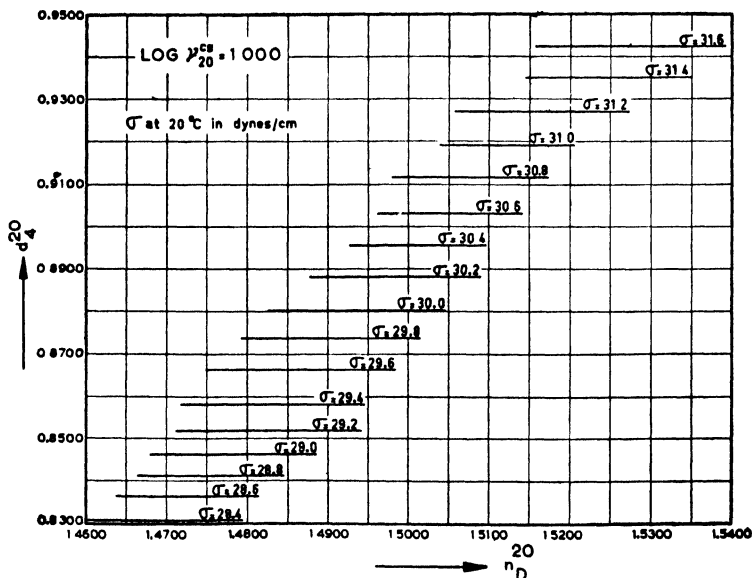


Fig. 40 Cross-section of the log ν - n - d space model at log $\nu_{20}^{cs} = 1.000$, for the determination of σ_{30} .

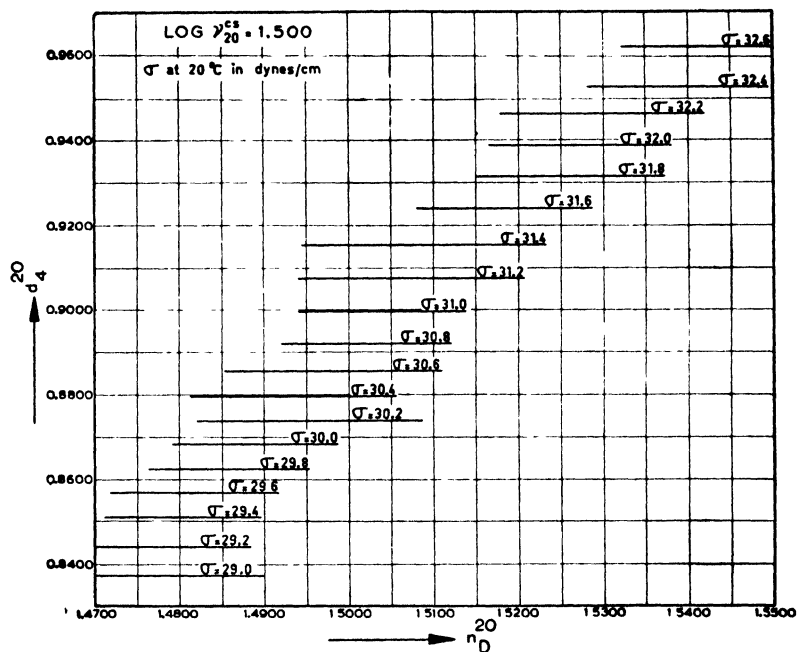


Fig. 41. Cross-section of the log ν - n - d space model at $\log \nu_{20}^{cs} = 1.500$, for the determination of σ_{20} .

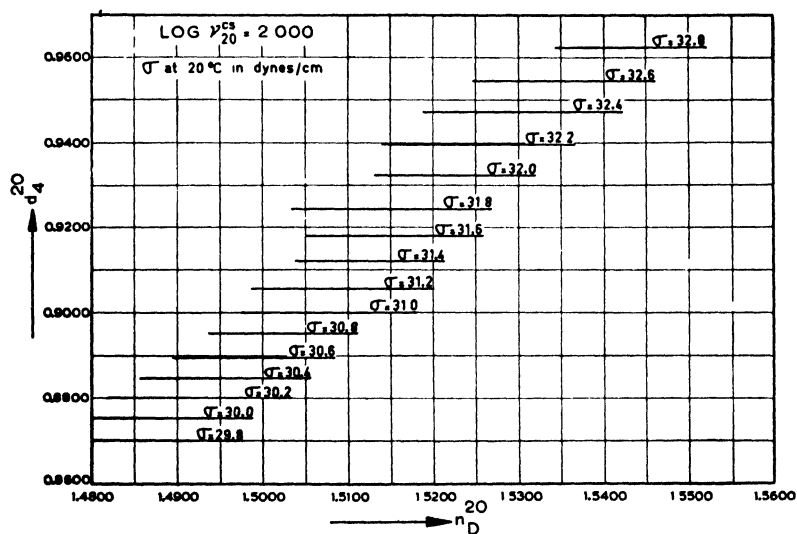


Fig. 42. Cross-section of the log ν - n - d space model at $\log \nu_{20}^{cs} = 2.000$, for the determination of σ_{20} .

(ii) *Application of a log ν - d graph*

The fact that only the two physical constants, viscosity and density, are necessary to determine the surface tension of mineral oil fractions, enabled CORNELISSEN, HARVA AND WATERMAN²¹ to construct a diagram with the coordinates $\log \nu_{20}^{cs}$ and d_4^{20} . This diagram has been constructed by projecting the surfaces of equal values of the surface tension in the $\log \nu$ - n - d space model on the $\log \nu$ - d coordinate plane. In the diagram lines of equal values of the surface tension σ_{20} (at 20°C) were constructed (Fig. 43).

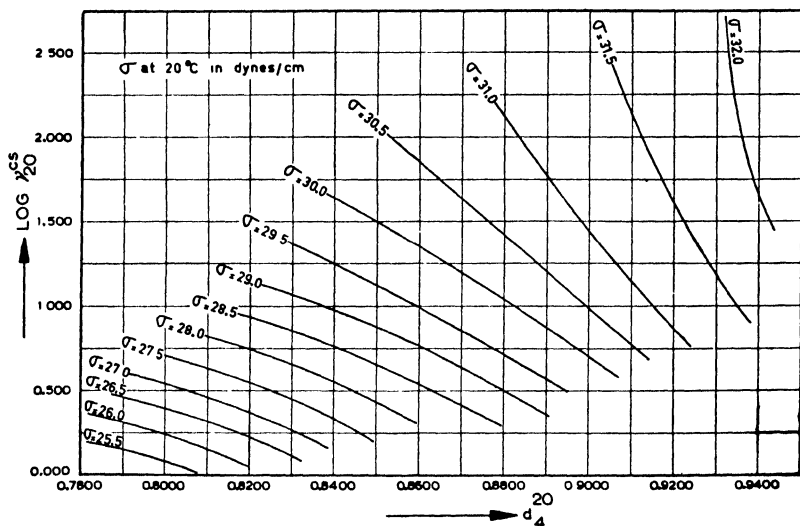


Fig. 43 $\log \nu_{20}^{cs}$ - d_4^{20} diagram for the determination of σ_{20} of mineral oil fractions.

This diagram makes it possible to determine σ_{20} from the measured values of the viscosity and the density. In general the results obtained have the same accuracy as those obtained by direct measurements.

It is a remarkable fact that only two physical constants (viscosity and density) are necessary to determine the surface tension of mineral oil fractions. The physical background of this phenomenon is not yet clear. Another remarkable fact is that the diagram presented in Fig. 43 can be applied not only to original mineral oil fractions, but also to hydrogenated mineral oil fractions, whereas in general different graphs must be used for these two groups.

c. Correlation of the ultrasonic sound velocity, the density and the surface tension of mineral oil fractions

A third example of the correlation of physical constants of mineral oil fractions is the determination of the surface tension from the ultrasonic sound velocity u and the density d^{22} .

This determination can be carried out by using a graph with the ultrasonic sound velocity u and the density d as coordinates, as shown in Fig. 44.

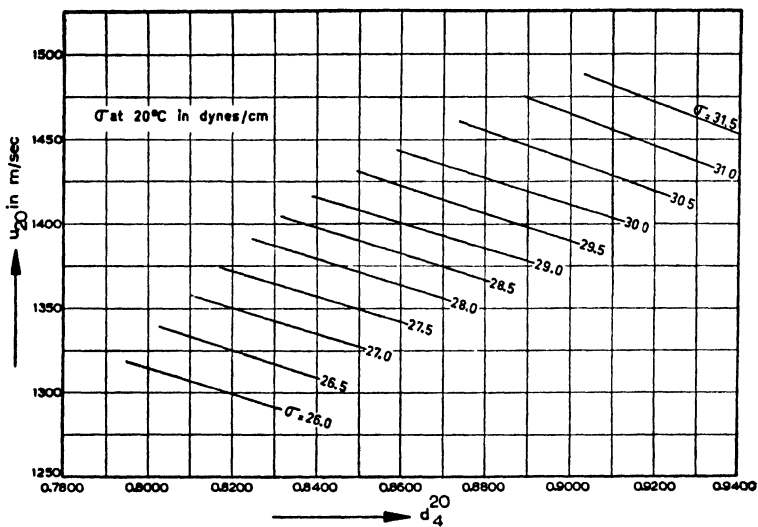


Fig 44 u - d graph for the determination of σ of mineral oil fractions

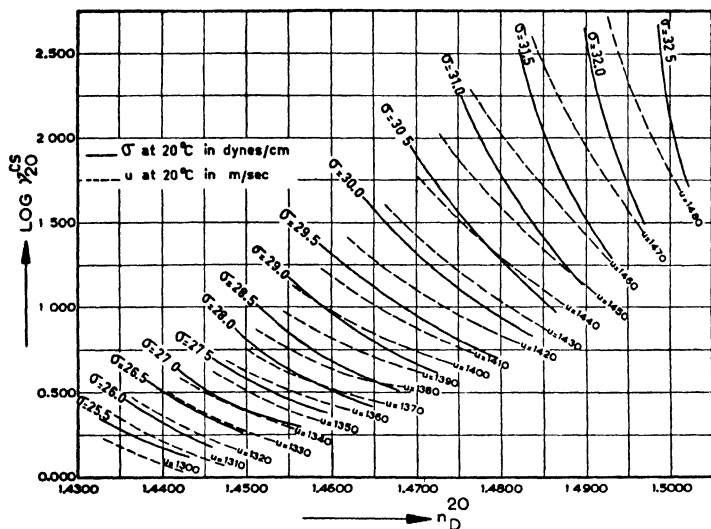


Fig 45 $\log v$ - n diagram for the determination of the ultrasonic sound velocity and the surface tension of saturated mineral oil fractions from their viscosity and refractive index

In the graph lines of equal values of u have been constructed. These lines are straight and parallel. Stress must be laid on the fact that the graph is only applicable to original mineral oil fractions and not to saturated mineral oil fractions.

d. Correlation of physical constants of saturated mineral oil fractions

It was found by CORNELISSEN, HARVA AND WATERMAN²³ that a $\log \nu$ - n diagram can be constructed for the determination of both the ultrasonic sound velocity and the surface tension of saturated mineral oil fractions. This was possible by constructing lines of equal values of the ultrasonic sound velocity and the surface tension, respectively, as shown in Fig. 45.

The graph shown in Fig. 45 is only valid for saturated mineral oil fractions and is *not* valid for the original mineral oil fractions.

It is also possible to determine the surface tension of hydrogenated fractions from the ultrasonic sound velocity and the density²². This can be done by means of a u - d diagram in which lines of equal values of the surface tension have been constructed. This diagram is shown in Fig. 46. See also Addendum 3, p. 113.

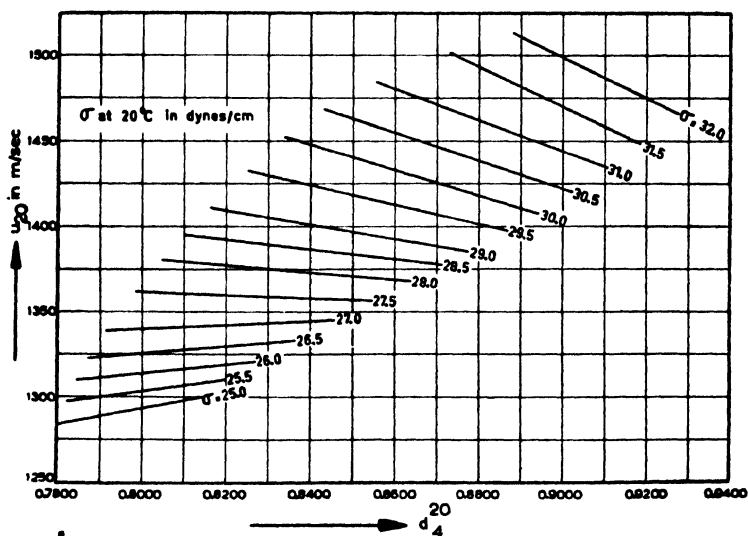


Fig. 46 u - d diagram for the determination of the surface tension of saturated mineral oil fractions

e. Temperature dependence of the viscosity

Not only the viscosity but also the temperature dependence of the viscosity can be related to the structure of mineral oil fractions

The viscosity-temperature relationship of mineral oil fractions, and in fact of many other liquids, can be represented by a formula proposed by CORNELISSEN AND WATERMAN²⁴

$$\log \nu = \frac{A}{T^x} + B \quad \dots \dots \dots (45)$$

where ν denotes the kinematic viscosity in centistokes (stokes = $\text{g}\cdot\text{cm}^{-1}\cdot\text{sec}^{-1}$) and T denotes the absolute temperature in $^{\circ}\text{K}$, A , B and x are constants. The formula has been experimentally tested over the temperature range from 10–100 $^{\circ}\text{C}$ and in some cases over wider ranges.

The constants A , B and x in the formula can be calculated from three viscosity values ν_1 , ν_2 and ν_3 , determined at three different temperatures T_1 , T_2 and T_3 , respectively.

The three following equations are obtained:

$$\log \nu_1 = \frac{A}{T_1^x} + B \quad \dots \dots \dots (a)$$

$$\log \nu_2 = \frac{A}{T_2^x} + B \quad \dots \dots \dots (b)$$

$$\log \nu_3 = \frac{A}{T_3^x} + B \quad \dots \dots \dots (c)$$

Subtracting (b) from (a) and (c) gives

$$\log \nu_1 - \log \nu_2 = A \left(\frac{1}{T_1^x} - \frac{1}{T_2^x} \right) \quad \dots \dots \dots (d)$$

$$\log \nu_2 - \log \nu_3 = A \left(\frac{1}{T_2^x} - \frac{1}{T_3^x} \right) \quad \dots \dots \dots (e)$$

Dividing (d) by (e) gives

$$\frac{\log \nu_1 - \log \nu_2}{\log \nu_2 - \log \nu_3} = \frac{\frac{1}{T_1^x} - \frac{1}{T_2^x}}{\frac{1}{T_2^x} - \frac{1}{T_3^x}} \quad \dots \dots \dots (46)$$

$$\text{If } Q = \frac{\log \nu_1 - \log \nu_2}{\log \nu_2 - \log \nu_3} \quad \dots \dots \dots (46a)$$

$$\text{and } Q = \frac{\frac{1}{T_1^x} - \frac{1}{T_2^x}}{\frac{1}{T_2^x} - \frac{1}{T_3^x}} \quad \dots \dots \dots (46b)$$

then the value of x can be calculated from that of Q using equation (46b). The value of Q is calculated by means of equation (46a) from the measured viscosity values.

The calculation of x from Q according to equation (46b) can be made with the aid of a table or a diagram if for the three temperatures T_1 , T_2 and T_3 , certain values are used, *e.g.* 20°C, 40°C and 70°C.

An example is given in Table II and Fig. 47.

TABLE II

$Q \begin{cases} 20 \\ 40 \\ 70 \end{cases} \quad x$	
0.78	1
0.84	2
0.91	3
0.99	4
1.07	5

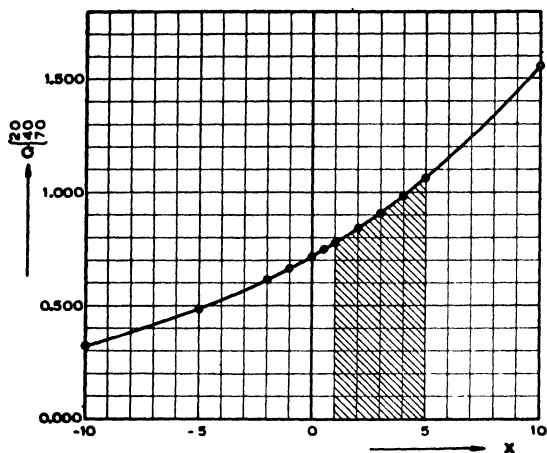


Fig 47 Q - x diagram for the determination of the value of x from the equation $\log \nu = \frac{A}{T^x} + B$, if the value of Q from equation (46a) is known.

A more detailed table than Table II has been published³⁵.

x can also be calculated^{35a} by means of the equation

$$x = \frac{2(\log Q - \log Q_0)}{\log T_3 - \log T_1}$$

in which

$$Q_0 = \frac{\log T_1 - \log T_2}{\log T_2 - \log T_3}$$

$$Q_0 = \lim_{x \rightarrow 0} Q$$

Once the value of x is known the value of A can be determined by means of the equation that can be derived from equations (a) and (c) by subtraction

$$\log \nu_1 - \log \nu_3 = A \left(\frac{1}{T_1^x} - \frac{1}{T_3^x} \right)$$

or

$$A = \frac{\log \nu_1 - \log \nu_3}{\frac{1}{T_1^x} - \frac{1}{T_3^x}} \quad \dots \dots \dots (47)$$

In many cases it is permissible to vary the experimental value of x about 0.5 unit, if the temperature range from 20°C to 100°C is being used, without unduly affecting the accuracy of the results of a calculation. Thus for a series of, for instance, lubricating oils with a value of x ranging from 3.0 to 4.0, the average group value of $x = 3.5$ can be chosen. In that case x may be considered as a constant for that group of oils, so that equation (47) can be altered to:

$$A = \frac{\log \nu_1 - \log \nu_3}{\text{constant}} \quad \dots \dots \dots (48)$$

Thus, the temperature dependence of the viscosity of these lubricating oils, being equal to A , is determined by $(\log \nu_1 - \log \nu_3)$ if the value of x is the same. If 20°C and 70°C are chosen for T_1 and T_3 this expression becomes $\log \nu_{20} - \log \nu_{70} = \log \frac{\nu_{20}}{\nu_{70}}$ (see also Fig. 48).

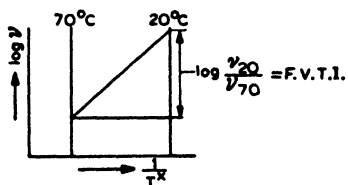


Fig 48 Schematic representation of the viscosity-temperature relationship of liquids with a certain constant average value of x , the slope A of the line is equal to $\frac{\log (\nu_{20} / \nu_{70})}{\text{constant}}$; therefore, for this group of oils with

constant x value, $\log \frac{\nu_{20}}{\nu_{70}}$ is a measure for the temperature dependence of the viscosity

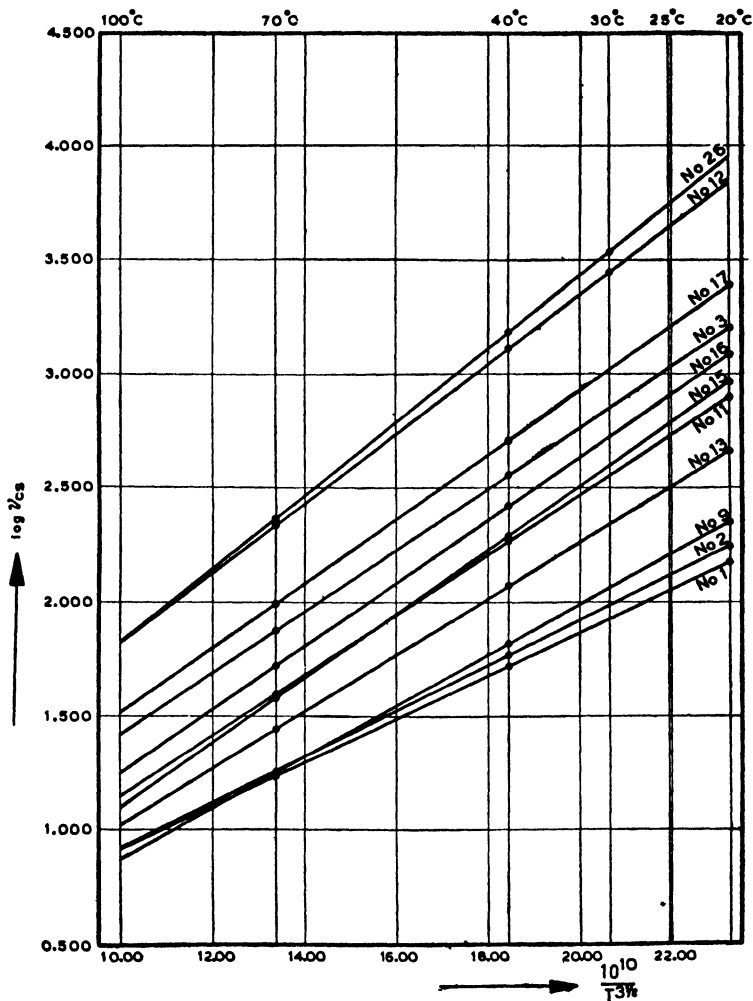


Fig. 49. $\log \nu - \frac{1}{T^x}$ graph for a series of lubricating oils

In a particular group of oils with constant average value of x , the expression $\log \frac{\nu_1}{\nu_2}$ can be considered as an absolute index for the temperature dependence of the viscosity $\log \frac{\nu_{30}}{\nu_{70}}$ has been given the name Fundamental Viscosity Temperature Index (F.V.T.I.).²¹

Only in the case of oils belonging to a group with a constant average x value may the values of the F.V.T.I. be compared. *E.g.* the values of the F.V.T.I. of a group of lubricating oils with an average group value of $x = 3.5$ (Figs. 49 and 50), cannot be compared with the values of the F.V.T.I. of a group of silicone oils with an average group value of $x = 1.0$ (Fig. 51).

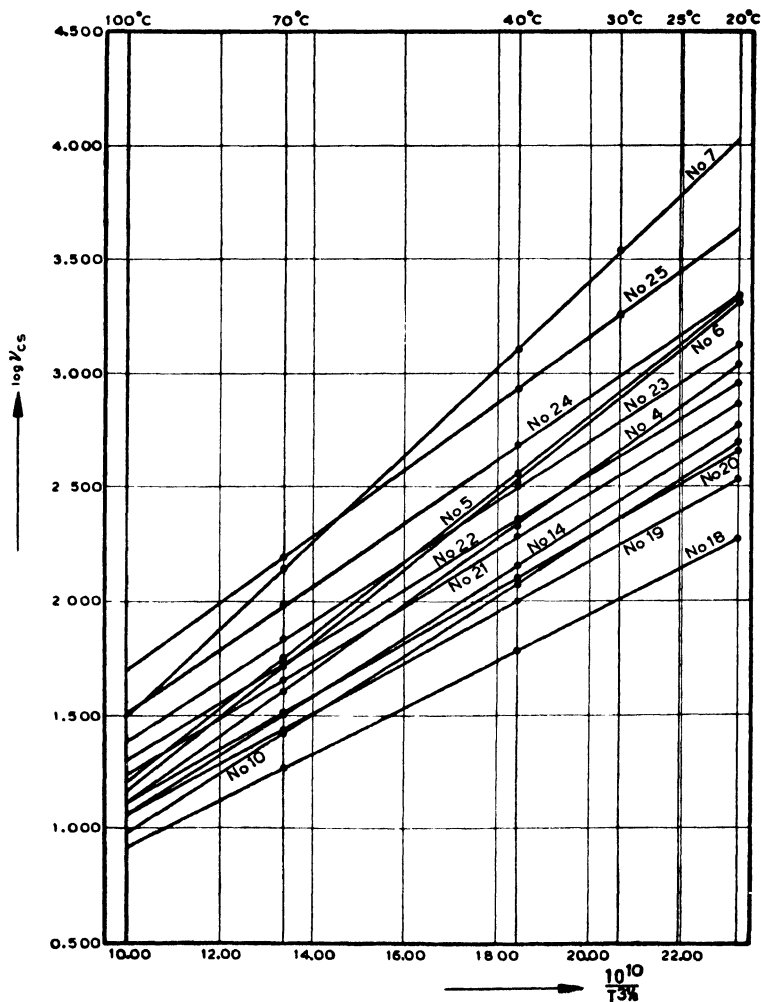


Fig. 50 $\log \nu - \frac{1}{T}$ graph for a series of lubricating oils

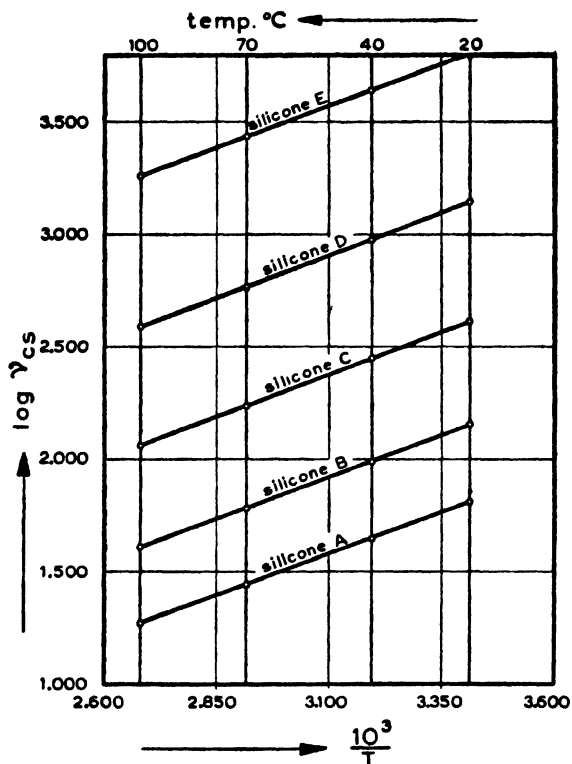


Fig 51 $\log \nu - \frac{1}{T}$ for a series of silicone oils.

The F.V.T.I. can be used to determine the number of rings in saturated fractions. CORNELISSEN AND WATERMAN constructed a diagram for this purpose²⁷, which diagram is shown in Fig. 52.

In the diagram the coordinates are $\log \frac{\nu_{20}}{\nu_{70}}$ and the refractive index at 20°C, n_D^{20} .

In the same way an $x - n_D^{20}$ diagram²⁵ can be constructed, which makes it possible to determine the ring content of saturated mineral oil fractions. This diagram is given in Fig. 53.

In this diagram x is the exponent in the formula

$$\log \nu = \frac{A}{T^x} + B \quad \dots \dots \dots (45)$$

This method has been applied by GEERARDS AND WATERMAN²⁸ to hydrocarbon oils obtained by hydrogenation of coal

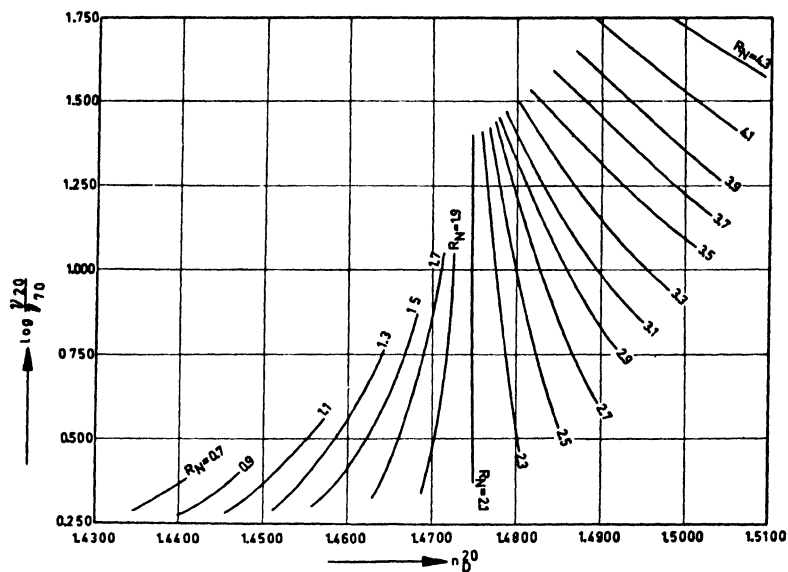


Fig. 52. $\log \frac{y_{20}}{y_{70}} - n_D^{20}$ diagram for the determination of the number of rings in saturated mineral oil fractions

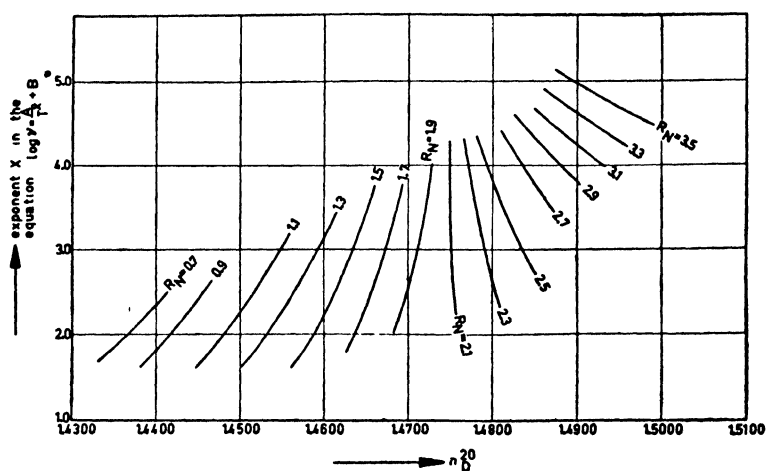


Fig. 53. $x - n_D^{20}$ diagram for the determination of the ring content of saturated mineral oil fractions.

4. ANALYSIS OF BRANCHED HYDROCARBON MIXTURES

a. Introduction

When determining the degree of branching of hydrocarbon mixtures by means of physical constants, especially those physical constants or functions thereof should be chosen that show the necessary sensitivity to the presence of branchings. Particularly the parachor and the magneto-optical rotation have found application.

There are mainly two problems that hamper the development of reliable methods for the analysis of branched hydrocarbon mixtures.

In the first place an unambiguous definition of the "degree of ramification" is very difficult, especially for naphthenic hydrocarbons, which are generally present in hydrocarbon mixtures. DE BOOIJ²⁹ gave the following definition:

φ = the number of *n*-alkyl groups building up the hydrocarbon molecule, minus one

thus trying to combine both paraffinic and naphthenic hydrocarbons in the same system. This, however, results in negative values of φ for cyclohexane, decalin, etc., and it is quite doubtful whether such hydrocarbons conform to a general system based on this relatively arbitrary definition of the degree of branching φ . WESTERDIJK *et al.*^{30,10a} defined the degree of branching N_v in saturated individual molecules as:

$$N_v = \frac{N_{CH_3} - 2 + 3 R_T}{N_c} \quad (49)$$

where N_{CH_3} = the number of methyl groups in the molecule

R_T = the number of naphthenic rings per molecule

N_c = the number of carbon atoms per molecule

N_v is related to one carbon atom

The naphthenic ring is thus considered as a form of branching that contributes three times as much as a side chain

Secondly there is no direct method for determining the degree of branching (φ or N_v) of mineral oil fractions or similar hydrocarbon mixtures. Direct correlation of φ or N_v with any particular physical constant is therefore impossible. The existing methods have all been based on correlating the data obtained from a limited number of individual hydrocarbons with their degree of branching, and consequently have a more or less limited and approximate character when applied to mineral oil fractions and other hydrocarbon mixtures. It should therefore be emphasized that the various methods of branching analysis are only qualitative, or at best semi-quantitative. For comparative studies they may be of some value, but quantitative data generally cannot be obtained.

b. The Faraday effect

The phenomenon of the rotation of the plane of polarization of light by substances when placed in a magnetic field is called the Faraday effect. The angle of rotation (α) depends on the nature of the substance:

$$\alpha = V H L \cos \beta$$

V is called the Verdet-constant, it depends only slightly on the temperature, but varies markedly with the wavelength of the light, measurements are normally carried out

with a sodium-lamp (Na-D line) at 20°C; V is generally given as $\frac{100 \text{ min}}{\text{cm-gauss}}$ and indicated in this case by $100 V_D^{20}$.

H is the strength of the magnetic field in gauss, L is the length of the path travelled by the light through the substance, β is the angle between the beam of light and the magnetic field lines.

Absolute determinations of V are extremely difficult. For routine measurements relative methods have been worked out^{29,31}, in which the experimental material is compared directly with a standard liquid (*e.g.* water), these methods also require a relatively complicated apparatus and skilled operators to obtain a reasonable accuracy ($\pm 0.05\%$).

WESTERDIJK *et al.*³⁰ have shown that the Verdet constant of saturated hydrocarbons is not so much related to the degree of branching φ as to the degree of branching defined by N_v . DE BOOIJ³² succeeded in correlating N_v and V for a large number of paraffinic and naphthenic hydrocarbons:

$$N_v = \frac{(N_{CH_3} - 2) + 3R_T}{N_c} = \frac{100V - 1.456 + \frac{1.56}{N_c}}{0.200} \dots (50)$$

thus indicating a method of estimating N_{CH_3} , the number of methyl groups of the individual saturated hydrocarbons, when V , N_c and R_T are known (*cf.* Fig. 54).

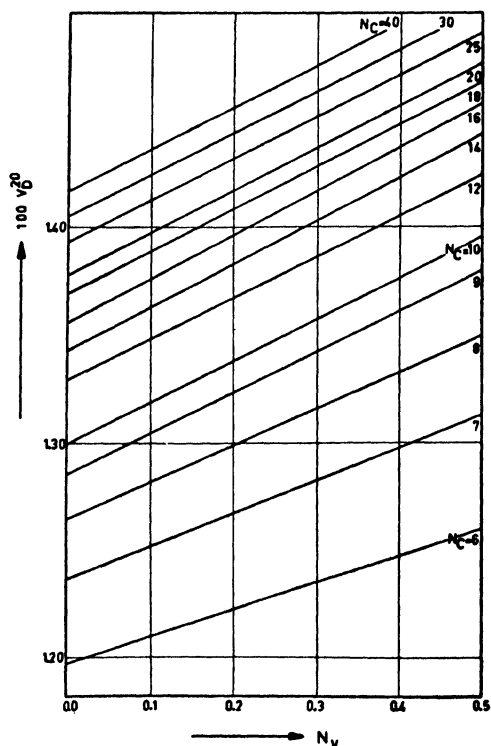


Fig. 54. Relation between N_v , V and N_c for naphthenic and paraffinic hydrocarbons.

The method can also be applied to aromatic- and olefin-free hydrocarbon mixtures (cf. Table III); in these cases N_c can be calculated from the average molecular weight M by means of the formula

$$N_c = \frac{M + 2 R_T - 2}{14.026} \dots \dots \dots (51)$$

c. The magneto-optical rotation³¹

The molecular magneto-optical rotation D is a function of the refractive index n , the density d , the Verdet constant V and the molecular weight M

$$D = \frac{9 n V M}{(n^2 + 2)^2 d} \dots \dots \dots (52)$$

This function shows a certain resemblance to that of the molecular refraction r_{mol}

$$r_{\text{mol}} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \dots \dots \dots (53)$$

However, in the analysis of saturated hydrocarbon mixtures, D has proved to be not only highly sensitive to the presence of rings (like r_{mol}), but also to ramifications in the molecules. When comparing D and r_{mol} of paraffinic or naphthenic hydrocarbons with those of corresponding n -alkanes of equal molecular weight ($D_{n\text{-alkane}}$ and $r_{\text{mol}}(n\text{-alkane})$, respectively), it can be stated that

$$\varphi = a(D - D_{n\text{-alkane}}) - b(r_{\text{mol}} - r_{\text{mol}}(n\text{-alkane})) \dots \dots (54)$$

where $D_{n\text{-alkane}} = 0.01309M + 0.1544$

$$r_{\text{mol}}(n\text{-alkane}) = 0.3309M + 1.424$$

M = the molecular weight.

a and b are constants depending on the nature of the homologous hydrocarbon series considered. In this equation φ is expressed in terms of $(D - D_{n\text{-alkane}})$ and $(r_{\text{mol}} - r_{\text{mol}}(n\text{-alkane}))$, the form of the equation follows from the consideration that for saturated hydrocarbons these two expressions are functions of both ring content and degree of branching, the dependency of $(r_{\text{mol}} - r_{\text{mol}}(n\text{-alkane}))$ on φ is, however, small in comparison with that of $(D - D_{n\text{-alkane}})$.

For *paraffinic hydrocarbons* the following expression is a good approximation

$$\varphi = 26.8 (D - D_{n\text{-alkane}}) - 6.71 (r_{\text{mol}} - r_{\text{mol}}(n\text{-alkane})) \dots \dots (55)$$

For *saturated mineral oil fractions* the following formula can be deduced

$$\varphi = 30.7 (D - D_{n\text{-alkane}}) - 3.08 (r_{\text{mol}} - r_{\text{mol}}(n\text{-alkane})) \dots \dots (56)$$

The method has been applied to saturated aromatic and olefin-free mineral oil fractions and hydrogenated polymers (cf. Table III and IV)

DE BOOIJ³² considered the degree of branching φ also in terms of the *apparent ring-numbers* R_T^{mol} and R_T^D , which, for distinct groups of non-branched hydrocarbons are equal to the real ring-number R_T ($R_T = R_T^{\text{mol}} = R_T^D$), but differ from it when branchings are present. According to DE BOOIJ φ is given by the general equation:

$$\varphi = p(R_T - R_T^D) + q(R_T - R_T^{r_{\text{mol}}}) \quad \dots \dots \dots (57)$$

in which p and q are constants depending on the nature of the hydrocarbons; $R_T^{r_{\text{mol}}}$ and R_T^D are given by equations (60) and (61).

Equation (57) shows the relation between φ and both the molecular magneto-optical rotation D and the molecular refraction r_{mol} , although r_{mol} is much less influenced by the presence of branchings:

$$R_T^{r_{\text{mol}}} - R_T \ll R_T^D - R_T \quad (\text{cf. Fig. 55})$$

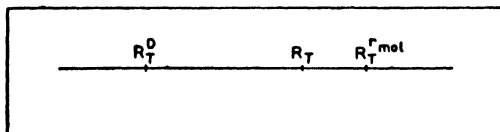


Fig. 55 Situation of the apparent ring-numbers $R_T^{r_{\text{mol}}}$ and R_T^D in respect to the real ring number R_T for saturated hydrocarbons, according to DE BOOIJ⁵⁰

For *saturated mineral oil fractions* the following holds within the limits of accuracy of determination:

$$R_T^{r_{\text{mol}}} = R_T \quad \dots \dots \dots (58)$$

and φ is given by.

$$\varphi = 5.1 (R_T^{r_{\text{mol}}} - R_T^D) \quad \dots \dots \dots (59)$$

$$\text{where } R_T^{r_{\text{mol}}} = \frac{0.3309M + 1.424 - r_{\text{mol}}}{1.654} \quad \dots \dots \dots (60)$$

$$R_T^D = \frac{0.01309M + 0.1542 - D}{0.1662} \quad \dots \dots \dots (61)$$

Since $R_T^{r_{\text{mol}}}$ and R_T^D can be graphically represented, estimation of φ from r_{mol} , D and M can be executed relatively easily when the proper graphs are available

d. The parachor

(i) The molecular parachor P was introduced as an additive function by SUGDEN⁵²:

$$P = \frac{\sigma^{\frac{1}{2}} \cdot M}{d - D_v} \quad \dots \dots \dots (62)$$

where σ = surface tension (dyne/cm)

d = density of the liquid

D_v = density of the vapor in equilibrium with the liquid under the conditions of measurement.

When P is determined at 20°C the value of D_v in the formula may be neglected for values of $M > 150$.

MUMFORD AND PHILLIPS⁵³ were the first to evaluate the influence of chain branching on the molecular parachor of hydrocarbons. They calculated values for the atomic parachors, which formed the basis for the specific parachor *vs.* molecular weight diagram of LEENDERTSE AND WATERMAN⁵⁴ (Fig. 56). In this diagram curves are drawn

representing non-branched paraffins, mono-cyclic six-carbon-ring naphthenes with *one* non-branched side-chain, etc. For non-branched hydrocarbon mixtures the average number of rings estimated with this diagram is equal to the value obtained with the aid of specific refraction and molecular weight in the ring analysis diagram (*cf.* Fig. 3); when branchings are present there appears to be a difference between the two ring-numbers, which, according to LEENDERTSE AND WATERMAN, amounts to about 0.1 ring per branching.

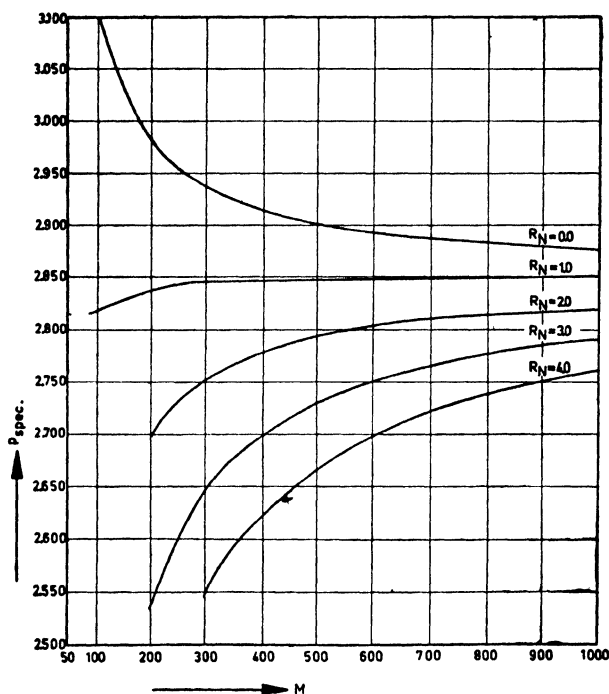


Fig. 56 Diagram for saturated non-branched hydrocarbons (based on values of the atomic parachor given by MUMFORD AND PHILLIPS) according to LEENDERTSE AND WATERMAN⁸⁴

(ii) WEBER *et al.*³⁵, in a study on the isomerization of paraffin wax, made use of analogous diagrams, which were, however, based exclusively on reliable data of a number of *n*-alkanes and *n*-alkyl-cyclohexanes at 20° and 70°C, taken from A.P.I.-project 44³⁶ (*cf.* Figs. 57 and 58). They concluded that the presence of one branching in a *n*-alkane causes a ring difference ΔR of 0.09 (about 0.1) rings between the values obtained from Figs. 57 and Fig. 58, respectively.

$$\varphi = 11 \Delta R \quad (63)$$

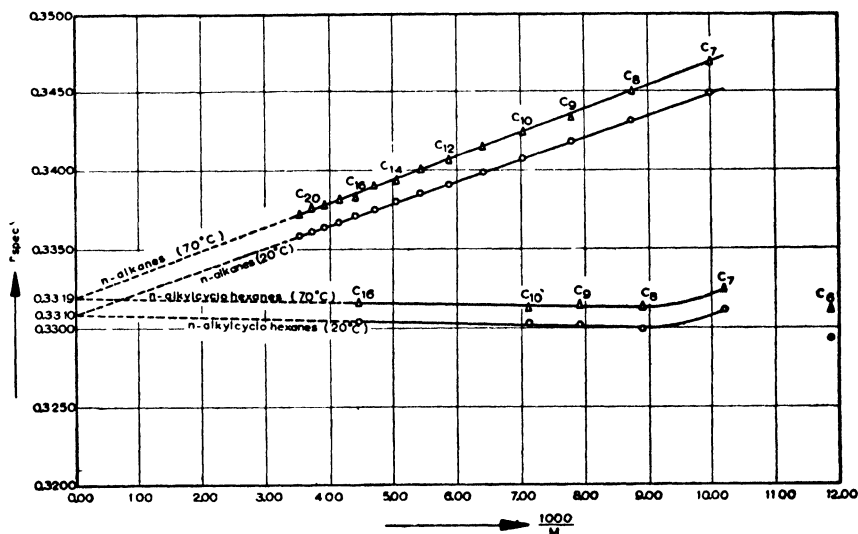


Fig 57

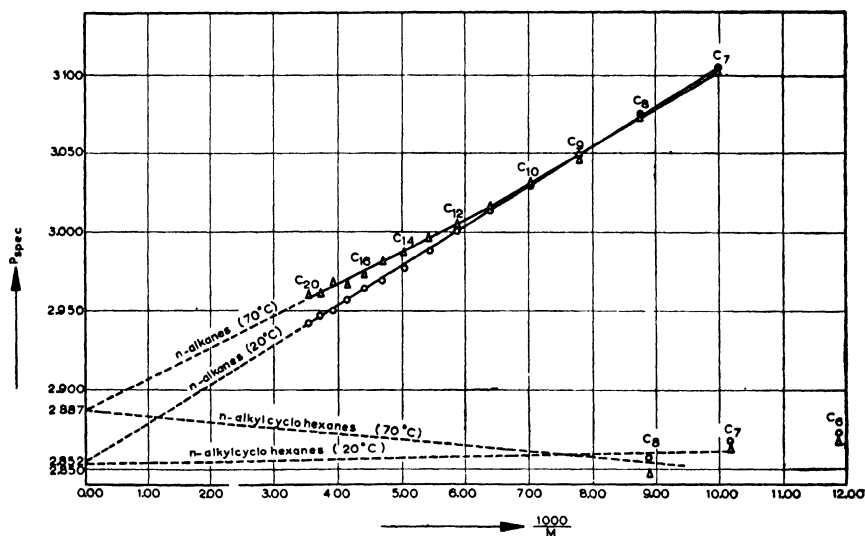


Fig 58

Figs 57 and 58 Diagrams representing specific refraction vs $\frac{1}{M}$ and specific parachor vs $\frac{1}{M}$ based on A P I data of *n*-alkanes and *n*-alkyl-cyclohexanes at 20° and 70°C⁸⁶

(iii) BOELHOUWER AND WATERMAN⁹ showed that the diagrams of WEBER form a valuable means for the ring analysis and branching analysis of saturated hydrocarbon mixtures of widely different degree of branching. Use was made of a general equation of GEELEN⁸ for relating a specific additive function A with the ring-number R_T and mol. weight M of saturated hydrocarbon mixtures

$$A = a + \frac{b + c R_T}{M} \quad \dots \dots \dots (64)$$

in which A represents a specific function ($r_{\text{spec}}^{\text{so}}$, $\frac{\sigma^{\text{I}}}{d}$, $\frac{\text{I}}{d}$, etc.) and a , b and c are constants.

The specific refraction *vs.* $\frac{\text{I}}{M}$ and the specific parachor *vs.* $\frac{\text{I}}{M}$ diagrams of WEBER *et al.* were extended according to equation (64) to bicyclic naphthenes, tricyclic naphthenes, etc. (*cf.* Figs. 59 and 60).

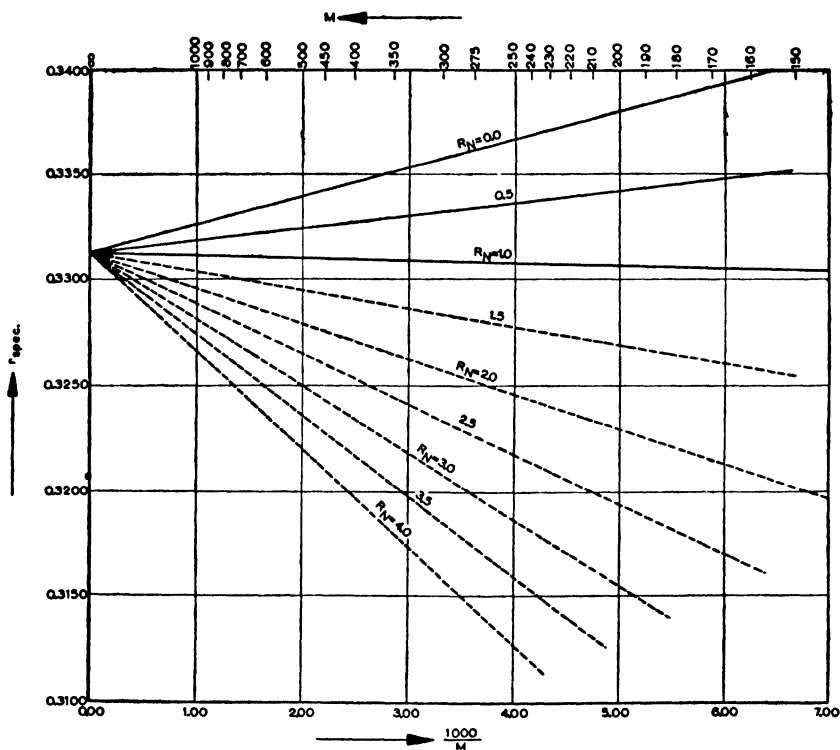


Fig 59

For *non-branched* saturated hydrocarbon mixtures the average number of rings per molecule can be read directly from one of these diagrams.

Chain branching causes a lowering of both the specific refraction and the specific parachor of saturated hydrocarbons, which corresponds, according to WEBER²⁵, with

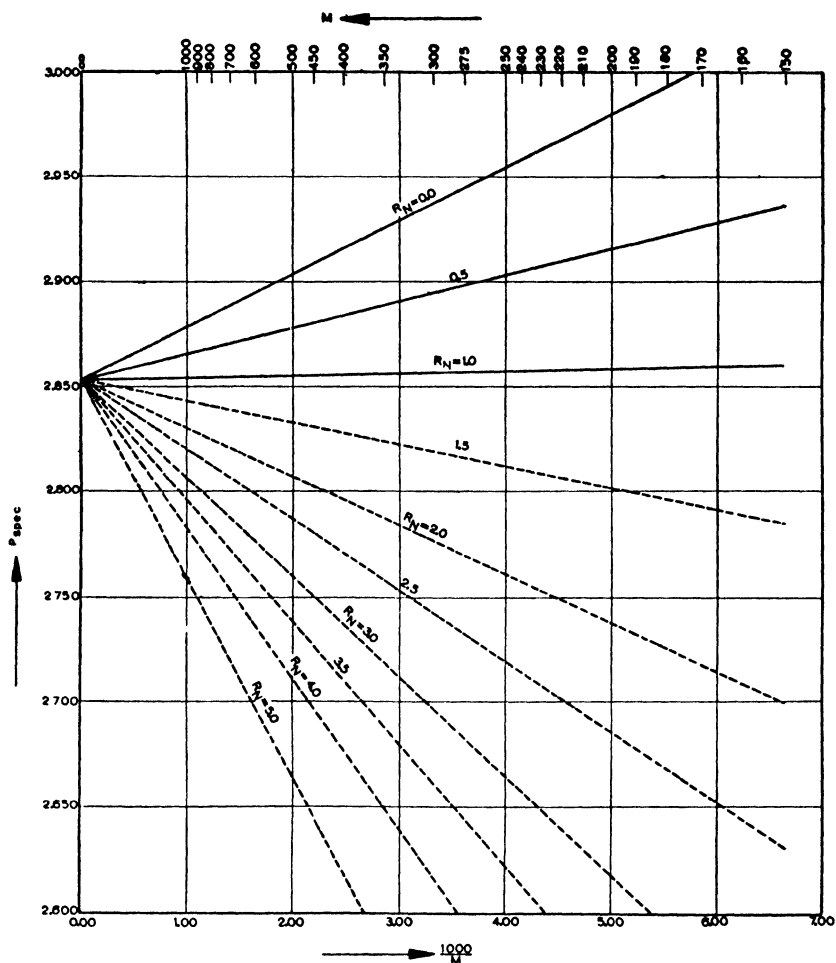


Fig 60

Figs 59 and 60 Diagrams representing specific refraction vs $\frac{I}{M}$ and specific parachor vs $\frac{I}{M}$, based on A P I data of *n*-alkanes, *n*-alkyl-cyclopentanes and *n*-alkyl-cyclohexanes at 20°C°.

approx. 0.05 rings per branching unit in the specific refraction vs. $\frac{I}{M}$ -diagram and with approx. 0.14 rings per branching unit in the specific parachor vs. $\frac{I}{M}$ -diagram. Approximately the degree of branching φ follows from the equation

$$\varphi = 10 (R_T^p - R_T^r) \quad \dots \dots \dots (65)$$

and R_T , the average number of rings per molecule, is given by

$$R_T = R_T' - \frac{1}{2}(R_T^p - R_T') \quad \dots \dots \dots (66)$$

in which R_T' and R_T^p are the apparent ring-numbers estimated from r_{spec} and $\frac{I}{M}$,

and from p_{spec} and $\frac{I}{M}$, respectively, in the diagrams of Figs. 59 and 60.

It should be pointed out that this method for ring analysis and branching analysis is based exclusively on reliable data of n , d , M and σ of pure individual hydrocarbons, and holds, within the limits of accuracy of the determination, for widely differing types of branched as well as non-branched saturated hydrocarbon mixtures. It is particularly recommended for the structural analysis of saturated polymers, where other statistical methods (n - d - M -method, v - n - d -method, etc.) fail because they have been developed for mineral oils, and are based on correlations of physical data of mineral oil fractions that always show approximately the same small degree of branching. 1-2 branchings per molecular weight = 100.

Examples are given in Tables III and IV.

(iv) DE BOOIJ²⁹ correlated the parachor values of branched and non-branched heptanes and octanes to form equations analogous to those based on molecular magneto-optical rotation and molecular refraction.

For *paraffinic hydrocarbons* the following equation can be derived:

$$\varphi = 0.402 (P_{n\text{-alkane}} - P) - 5.75 (r_{\text{mol}}(n\text{-alkane}) - r_{\text{mol}}) \quad \dots \dots (67)$$

for *hydrogenated mineral oil fractions*

$$\varphi = 0.186 (P_{n\text{-alkane}} - P) - 2.84 (r_{\text{mol}}(n\text{-alkane}) - r_{\text{mol}}) \quad \dots \dots (68)$$

in which $P_{n\text{-alkane}} = 2.852M + 25.22$,

$$r_{\text{mol}}(n\text{-alkane}) = 0.3309M + 1.424,$$

M = average molecular weight.

In the case of *aromatic fractions* an empirical correction for %C_A, the percentage of carbon in aromatic structure, can be applied

$$\varphi = 0.186 (P_{n\text{-alkane}} - P) - 2.84 (r_{\text{mol}}(n\text{-alkane}) - r_{\text{mol}}) - 0.00126 M \cdot \% C_A. \quad (69)$$

With this equation a simple approximate determination can be made of φ in natural mineral oil fractions of not too extreme aromatic character (%C_A < 30%). The above-mentioned correction was obtained by comparing the parachor values of a large number of aromatic mineral oil fractions with those of the corresponding hydrogenated fractions.

It can easily be shown that the formulas for the determination of φ can also be represented graphically by using the specific refraction r_{spec} ($= \frac{r_{\text{mol}}}{M}$) and the specific

parachor p ($= \frac{P}{M}$) and plotting the function

$$\frac{p - 2.852 + 0.00375\%C_A}{r_{\text{spec}} - 0.3309 - 0.0002\%C_A} \quad \dots \dots \dots (70)$$

versus the total number of rings per molecule R_T (cf. Fig. 61).

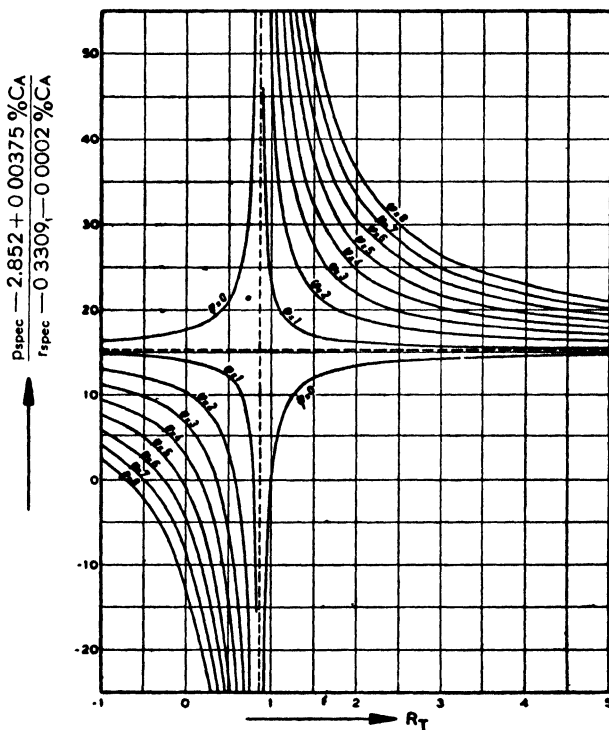


Fig 61 Determination of the degree of branching ϕ in mineral oil fractions from specific refraction, specific parachor and ring-number R_T

e. Applications

(i) Mineral oil fractions

In Table III are collected data concerning a number of fractions of a Rumanian crude²⁷, before and after complete hydrogenation. It can be concluded that the results of the different methods for branching analysis show qualitatively the same picture. The number of branchings is relatively small and does not differ very much for the different fractions. This holds for a large number of crudes of different origin²⁸. Therefore it is possible to determine the surface tension σ of natural and hydrogenated mineral oil fractions from n , d and ν (cf. Section II, 3, p. 45).

In the case of aromatic fractions it is generally impossible to measure the Verdet constant owing to the considerable absorption of visible light by even slightly coloured liquids. Therefore in non-hydrogenated fractions only parachor measurements can serve to determine the degree of branching. As follows from Table III, there is a reasonable agreement between the values of ϕ for hydrogenated and non-hydrogenated fractions.

(ii) *Saturated liquid polymers*

Table IV contains data on hydrogenated polymers of propylene, isobutene and cyclohexene obtained by polymerization under various conditions³⁸. The Direct Method (ultimate analysis and molecular weight) shows that the polymers of propylene and isobutene are paraffinic; for the estimation of ϕ the appropriate formulas were used. In the case of the highly cyclic saturated cyclohexene-polymers the formulas for hydrogenated mineral oil fractions were applied. In the table are also given values of ϕ and R_T determined with the ring analysis diagrams of Figs. 59 and 60 (p. 64-65).

For these polymers also there is a reasonable agreement between the values of NCH_3 , the number of methyl groups per molecule, and ϕ , the number of alkyl groups minus 1.

If in the cyclohexene polymers no methyl groups are present then ϕ should approach the value -1 . In Table IV the ϕ values amount to 0.2 and 1.3 respectively, the NCH_3 values are 0.3 and -0.2 .

(iii) *Isomerization phenomena*

Although the methods discussed for branching analysis have only a semi-quantitative character, they may be especially useful in comparative experiments, *e.g.* for selecting optimal reaction conditions for isomerization processes. As an example data are given in Table V on isomerization products of paraffin wax, processed on a semi-commercial scale with a Pt-Al₂O₃-Cl platforming catalyst at 52 ata and different temperatures in the vapor phase (in the presence of hydrogen)³⁵. The main reactions in this process are branching, cracking and to a minor extent also cyclization.

The reaction products were first hydrogenated to saturate small amounts of olefins, and then split up into fractions by distillation *in vacuo*.

Table V shows the influence of the reaction temperature especially in connection with the course of isomerization reactions. Higher reaction temperatures favour the process of branching.

5. DETERMINATION OF MONO- AND DI-AROMATICS IN MINERAL OILS

a. Introduction

The application of several methods for structural analysis of mineral oils is, in general, limited to those fractions in which no structural elements are present in larger quantities than normally occur in mineral oil fractions. In highly aromatic concentrates, for instance, the normal analytical methods ($n-d-M$; $v-n-d$) may give inaccurate results, because different types of aromatics may influence the physical constants of the oil differently.

The development of newer techniques (chromatography, thermodiffusion) for the separation of the different groups of hydrocarbons from mineral oil fractions allows a better characterization of such "type-concentrates" with the aid of physical constants. Combination of physical methods of separation with the statistical analysis of the products obtained, may lead to a more detailed and more complete knowledge of the composition of oils.

By a simple percolation through silicagel a sharp separation into non-aromatic and aromatic compounds is achieved. By the same percolation approximate separations into mono-, di- and tri-aromatics have been obtained^{39,40}. The result is a semi-quantitative

TABLE V
BRANCHING ANALYSIS OF HYDROGENATED PLATFORMING PRODUCTS OBTAINED BY HYDROISOMERIZATION OF PARAFFIN WAX

Product	Revol of vacuum distillation		Physical constants				Specific refract. n_D^{20}	Specific paraffin p^m	Apparent ring-number estimated from		$\varphi = 11 \times \Delta \text{ring}$
	fraction	weight %	n_D^{20}	d_4^{20}	M	σ^m dyn/cm			r^m and M D (Fig 57)	p^m and M (Fig 58)	
Starting material paraffin wax	1	5.6	1.4269	0.7642	315	25.3	0.3359	2.935	0.12	0.1	0.1
	2	15.7	1.4273	0.7645	325	25.4	0.3360	2.936	0.13	0.14	0.1
	3	17.7	1.4288	0.7675	340	25.8	0.3358	2.937	0.13	0.14	0.1
	4	20.6	1.4306	0.7718	362	26.1	0.3351	2.929	0.14	0.15	0.1
	5	16.9	1.4328	0.7750	396	26.5	0.3352	2.928	0.16	0.17	0.1
	6	23.3	1.4364	0.7826	467	27.0	0.3343	2.913	0.21	0.20	-0.1
Starting material paraffin wax, platformed at 410°C, 52 ata, contact time 10 sec	1	15.4	1.4241	0.7599	287	24.8	0.3359	2.937	0.21	0.23	0.2
	2	19.0	1.4283	0.7666	347	25.5	0.3358	2.931	0.09	0.18	1.0
	3	16.8	1.4299	0.7698	355	25.6	0.3355	2.922	0.15	0.30	1.7
	4	19.3	1.4319	0.7734	365	26.3	0.3353	2.928	0.16	0.20	0.4
	5	29.5	1.4354	0.7807	459	26.8	0.3345	2.914	0.21	0.30	1.0
Starting material paraffin wax, platformed at 420°C, 52 ata, contact time 10 sec	1	12.7	1.4221	0.7562	271	24.0	0.3361	2.927	0.23	0.39	1.8
	2	15.4	1.4280	0.7663	341	25.4	0.3357	2.930	0.13	0.21	0.9
	3	16.7	1.4294	0.7688	349	25.6	0.3356	2.926	0.14	0.25	1.2
	4	19.7	1.4310	0.7722	376	25.9	0.3352	2.921	0.17	0.28	1.2
	5	18.0	1.4329	0.7758	392	26.2	0.3349	2.916	0.20	0.34	1.5
	6	17.5	1.4363	0.7828	460	26.5	0.3342	2.898	0.29	0.60	3.4
Starting material paraffin wax, platformed at 435°C, 52 ata, contact time 10 sec	1	8.8	1.4119	0.7376	193	21.8	0.3373	2.929	0.28	0.50	2.4
	2	12.6	1.4258	0.7641	302	24.5	0.3352	2.912	0.32	0.52	2.2
	3	16.9	1.4286	0.7685	314	24.9	0.3352	2.907	0.30	0.56	2.9
	4	24.7	1.4295	0.7702	336	25.2	0.3351	2.909	0.28	0.51	2.5
	5	17.3	1.4319	0.7757	373	25.6	0.3343	2.900	0.39	0.61	2.4
	6	19.7	1.4356	0.7819	406	25.9	0.3341	2.885	0.40	0.85	5.0

titative determination of the weight percentages of 1 ring and 2 ring aromatics in distillation fractions of crude oils. A further separation of the molecules according to their ring-number is possible by thermal diffusion of the fractions obtained by percolation⁴¹.

Along these lines a more or less complete separation is possible of paraffins, naphthenes with 1 ring, 2 rings, etc., benzene derivatives, mono-aromatics with 1 ring, 2 rings, etc., as shown in Table VI. The physical data for each fraction enable the corresponding amounts of structural compounds present to be calculated, as will be discussed below.

TABLE VI

TYPE ANALYSIS OF A BORNEO CRUDE OIL FRACTION (MOL WT 267) BY CHROMATOGRAPHIC SEPARATION AND THERMODIFFUSION⁴⁰

Type	Non-aromatic	Mono-aromatic	Di-aromatic	Tri-aromatic	Total
Non-cyclic	2	—	—	—	2
Monocyclic	10	1	—	—	11
Dicyclic	7	2	6	—	15
Tricyclic	12	9	18	7	46
Tetracyclic	7	8	7	—	22
Pentacyclic	1	1	2	—	4
Total	39	21	33	7	100

GEELEN⁸ investigated the influence of mono-aromatic and di-aromatic rings on several physical constants of mineral oils.

He considered as *mono-aromatics* molecules with one or more non-condensed benzene nuclei, e.g. alkyl-benzenes, tetralin-derivatives, diphenyl. *Di-aromatics* he defined as molecules with one or more naphthalene nuclei not condensed with each other or with a benzene nucleus.

GEELEN especially examined several specific functions (specific refraction r , specific sound velocity u , specific volume $1/d$). The use of these functions together with the hydrogen content (%H) enables the structural composition of aromatic hydrocarbons to be determined. From data on homologous series of pure mono- and di-aromatic hydrocarbons⁴² he deduced the following equations for r , d and %H (20°C).

$$r = 0.3310 + \frac{1}{M} (1.419 - 1.654 R_N + 0.76 R_A^I - 0.38 R_A^{II}) \quad . \quad (71)$$

$$\frac{1}{d} = 1.1747 + \frac{1}{M} (27.56 - 16.32 R_N + 28.9 R_A^I + 26.9 R_A^{II}) \quad . \quad (72)$$

$$\%H = 14.37 + \frac{1}{M} (172.6 - 172.6 R_N + 690 R_A^I + 604 R_A^{II}) \quad . \quad (73)$$

where M = molecular weight,

R_N = number of naphthenic rings per molecule,

R_A^I = number of mono-aromatic rings per molecule, e.g. $R_A^I = 1$ for benzene and 2 for diphenyl,

R_A^{II} = number of aromatic rings per molecule present in di-aromatic hydrocarbons, e.g. $R_A^{II} = 2$ for alkylnaphthalenes.

With these equations R_N , R_A^I and R_A^{II} can be calculated, when n , d , M and %H are given:

$$R_N = 1.95 + M (0.138 \Delta r + 0.0876 \Delta \frac{1}{d} - 0.00382 \Delta H) \quad . . . (74)$$

$$R_A^I = -1.60 + M (0.632 \Delta r - 0.129 \Delta \frac{1}{d} + 0.00616 \Delta H) \quad . . . (75)$$

$$R_A^{II} = 1.56 - M (0.762 \Delta r - 0.123 \Delta \frac{1}{d} + 0.00429 \Delta H) \quad . . . (76)$$

$$\text{where } \Delta r = 0.3310 - r,$$

$$\Delta \frac{1}{d} = 1.1747 - \frac{1}{d},$$

$$\Delta H = 14.37 - \%H.$$

These formulas, which have been deduced for individual aromatic compounds, are also suitable for the characterization of aromatic mineral oil fractions, aromatic concentrates, etc., provided that only small amounts of tri-aromatics and higher aromatic compounds are present. For sulphur-containing oils the value of R_N should be corrected

$$\Delta R_N = -0.001M \cdot \%S \quad (77)$$

No corrections are necessary for R_A^I and R_A^{II} .

b. Applications

(i) Analysis of aromatic oil fractions

According to GEELEN⁸ usually approximately equal amounts of mono- and di-aromatic compounds are present in natural mineral oil fractions

$$2 R_A^I \approx R_A^{II} \quad (78)$$

Thus the contributions of these compounds to the specific refraction r of the fractions cancel out [cf. eqn. (71)]; this is the reason that diagrams for the ring analysis of saturated mineral oil fractions based on specific refraction and molecular weight are also valid for the estimation of naphthenic rings in aromatic fractions (cf p. 24).

For the analysis of highly aromatic oils (chromatographic concentrates, products of solvent extraction, distillation fractions of oil residues) where the ordinary analytical methods ($n-d-M$, $r-n-d$, etc.) fail, the formulas of GEELEN are of great value because they allow a reasonable type-analysis of these products. When tri-aromatics are present the equations do not hold exactly, however, in these cases also, the total number of aromatic rings is given in a good approximation by

$$R_A = R_A^I + R_A^{II} \quad (79)$$

As an illustration, some data on the analysis of type concentrates obtained by chromatographic separation of a "Kerex" kerosine extract, are given in Table VII.

It can be seen that the analytical results of both the methods mentioned in Table VII agree reasonably well for saturated fractions, which was to be expected; for the

TABLE VII

ANALYSIS OF SATURATED, MONO-AROMATIC AND DI-AROMATIC FRACTIONS OBTAINED BY CHROMATOGRAPHIC SEPARATION OF A "KEREX"

	n_D^{20}	d_4^{20}	r_D^0	Mol wt	%H	%S	R_A^I	R_A^{II}	R_N	R_T	R_A	R_T
(according to GEELLEN)												
	(n, d, M)											
Saturated* fraction	1 4546	0 8213	0 3301	206	14 04	—	0 08	0 04	0 94	1 06	0 09	1 07
Mono-aromatics	1 5071	0 8982	0 3314	181	10 95	0 03	0 73	0 33	0 55	1 61	0 77	1 64
Di-aromatics	1 5958	0 9940	0 3423	167	7 83	0 11	0 30	1 78	0 01	2 07	1 91	1 55

* After elimination of oxygen compounds by percolation through Al_2O_3 .

mono- and di-aromatic concentrates the results of the $n-d-M$ -method show deviations in particular for R_T .

(v) Hydrogenation of aromatic mineral oil fractions

The analytical hydrogenation is very important for the study of natural mineral oils.

VAN NES AND VAN WESTEN⁴² described the physical constants and elementary composition of intermediates in the complete hydrogenation of a large number of mineral oil fractions. These data were used by GEELLEN⁸ to study the behaviour of mono- and di-aromatics during catalytic hydrogenation.

In Fig 62 the course of the selective hydrogenation experiments is represented schematically in terms of the aromatic composition of the partially hydrogenated intermediates. Generally there is a pronounced selectivity in connection with the saturation of di- and mono-aromatic compounds: saturation of the latter does not occur to a significant degree before larger amounts of di-aromatics have been transformed by partial hydrogenation into the corresponding mono-aromatics.

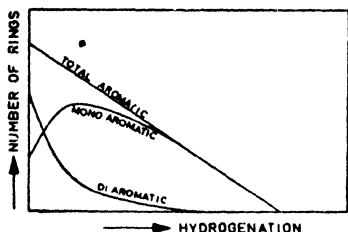


Fig 62 Schematic representation of the analytical hydrogenation of a mineral oil fraction

6 SULPHUR COMPOUNDS IN MINERAL OILS

Mineral oils contain, besides hydrocarbons, certain amounts of foreign elements, of which sulphur, nitrogen and oxygen are the most important ones. Whereas, in general, nitrogen and oxygen are present in very small quantities only, sulphur compounds may be present in larger quantities. Especially in recent years has the production of crudes with high sulphur contents (5% S and more) been increased and the significance of desulphurization processes in the petroleum technology is still gaining in importance.

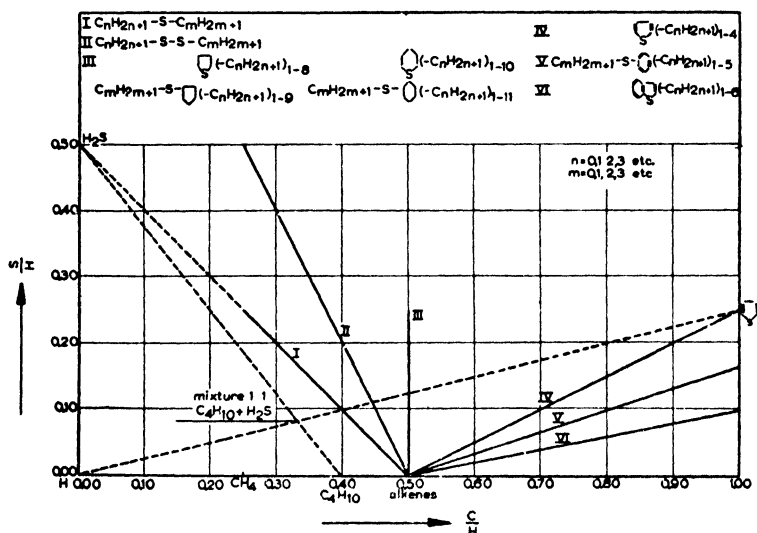
The weight% of sulphur does not give an impression of the amount of sulphur compounds, that may be present. For example, with a sulphur content of 5% and an av. mol wt. of 320 the mineral oil contains $5 \cdot \frac{320}{32} = 50\%$ sulphur compounds on an average, if it is assumed that in molecules that contain sulphur only one atom of sulphur is present.

It is of great value to know which types of sulphur compounds are present in a crude oil, because the various types may behave quite differently in respect to the properties of the crude and of the products that can be obtained from it by physical or chemical methods. According to recent investigations, in lower molecular oil fractions sulphur appears mainly in the form of alkane-thiols, cyclohexane-thiols and thioalkanes, in higher molecular fractions cyclic sulphur compounds of the thiophen type predominate.

In the case of statistical methods of analysis of sulphur-containing crude oil fractions one generally confines oneself to small corrections on the applied graphs or equations. These corrections, which have been estimated empirically, are valid only for small percentages of sulphur and do not take into account the nature of the sulphur compounds present in the fractions.

In recent years the intensive study of sulphur compounds, sponsored by several oil companies⁴³, has led to a collection of physical data on many of these compounds, which enables us to predict several properties of sulphur compounds not yet investigated^{44,45}.

VAN ZIJLL LANGHOUT developed graphs for compounds consisting of C, H and S, analogous to the graphical representation of C-H-O compounds of VAN KREVELEN⁴⁶. These graphs, of which Fig 63 is an example, are based on the ultimate analysis, and can be applied to identify pure sulphur compounds and to analyse simple mixtures



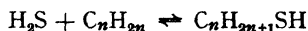
thereof; they are also useful to represent distinct chemical transformations in which sulphur compounds are involved.

The following examples may serve to illustrate the use of the graph:

- (a) from H_2S (C:H = 0, S:H = 0.5) and C_4H_{10} (C:H = 0.4, S:H = 0) thiophen (C:H = 1.0, S:H = 0.25) can be obtained as the result of a dehydrogenation.



- (b) by the addition of H_2S (C:H = 0, S:H = 0.5) to alkenes (C:H = 0.5, S:H = 0) thiols are formed:



which are represented in the diagram by points on line I.

In Fig. 64 the *specific refraction* is plotted *versus* the weight percentage of sulphur. On the lines that represent different groups of sulphur compounds values of n_D^{20} are indicated, thus making an easy orientation possible. Similar graphs based on other physical constants can be constructed, permitting the prediction, by interpolation or extrapolation, of physical constants of still unknown members of homologous series of compounds. The accuracy and usefulness of these graphs will increase as more reliable physical constants become known.

These diagrams may also be useful for the characterization of sulphur compounds in crude oil fractions, provided that separation of the fractions into two parts, i.e. the hydrocarbons and the sulphur compounds, is possible. However, the sulphur compounds in mineral oils, especially those containing high percentages of carbon and hydrogen, resemble the corresponding hydrocarbons very closely, both physically and chemically. This greatly hampers their complete separation, although modern analytical techniques⁴⁷ have made considerable progress in this direction

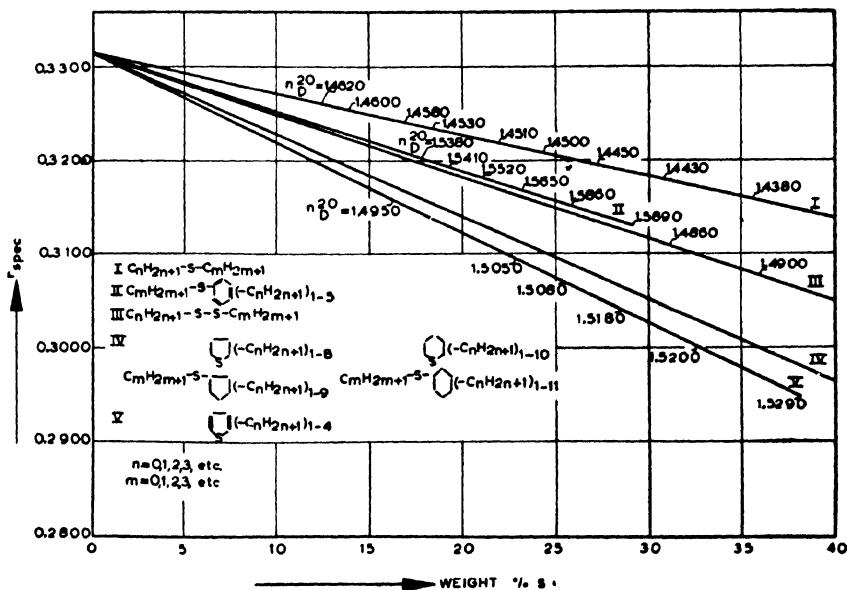


Fig 64 Graphical representation of sulphur compounds

III APPLICATION OF GRAPHICAL STATISTICAL METHODS IN THE DETERMINATION OF THE COMPOSITION OF GLASSES AND SILICONES

I. INTRODUCTION

In the last few years the graphical statistical methods have been successfully applied not only to petroleum, fatty oils and coal, but also to glass and silicones. Though the recently developed methods for glass and silicones are still in their initial stages, some remarkable results have already been obtained.

In order to develop methods that can be applied to glass, it is necessary to study homogeneous glasses with a known composition. To obtain a known composition the glass mass has to be dealt with in a *quantitative* way during the homogenizing process and much of the work to prepare the glass is done with this purpose in mind.

The method worked out by VAN LEEUWEN at the Department of Chemical Engineering of the Technological University of Delft, can be used to prepare homogeneous glasses with known composition.

Certain amounts of chemically pure oxides or in many cases the corresponding carbonates are weighed and intimately mixed in a platinum crucible. The mixture is *slowly* heated to 700°C* in the course of one day. In this period a reaction between the solid substances takes place and CO₂ is expelled. After this a porous cake has been formed, which stands free from the crucible wall and therefore contains the starting material quantitatively. Then it is possible to increase the temperature *quickly* to 1300°C*, in order to melt the glass without drops of glass being formed on the wall. This temperature, which is maintained for some hours, may neither be too high because of possible losses by evaporation, nor too low in order to ensure sufficient homogenization of the glass.

The crucible with the glass is quenched in cold water, a rubber stopper is put on the crucible and the glass is loosened from the inner wall by softly knocking with a small hammer on the outer wall. In this way the glass can be taken out of the crucible quantitatively.

The homogeneity of the glass can be checked by determining the density of some of the separate pieces of glass, which on inspection with a magnifying glass should not show small cracks. If the values of the density differ 0.0004 or less, the glass is considered to be homogeneous. In most cases it is necessary to repeat the melting of the glass once or twice after grinding.

After the preparation of the glass the refractive index and the density are measured.

a Determination of the density of glass

For the determination of the density a small piece of glass is brought into a mixture of dibromoethane Br-CH₂-CH₂-Br and bromoform CHBr₃** The density of the former liquid is lower and that of the latter is higher than the density of the glass. At a certain

* This temperature is determined by the composition of the glass being prepared, and is only given as an example

** The choice of the two liquids depends on the nature of the glass and on its density

temperature the proportion of these liquids is adjusted in such a way that the piece of glass neither sinks nor floats. Then the density of the liquid mixture is determined at the same temperature. This density is equal to the density of the glass.

Care must be taken that no moisture is present in the dibromoethane and in the bromoform. This is especially important for glasses of which the surfaces are easily attacked by water. This presence of moisture may give rise to inaccurate results in the subsequent determination of the refractive index. For the same reason it is advisable to keep the pieces of glass stored in a desiccator.

b. Determination of the refractive index of glass

The refractive index is measured according to a method developed by FAICK AND FONOROFF⁴⁸. The principle of the method can be described as follows.

A parallel, monochromatic beam of light is passed through a tube (Fig 65) containing two adjustable knife-edge diaphragms A and B, each of which removes about one half of the light.

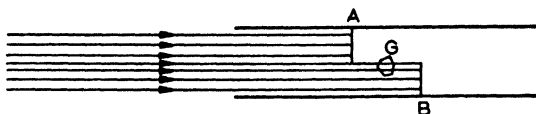


Fig 65 Principle of the method of FAICK AND FONOROFF for measuring the refractive index of glass

A cylindrical glass tube containing the immersion liquid and the piece of glass of which the refractive index has to be determined, is placed between the two diaphragms. The immersion liquid consists of petroleum ether (or dioxane) and α -chloronaphthalene. The temperature of the immersion liquid is controlled by circulating water around the tube.

If the refractive index of the glass is equal to that of the liquid, only dim light is allowed to pass along the two diaphragms.

If the refractive index of the glass is different from that of the liquid, light can be seen through a telescope placed to the right of B. This can be made clear as follows.

In Fig 66 two cases are considered, namely I and II.

I. The refractive index n_1 of the immersion liquid is larger than the refractive

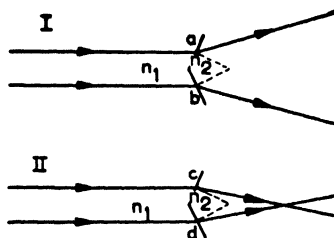


Fig 66 How the light is dispersed if the refractive indices of the glass and the immersion liquid are different

index n_2 of the piece of glass ($n_1 > n_2$). Light falling on surface a can be seen through the telescope, light falling on surface b cannot be seen.

II. $n_1 < n_2$. Light falling on surface d can be seen through the telescope, light falling on surface c cannot be seen.

It can be concluded that if $n_1 \neq n_2$ light can be seen, whereas if $n_1 = n_2$ no light can be seen. The immersion liquid is adjusted so that this last condition is fulfilled. The refractive index of the immersion liquid is then determined at the same temperature by means of an Abbe refractometer. The value found is equal to the refractive index of the glass.

2. THE THERMAL BEHAVIOUR OF POTASSIUM AND SODIUM SILICATES

It is a well-known fact that the physical constants of glasses depend on the temperature to which the glass has been exposed⁴⁹. This treatment can be carried out by keeping a small piece of the glass for a sufficient time at a certain constant temperature to obtain a constant value of the physical constants. At 600°C a few minutes may suffice, at 350°C hundreds of hours may be necessary. After this period the pieces of glass are either quenched in benzene at 6°C (if the glass has been exposed to a relatively low temperature) or in toluene at 100°C (if the glass has been treated at a relatively high temperature).

A few types of glasses have been investigated in this way. They were composed either of Na_2O and SiO_2 or of K_2O and SiO_2 . Their composition is given in Table VIII.

TABLE VIII
COMPOSITION OF GLASSES J_1 , F, K_1 AND K_2

Composition of glass	Weight percentage of			Molecular percentage of		
	SiO_2	Na_2O	K_2O	SiO_2	Na_2O	K_2O
J_1	71.38	28.62		72.03	27.97	
F	77.38	22.62		77.95	22.05	
K_1	72.31		27.69	80.37		19.63
K_2	78.58		21.42	85.18		14.82

The density of these glasses was determined after thermal treatment at different temperatures. The values of these densities for the different glasses are reported in Tables IX, X, XI and XII. The density values of the glasses have also been plotted as a function of the temperature of treatment in Figs. 67, 68, 69 and 70.

It appears that relatively low temperatures of treatment do not lead to a change in the density measured at 20°C. For the types of glass tested, from a certain temperature between 400°C and 450°C onwards there is a sharp fall in the density value until a temperature between 500°C and 650°C is reached. Beyond this temperature no further change takes place in the density value.

In Tables IX to XI the values of the refractive index, n_D^{20} , for a number of temperatures of treatment are also given. The specific refraction defined according to

LORENTZ-LORENZ as $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, was calculated and the values obtained are also included in the tables. It is very remarkable that for a glass of definite composition the value

TABLE IX
THERMAL TREATMENT OF GLASS J₁

Temperature °C	d_{40}^{20}	n_D^{20}	$r_{spec} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$
365	2 4557	1 5011	0 1200
392	2 4556		
414	2 4555	1 4997	0 1200
430	2 4546		
458	2 4497		
471	2 4476		
473	2 4473		
493	2 4453		
532	2 4443		
576	2 4442		

TABLE X
THERMAL TREATMENT OF GLASS F

Temperature °C	d_{40}^{20}	n_D^{20}	$r_{spec} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$
360	2 4079	1 4940	0 1210
387	2 4079		
412	2 4076	1 4942	0 1210
438	2 4070		
483	2 4024	1 4921	0 1211
539	2 3964		
586	2 3948		
602	2 3947		

TABLE XI
THERMAL TREATMENT OF GLASS K₁

Temperature °C	d_{40}^{20}	n_D^{20}	$r_{spec} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$
366	2 3887	1 4931	0 1217
398	2 3885		
452	2 3885	1 4931	0 1217
495	2 3827		
513	2 3809		
547	2 3763		
593	2 3706		
623	2 3681		
663	2 3663		

of the *specific refraction* appears to be *independent* of the *temperature of treatment*.

It is furthermore interesting to note that in a specific refraction-composition diagram (Fig. 71) for the potassium- and sodium-silicate glasses studied, the points are

TABLE XII
THERMAL TREATMENT OF GLASS K₃

Temperature °C	d_4^{20}	n_D^{20}	$r_{spec.} = \frac{n^2 - 1}{n^2 + 1} \frac{1}{d}$
408	2 3500		
470	2 3496	1 4863	0 1223
487	2 3487		
500	2 3473	1 4860	0 1223
513	2 3452	1 4855	0 1223
541	2 3411	1 4852	0 1224
558	2 3403	1 4849	0 1224
575	2 3397		
588	2 3398		
615	2 3395		

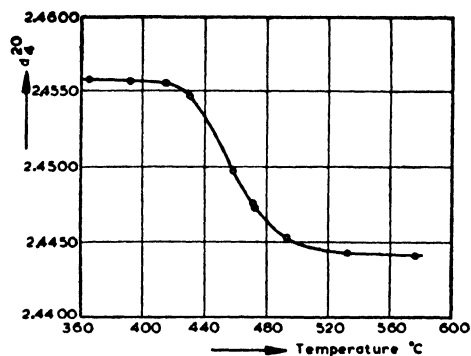


Fig. 67. The density of glass J₁ as a function of the temperature of treatment

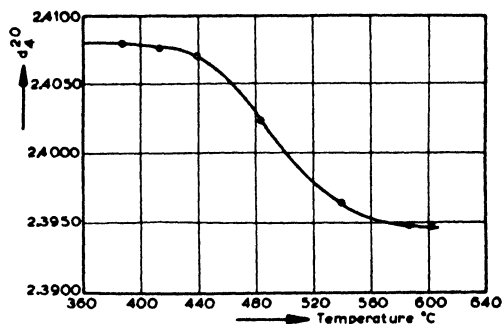


Fig. 68 The density of glass F as a function of the temperature of treatment

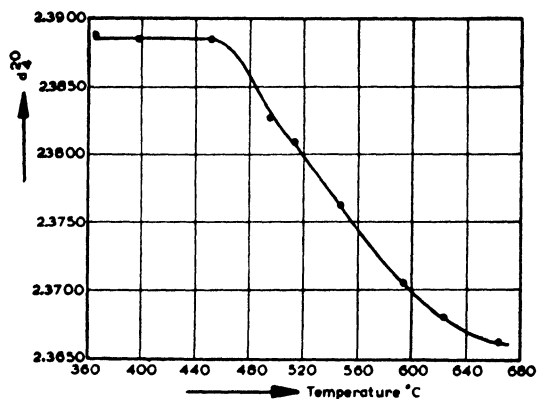


Fig. 69 The density of glass K₁ as a function of the temperature of treatment

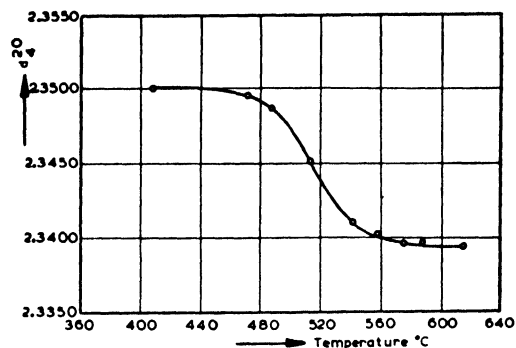


Fig. 70 The density of glass K₂ as a function of the temperature of treatment

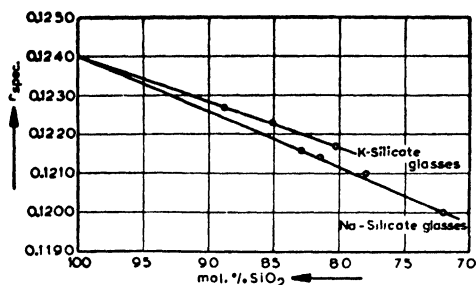


Fig. 71 Relation between composition and specific refraction of sodium and potassium silicate glasses (own preparations)

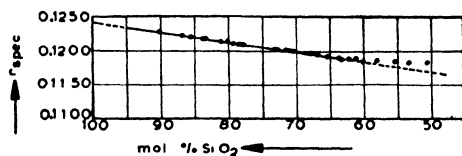


Fig. 72. Relation between composition and specific refraction of a large number of sodium silicates (prepared by different authors)

on two straight lines, which intersect at the specific refraction value of molten quartz. A reliable value of n of glassy quartz is given by SOSMAN⁶⁰.

The results obtained are in agreement with reliable values, which have been reported in the literature for $\text{Na}_2\text{O}-\text{SiO}_2$ glasses. These values are represented in Fig. 72.

The straight lines permit the determination of the composition of potassium and sodium glasses by determining their density and refractive index and calculating their specific refraction.

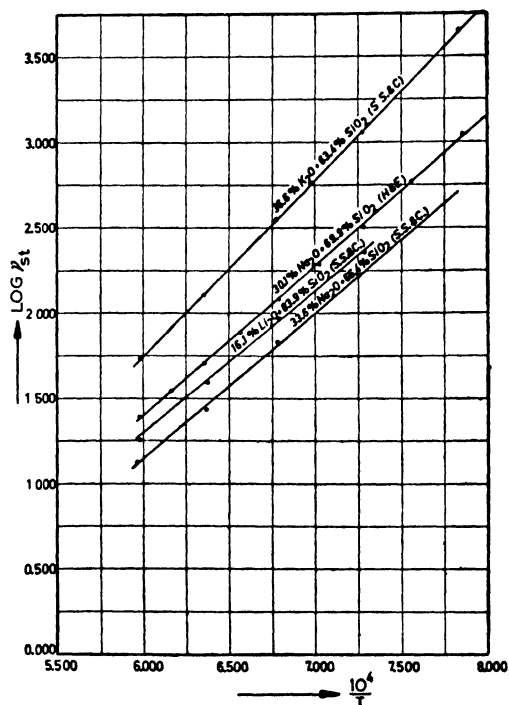


Fig. 73. $\text{Log } v - \frac{1}{T}$ graph for some $\text{K}_2\text{O}-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{SiO}_2$, and $\text{Na}_2\text{O}-\text{SiO}_2$ glasses

3. TEMPERATURE DEPENDENCE OF THE KINEMATIC VISCOSITY OF GLASSES

On studying the temperature dependence of the kinematic viscosity of glasses it appears that the formula

$$\log \nu = \frac{A}{T^x} + B \dots \dots \dots (45)$$

discussed in Section II, 3, not only holds for liquid hydrocarbons and their mixtures (natural or synthetic), water, molten metals, sugar and sulfuric acid solutions in water and for silicones, but also for molten glasses⁹² To investigate the validity of formula (45) in this field, data have been used that have recently been published by HEITKAMP AND ENDELL⁵¹, SHARTSIS, SPINNER AND CAPPS⁵² and LILLIE⁵³. For these glasses $\log \nu = f(\frac{1}{T^x})$ graphs were constructed⁴⁹, the value of x being calculated as described previously (Section II). Some of these graphs are given in Figs. 73, 74, 75 and 76.

It appears that the value of x varies from 1 to 3 for the different glasses. The accuracy with which x can be determined is a few units in the first decimal place, owing to the

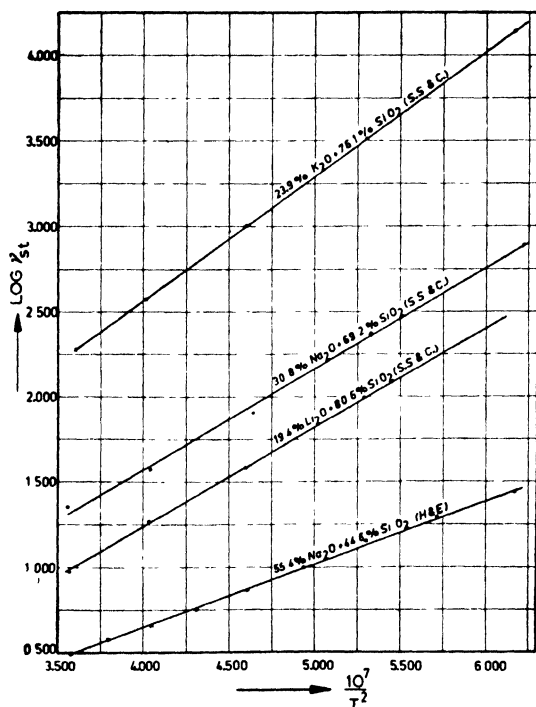


Fig 74 $\log \nu - \frac{1}{T^2}$ graph for some K_2O-SiO_2 , Li_2O-SiO_2 and Na_2O-SiO_2 glasses.

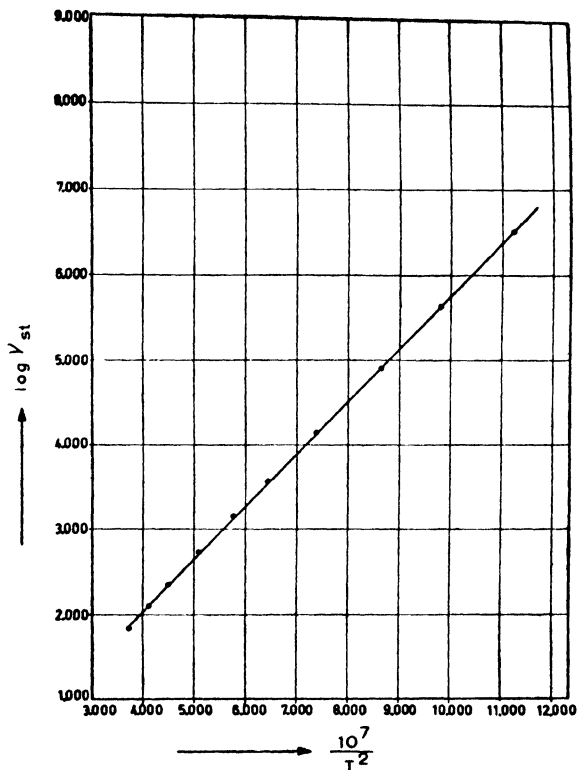


Fig 75 $\log \nu - \frac{1}{T^2}$ graph for a lead glass

fact that the viscosity of molten glasses cannot be determined with any great accuracy at the high temperatures in question.

The relationship between the A , B and x values of glasses and their composition is not yet clear, in contrast to the relationship between x and the composition of saturated mineral oil fractions. The lack of accuracy of x apparently hampers the establishment of this relationship for glasses. This can only be an incitement to determine the viscosity of glasses with greater precision than has been possible so far, thus enabling the x values in the case of the glasses to be calculated more precisely.

4. THE STRUCTURE OF SILICONES

Silicones are polymeric compounds in which molecules with $-\text{Si}-\text{O}-\text{Si}-\text{O}-$ bonds occur, organic groups being attached to the Si-atoms. Many silicones have found practical application, the particular application being dependent on the chemical structure. HUNTER, HYDE, WARRICK AND FLETCHER⁵⁴ found regularities in the case of some cyclic

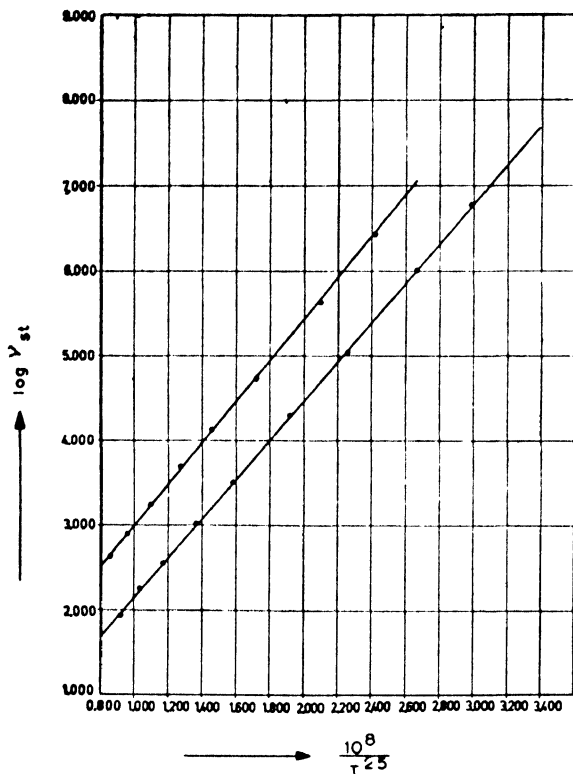


Fig. 76 $\log \nu - \frac{1}{\lambda}$ graph for a B_2O_3 glass (upper curve) and a $Na_2O-CaO-SiO_2$ glass (lower curve)

silicones, of which several physical constants have been measured. Of these, the refractive index, density, surface tension (all at 25°C) and the derived functions, specific refraction according to LORENTZ-LORENZ $\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \right)$ and specific parachor $\frac{\sigma^{1/4}}{d}$, are collected in Table XIII

It appears that for these cyclic polymers the values of the specific refraction and the specific parachor are almost constant, though the refractive index, the density and the surface tension vary notably. The specific refraction and the specific parachor are independent of the degree of polymerization.

Although this result is only the first step in establishing relationships between chemical structure and physical constants of silicones, it is very promising. New investigations with the aim of establishing new relationships have been started in the

TABLE XIII
PHYSICAL CONSTANTS OF CYCLIC SILICONES

	<i>Tetramer</i> [(CH ₃) ₂ SiO] ₄	<i>Pentamer</i> [(CH ₃) ₂ SiO] ₅	<i>Hexamer</i> [(CH ₃) ₂ SiO] ₆	<i>Heptamer</i> [(CH ₃) ₂ SiO] ₇
d_{4}^{25}	0.9497	0.9531	0.9613	0.9664
n_D^{25}	1.3935	1.3958	1.3996	1.4018
σ_D^{25}	17.37	17.42	17.61	18.30
$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$	0.2512	0.2516	0.2515	0.2514
$\frac{\sigma^{1/4}}{d}$	2.145	2.140	2.130	2.140

laboratories of the Department of Chemical Engineering of the Technological University at Delft⁹³

It must be borne in mind that, for glass of a certain composition, the specific refraction according to LORENZ-LORENZ is independent of the temperature of treatment. The results discussed above suggest that this phenomenon may also be connected with polymerization and depolymerization of the glass in question

5 TEMPERATURE DEPENDENCE OF THE KINEMATIC VISCOSITY OF SILICONES

This subject has been treated in Section II, but more details are given here

We have already discussed the temperature dependence of the kinematic viscosity of silicones with relatively large viscosity values (silicone lubricants). The silicones concerned are chain polymers and in Table XIV the values of their F.V.T.I. is given together with their ν_{20} and α values.

TABLE XIV
VISCOSITY PROPERTIES OF SILICONE LUBRICANTS

<i>Silicone fluid</i>	ν_{20} cS	F.V.T.I. = $\log \frac{\nu_{20}}{\nu_{15}}$	α
A	64.83	0.368	1.0
B	143.1	0.371	1.1
C	410.2	0.375	0.7
D	1393	0.378	0.9
E	6400	0.370	0.8

The F.V.T.I. values prove to be practically constant, viz. 0.37 to 0.38, which means that (since α is almost equal to 1) the temperature dependence for these silicone oils is practically the same for the whole viscosity range from 65 to 6400 cS.

This is not the case for lower viscosity values of the same series of silicones and for cyclic polymers. Viscosity values at 20°C, F.V.T.I. and α values of both these groups are given in Table XV

TABLE XV
VISCOSITY PROPERTIES OF SILICONES

Compound	Indicated in Fig 77 as	$\log \nu_{20}$	$\log \frac{\nu_{20}}{F V T I}$	z
<i>Cyclic polymers</i>				
$[(CH_3)_2SiO]_3$ cyclic trimer	D 3	0 018*	0 289*	1 7*
$[(CH_3)_2SiO]_4$ cyclic tetramer	D 4	0 405	0 347	1 5
$[(CH_3)_2SiO]_5$ cyclic pentamer	D 5	0 638	0 377	1 3
<i>Linear polymers</i>				
$(CH_3)_2Si-O-Si(CH_3)_2$ hexamethyldisiloxane	MM	—0 178	0 204	1 1
MS 200/ 1 cs commercial product	MS 200/1	0 038	0 230	1 1
MS 200/ 2 cs commercial product	MS 200/2	0 346	0 275	1 0
MS 200/ 3 cs commercial product	MS 200/3	0 542	0 297	0 9
MS 200/ 5 cs commercial product	MS 200/5	0 764	0 316	1 1
MS 200/10 cs commercial product	MS 200/10	0 893	0 323	1 1

* Extrapolated

It appears that for the silicones given in Table XV the F.V.T.I. is no longer a constant. In Fig. 77 the F V.T.I. is plotted against $\log \nu_{20}$.

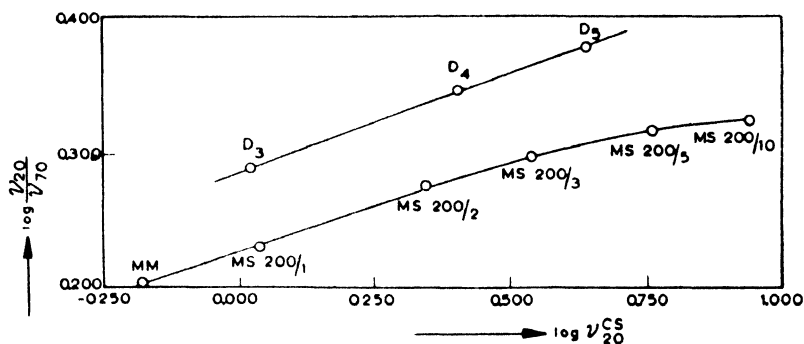


Fig 77 F V T I of silicones plotted against their $\log \nu_{20}$ values

It can be seen from the figure that the F V T I. of the chain polymers increases with increasing $\log \nu_{20}$ value until it reaches the limiting value 0.380 for higher $\log \nu_{20}$ values. The F.V.T.I. values of the cyclic polymers are invariably higher than the F.V.T.I. values of the chain polymers of the same viscosity value

IV ANALYSES IN THE FIELD OF FATTY OILS

1 INTRODUCTION

The fatty oil industry has not yet made the same progress in the chemical processing of its products as is the case in the petroleum industry. After the initial success attained in the development of the fat-hardening technique, this industry has remained stationary for many years. However, the chemical modification of fatty oils is of vital importance and the development of modern processes in the fatty oil industry will depend to a large extent on the basic knowledge of its raw materials and the fundamental study of possible chemical transformations.

The development of analytical methods is essential for the study of these processes. Chemical methods of analysis (BERTRAM's determination of saturated fatty acids⁵⁵, estimation of olefinic unsaturation by means of hydrogen value^{56,1} and ozone addition²) have found widespread use. In addition physical analytical techniques (spectrochemical methods, chromatographic separations, etc.) have proved to be valuable for fatty oil analysis. In particular molecular distillation⁵⁷ must be mentioned, which has turned out to be of great value for the investigation of polymerized oils and for the industrial concentration of vitamins from animal oils. The cascade fractionating molecular still⁵⁸ permits an efficient separation of higher molecular fatty acid derivatives (Fig. 78).

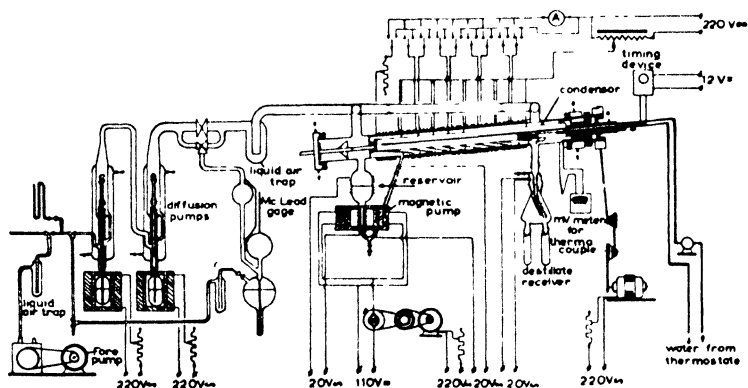


Fig. 78 Fractionating still with high separating power, according to BOOIJ

On comparing the chemical composition of hydrocarbons and fatty oils, a certain parallelism between these two groups of products is found. Actually the difference is only due to the presence of a relatively small amount of oxygen in the esters. Thus, in principle, the structural analysis of fatty acid derivatives can be carried out by removing the oxygen and transforming the products into saturated hydrocarbons of

corresponding structure. The proper methods of hydrocarbon analysis can then be applied to the hydrocarbon mixtures obtained. Several methods for deoxidation of fats have been recommended of which especially the direct high pressure hydrogenation and the Grignard method are mentioned here

For the direct graphical representation of non-branched, non-conjugated and non-polymerized fatty oils, a general diagram has recently been constructed by TELS *et al.*⁵⁹. In this diagram the specific refraction r_{spec}^{20} is plotted *vs.* the iodine value (*cf.* Fig 79). Triglyceride mixtures containing per average molecule the same number of carbon atoms are represented by a set of parallels, the average number of double bonds follows from a bundle of curves converging to the limiting point of the graph, which point indicates the values of r_{spec}^{20} and the iodine value ($r_{\text{spec}}^{20} = 0.3309$, iodine value = 0) when the molecular weight of the mixture approaches infinity.

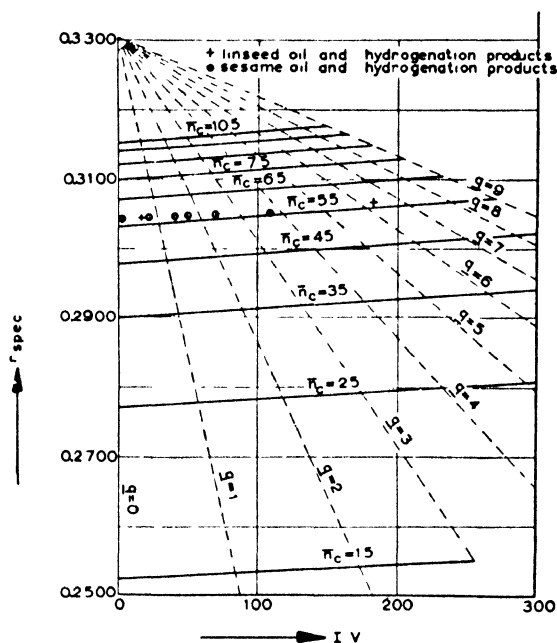


Fig 79 General diagram for the representation of non-branched, non conjugated and non-polymerized fatty oils $\bar{n}_c$ = number of carbon atoms per average triglyceride molecule, $\bar{q}$ = number of double bonds per average triglyceride molecule

It should be remarked, that in several respects fatty oils and related products usually have a far less complicated character than have mineral oil products. The number of fatty acids occurring in natural fats is limited and certain structural elements, which contribute considerably to the composition of mineral oils (cyclic compounds, branchings) hardly occur. On the other hand, phenomena such as *cis-trans* isomerism, al-

though certainly occurring in different cases in the field of mineral oils, play a more important part in fatty oil technology and have found valuable applications.

The chemical and physical properties of fatty oils depend largely on the nature of the fatty acids of which they are composed. This is reflected in the methods of classification of oils and fats, which methods are mainly based on two important structural characteristics

(a) *The degree of unsaturation*, indicated, for example, by the *iodine value*, which gives the amount of iodine taken up, following standard methods. VAN DER STEUR⁶⁰ showed that the addition of halogen is an equilibrium reaction. The equilibrium constant depends on the nature and position of the double bond, yet in the majority of oils the various methods of iodine addition usually employed give values that vary little amongst themselves. In the fat-hardening industry especially, the iodine value is an important means of following the course of the reaction. When conjugated double bonds are present the normal addition of halogen fails, in these cases determination of the *hydrogen value* by quantitative hydrogenation with platinum- or palladium-catalysts^{56,1}, or quantitative ozonization² are to be preferred

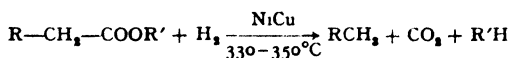
(b) *The mean average molecular weight*, for which the *saponification value* can be taken as a measure

Several physical constants (density, refractive index, melting point) are closely related to the structural properties of fatty oils and are therefore used, not only for their classification, but also for following their chemical transformations (hydrogenation, polymerization, isomerization⁶¹). A more detailed study of these correlations will be of great help in obtaining more fundamental knowledge of the fatty oils and in developing new technical applications. The experiences and results obtained in the field of mineral oils may be very useful in this respect

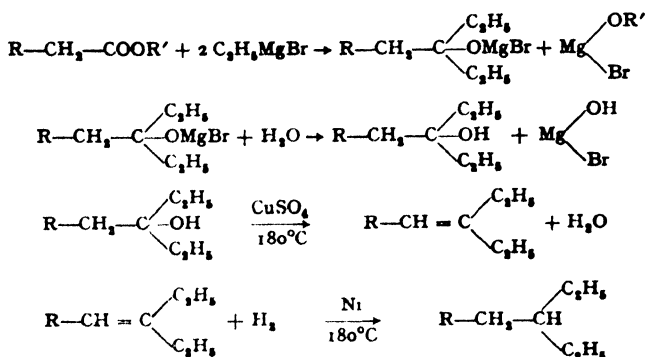
2 TRANSFORMATION OF FATTY ACID ESTERS INTO SATURATED HYDROCARBON MIXTURES

For the structural analysis of cyclic fatty acid derivatives (polymerized drying oils, copolymerization products of fatty oils with various hydrocarbons), in principle the same graphical methods can be developed as have been described for the investigation of hydrocarbon mixtures. However, the construction of useful graphical representations is hampered by the fact that reliable data on physical constants are restricted to the normal saturated fatty acids and their methyl and ethyl esters, the synthesis of pure unsaturated fatty acids is already extremely difficult, to say nothing of more complicated cyclic or branched compounds

Therefore in many cases the structural analysis of fatty oils has been carried out by expelling the oxygen and transforming the fatty acid esters into saturated hydrocarbons of corresponding structure. The proper graphical analytical methods can then be applied to these products. This deoxidation can be performed either by a high pressure hydrogenation⁶² (330–350°C, 200 atm., 30% of a nickel-copper on kieselguhr catalyst)



or by a Grignard operation⁶³ with alkyl magnesium halide, dehydration of the resulting tertiary alcohols and saturation of the olefinic double bonds, e.g.



The direct hydrogenation to deoxidize fatty acid esters results in hydrocarbons with one carbon atom less than the number present in the hydrocarbon chain of the original ester. The reaction can be carried out quantitatively, but it is a relatively drastic chemical operation. In the Grignard method the hydrocarbon chain of the molecule is lengthened, the reactions are executed at relatively low temperatures; the overall yield amounts to 70-90% of the theory.

These procedures are especially useful for the investigation of polymerization phenomena of drying oils. The formation of rings during the thermal polymerization of linseed oil and tung oil, evidence for KAPPELMEIER's theory⁴⁵ of the diene type condensation reaction of drying oils at elevated temperatures, was confirmed by means of these methods^{43,44}. Fig. 80 shows that thermal polymerization of linseed oil and

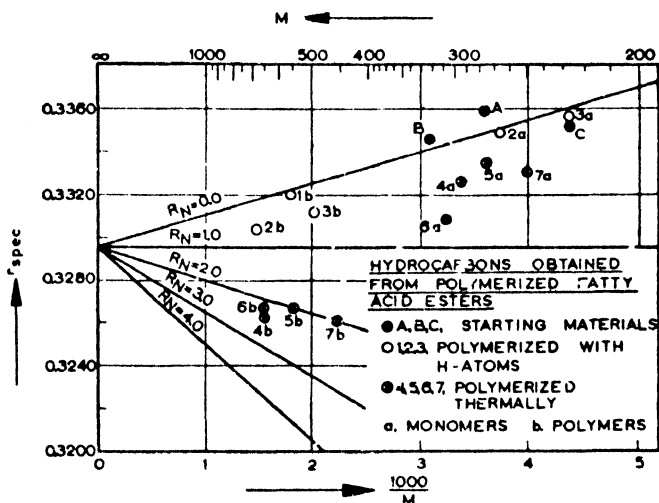


Fig. 80 Ring analysis of hydrocarbons obtained from polymerized fatty acid esters.

tung oil fatty acid esters leads chiefly to formation of dimers, containing approximately two rings per molecule; some cyclization of the esters also occurs. A possible reaction scheme can be represented as follows

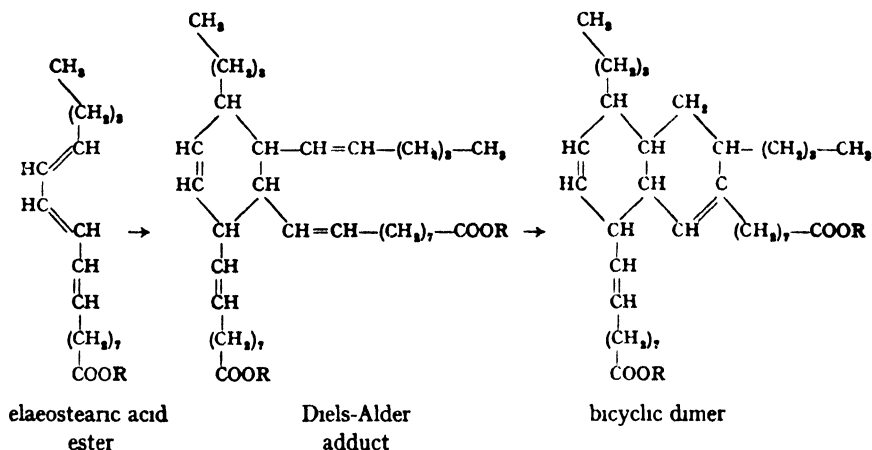


TABLE XVI

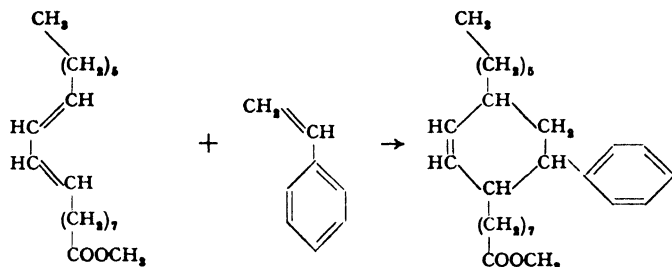
ANALYSIS OF COPOLYMERIZATION-PRODUCT OF STYRENE WITH METHYL LINOLEATE

	Properties of addition compound		Properties of saturated hydrocarbon obtained from the addition compound by the Grignard method	
	observed	theoretical for Diels-Alder adduct	observed	calculated for $\text{C}_{20}\text{H}_{34}$
n_D^{20}	1.5067	—	1.4768	—
d_4^{20}	0.9631	—	0.8668	—
r_{spec}^{20}	0.3088	0.3067 (Eisenlohr) 0.3084 (Vogel)	0.3257	0.3253
Mol wt	403	398.6	395	390.7
Saponif value	140.0	140.7	—	—
Iodine value (Wijs)	64.8	63.7	—	—
%C	81.27	81.35	86.11	86.07
%H	10.49	10.62	13.94	13.93
Average number of rings per molecule	from %H and mol wt		1.99	2.00
	from n , d and mol wt		2.07	2.00

In the low temperature polymerization of these esters by the action of hydrogen atoms at room temperature cyclization is, on the contrary, of little importance⁶⁶. Thus

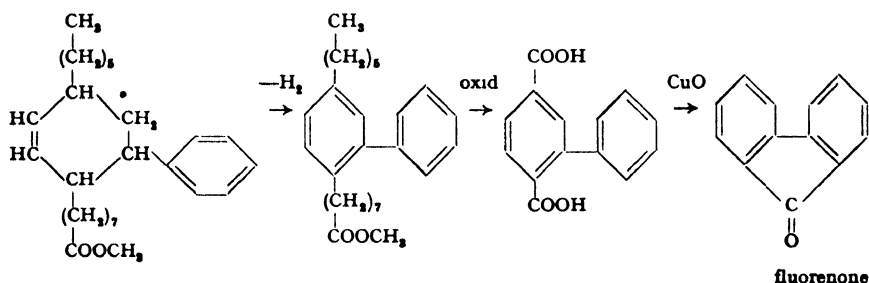
the application of the ring-analysis method to hydrocarbon mixtures obtained from polymerized esters by deoxidation, allows one to compare the structure of polymerization products obtained under different conditions.

SIE⁸⁷ allowed methyl linoleate to react with gaseous styrene at 280°C and isolated an addition compound by molecular fractionation of the reaction products in the cascade fractionating still (Fig. 78). From the analytical data of the addition compound he concluded that a Diels-Alder mechanism was involved in the copolymerization reaction of styrene with the primarily conjugated linoleic ester (*cf.* Table XVI)

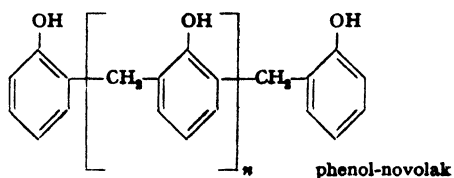


In order to establish the structure of the addition compound it was converted into the corresponding saturated hydrocarbon $C_{28}H_{54}$ by means of the above-mentioned Grignard reaction with methyl magnesium iodide, in this way the bicyclic character of the compound was proved (*cf.* Table XVI).

The structure was confirmed further by the following degradation reactions of the adduct⁸⁷:



Another example of the use of deoxidation of oxygen-containing compounds for their structural analysis was given by WIJNANDS *et al.*⁸⁸, who investigated the structure of novolaks, prepared by polycondensation of formaldehyde with phenol, *p*-cresol and *m*-cresol. The novolaks were transformed into saturated hydrocarbon mixtures by direct hydrogenation. Ultimate analysis of the hydrocarbons confirmed the linear structure of the novolaks:



3. DIRECT GRAPHICAL TRACING OF TRANSFORMATIONS OF FATTY OILS

a. Hydrogenation of fatty oils

For a long time it was impossible to obtain satisfactory insight into several aspects of the fat hydrogenation process owing to the lack of reliable analytical methods. This was for example the case with the separation of saturated and unsaturated fatty acids. For this separation several inconvenient methods were used that did not favour the drawing of reliable conclusions from hydrogenation data, although they enabled WILLIAMS⁶⁶ to represent the theoretical limits of possible ways of hydrogenation in a general diagram and to study the influence of hydrogenation conditions on the selectivity of the process more closely.

An accurate investigation of these problems was, however, only possible after the development of reliable methods of analysis. Particularly BERTRAM's method⁶⁵ for the determination of saturated fatty acids should be mentioned. VAN VLODROF⁷⁰ proved its usefulness for the study of the hydrogenation of several fatty acid esters (oleic, linoleic, elaeostearic).

The importance of the hydrogenation of fatty oils lies chiefly in the fact that the melting point rises owing to partial saturation of the double bonds of the unsaturated fatty acid groups present in the glycerides. For practical reasons, especially in the case of the margarine industry, it is very important that the starting material, consisting for the greater part of mixed glycerides of mono-, di- and possibly tri-unsaturated fatty acids, should be hydrogenated in such a way that a product is obtained with a homogeneous consistency. This is possible by using a *selective* hydrogenation process, in which the poly-unsaturated fatty acids (linolenic, linoleic) are transformed into mono-unsaturated ones, while the percentage of saturated acids remains constant, a good selectivity is also desirable in connection with the stability of the product. Although side reactions influence the properties of the end-product (particularly *cis-trans* isomerism of mono-unsaturates is accompanied by a considerable increase in the melting point), the diagram of WILLIAMS appears to be a valuable representation of selectivity problems of the fat hydrogenation process.

In Fig. 8r the course of the hydrogenation of linoleic acid esters at various temperatures, pressures, quantities of catalyst and contact conditions, is represented. This figure gives a clear picture of the influence of reaction conditions on the selectivity of the process: higher temperatures and low hydrogen pressures promote the selectivity of the hydrogenation. The particular importance of the diagram is, that it shows under which conditions any desired point of the diagram — that is to say any desired composition of esters — may be obtained from the starting material. In Section VI the selective hydrogenation of linoleic esters is described in more detail, in connection with the characterization of hydrogenation catalysts (see p. 105).

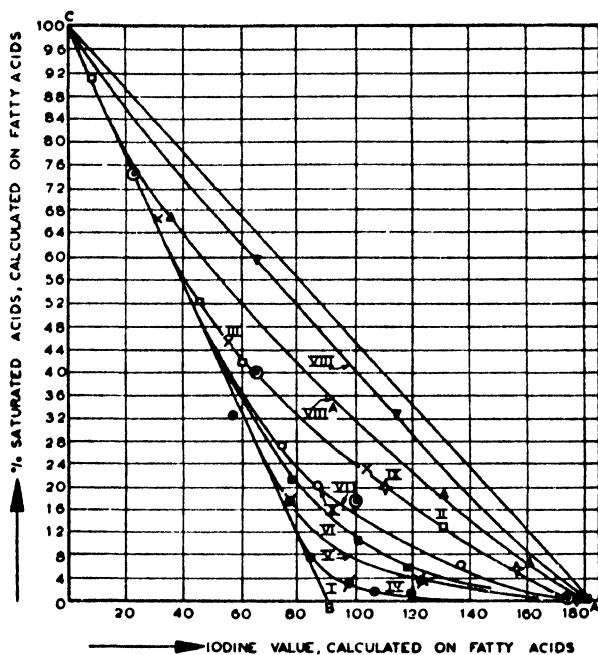


Fig 81 Hydrogenation of linoleic esters

- × 3 % Ni-guhr, 50°C, 100 atm
- 2.5% Ni-guhr, 90°C, 1 atm.
- 2 % Ni-guhr, 180°C, 1 atm.
- 2 % Ni-guhr, 180°C, 100 atm
- × 30 % Ni-guhr, 180°C, 1 atm
- ▲ 10 % Pt-carbon, 20°C, 100 atm
- ◆ 10 % Pt-carbon, 30°C, 0.1 atm.
- 10 % Pt-carbon, 30°C, 1 atm
- ▼ 10 % Pt-carbon, 50-65°C, 100atm
- 10 % Pt-carbon, 180°C 1 atm

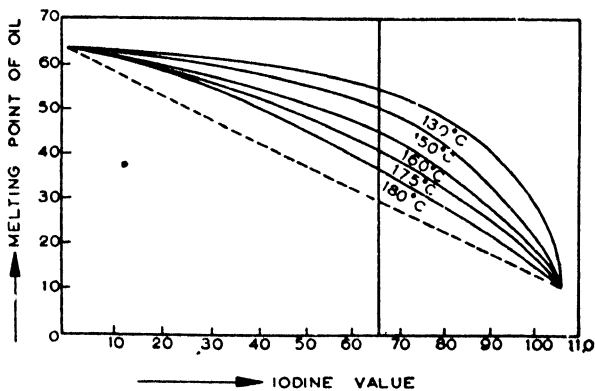


Fig 82 Melting points and iodine values of cottonseed oil, hydrogenated at different temperatures, according to WILLIAMS⁶⁶

It will be clear that the change in the melting point is closely connected with the conditions under which the hydrogenation process has been carried out. Not only the amount of solid saturated fatty acids, but also the amount of solid unsaturates formed during the process by isomerization, influences the melting point of the reaction pro-

duct, hence no definite relationship can be given between iodine value and melting point (*cf* Fig. 82). In practice, the refractive index is generally used besides the melting point for a rapid control of the saturation process, because the relationship between refractive index and iodine value is about the same for a large number of oils (Fig. 83).

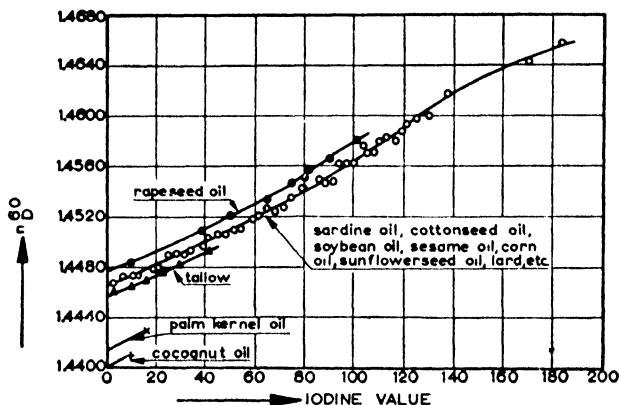


Fig 83 Iodine value vs refractive index for various hydrogenated oils, according to BAILEY⁷¹.

b Polymerization of drying oils

According to KAPPELMEIER⁶⁵ the thermal polymerization of non-conjugated oils (linseed, perilla) takes place by a primary conjugation of the linoleic and linolenic acid groups, followed by a Diels-Alder type condensation reaction of the conjugated fatty acid groups (*cf* p 91). For the conjugation of the molecules a relatively high reaction temperature is necessary (approx 300°C), unless proper conjugation catalysts are present, this explains the fact that thermal polymerization of conjugated oils like tung oil or catalytically conjugated linseed oil can be performed at much lower temperatures (200–250°C). Extensive research has shown that several active conjugation catalysts (sulphur dioxide, nickel, selenium) can be used as effective polymerization catalysts for non-conjugated drying oils, but do not influence the polymerization of conjugated oils to a large extent.

The action of sulphur dioxide in the conjugation (activation) of linseed oil and similar oils was studied by VAN VLODROP *et al* ⁷². In general relatively high pressures (100–150 atm) are required to obtain a reasonable conjugation at lower temperatures (160–180°C). Later experiments⁷³ showed that linseed oil can also be activated at normal pressure by introducing gaseous SO₂ at 285–300°C, however, efficient precautions should be taken to avoid any influence of traces of oxygen which strongly promote polymerization of the activated oil at these high temperatures.

Graphical representation of the activation and polymerization phenomena of drying oils is possible by means of the specific refraction and the iodine value⁷⁴, as shown in Fig. 84

In this diagram the triglycerides of pure linolenic, linoleic, oleic and stearic acid are represented by the points D, C, B and A, respectively, the values for the specific

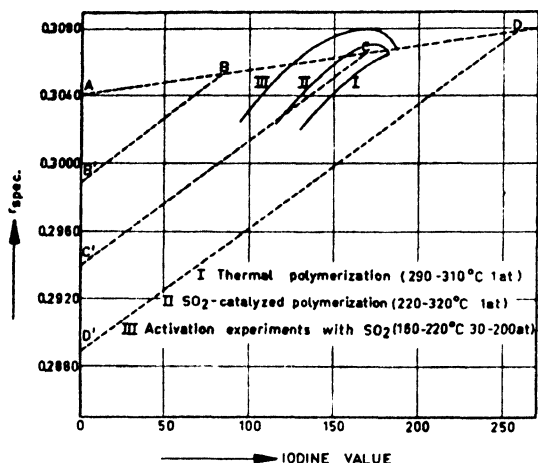


Fig 84 Polymerization and isomerization of linseed oil

refractions were calculated according to an equation recently given by TELS *et al.*⁵⁰ for non-conjugated, non-branched and non-polymerized glycerides:

$$n_{\text{spec}}^{20} = 0.3307 + 1.68 \cdot 10^{-5} \text{ I.V.} - 1.41 \cdot 10^{-4} \text{ S.V.} \quad \dots \quad (80)$$

in which I.V. = the iodine value
S.V. = the saponification value.

Hydrogenation experiments with the triglycerides are given by the curve D-C-B-A; theoretical polymerization curves of the esters (assuming removal of the double bonds without any change in the elementary composition) can be represented by D-D', C-C' and B-B'.

Conjugation of double bonds is demonstrated by an increase in the specific refraction of the experimental material. The role of this reaction in the polymerization of drying oils is shown by curves I, II, and III of Fig. 84. Curve I represents the thermal polymerization of linseed oil at 300°C. Owing to the low conjugation velocity, an increase in the specific refraction can hardly be detected, the conjugated molecules polymerize immediately at this relatively high process temperature. Curve II gives the course of sulphur dioxide-catalysed polymerization reactions. A considerable formation of conjugated molecules can be observed, especially in the initial stage of the process. Some typical conjugation (activation) experiments are shown by curve III.

Although the diagram does not give a quantitative interpretation of the heat-bodying phenomena of linseed oil it allows an easy comparison of the conjugation and polymerization reactions under different conditions. Chemical and physical analytical methods for the determination of conjugated double bonds (diene value, ultraviolet absorption spectra) confirmed the conclusions about the conjugation phenomena.

It should be remembered that the iodine value gives no reliable information about the unsaturation of polymerized and conjugated oils^{50,51}; the diagrams discussed above

should therefore be treated with some reserve. The application of improved analytical methods (hydrogen value, ozone addition) will improve the graphical analysis of conjugation and polymerization phenomena in this respect.

c. *Cis-trans isomerism of fatty oils*

The hardening action of sulphur dioxide on several fatty oils was observed by WATERMAN *et al.*⁷⁵ and DAHMEN^{75a}. Although, in principle, *cis-trans* isomerization is possible with any unsaturated fatty oil, the elaidinization process is of special interest for the non-drying and semi-drying oils, where it brings about a considerable increase in melting point due to the conversion of oleic acid (and other mono-unsaturated fatty acid) esters into the higher melting elaido-forms.

Several active elaidinization catalysts are known⁷⁶ of which selenium and sulphur dioxide certainly are the most attractive ones. With liquid sulphur dioxide optimum results are obtained under relatively mild conditions (110–115°C, 35 atm., 3 h), the low reaction temperature is favourable for the application of the hardened oils in the margarine industry.

The hardening effect of fatty oil isomerization processes is limited by the fact that *cis-trans* conversion of the double bond of mono-unsaturated fatty acids is an equilibrium reaction, in the case of oleic and elaidic acid esters the equilibrium mixture consists of 67% elaidic acid and 33% oleic acid, thus equilibrium ratio is practically independent of the isomerization temperature⁷⁷.

The course of the elaidinization reaction can be followed graphically by means of the critical demixing temperature of the oil, using, for example, aniline as a solvent. According to DAHMEN the rise in the critical demixing temperature is approximately proportional to the degree of elaidinization (*cf.* Fig. 85).

In Fig. 85 the critical demixing temperature of isomerized olive is plotted against the percentage of elaidinized oil (calculated on the amount of elaidic acid that can

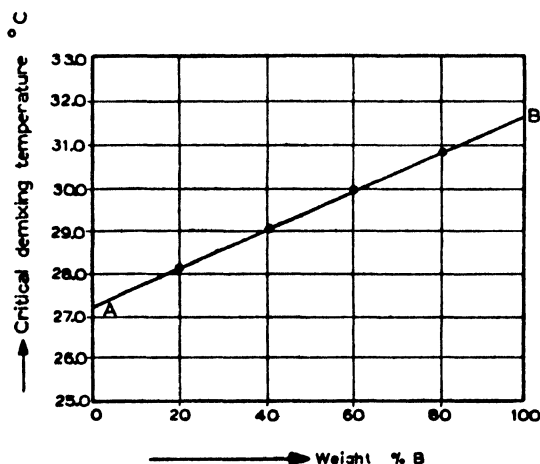


Fig. 85 Elaidinization of olive oil Critical demixing temperatures (oil-aniline) plotted against composition of mixtures of refined olive oil A and a strongly elaidinized product B

in practice be reached in the final product). Although this graphical method does not give the absolute percentage of elaidinic esters it allows a quick comparison of the *cis-trans* conversion under different conditions. The critical demixing temperature can be determined with good reproducibility and therefore should be preferred to melting point determinations.

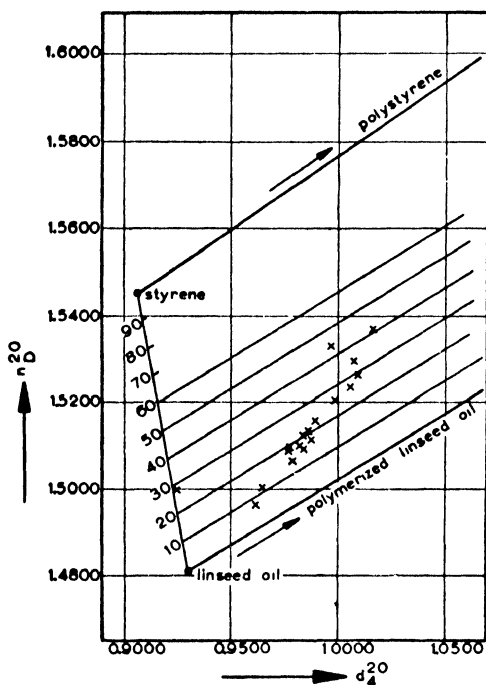


Fig 86 Analysis of styrenated linseed oils

4. GRAPHICAL ANALYSIS OF STYRENATED OILS

Copolymerization products of fatty oils and unsaturated hydrocarbons have become very important in recent years for the manufacture of varnishes, plasticizers, etc.

WATERMAN *et al.*⁷⁸ described a method for the preparation of homogeneous copolymerization products of drying oils with styrene, according to which styrene vapours are brought into contact with the oils at temperatures of 220–280°C. This method prevents the formation of high-molecular polystyrene and favours the chemical combination (copolymerization) of styrene with the oils⁷⁹.

To facilitate a rapid determination of the percentage of styrene in copolymerization products with linseed oil, a graphical method was based on the observation⁸⁰ that polymerization reactions of pure styrene and pure linseed oil can be represented by two parallel lines in a refractive index (n_D^{20}) vs. density (d_4^{20}) diagram (*cf.* Fig. 86).

Analysis of a large number of styrenated linseed oils showed that parallels, drawn between these two lines, indicate immediately the percentage of styrene in the products.

V COMPOSITION OF COAL

Coal is mainly composed of carbon, hydrogen and oxygen and is formed from plants by a coalification process. During this process the oxygen, constituting about 40% of the plant material, is split off as, for example, H_2O and CO_2 . The process can be represented by graphical tracing in a $\frac{H}{C} - \frac{O}{C}$ diagram, introduced by VAN KREVELEN^{81,82} (Fig. 87). The $\frac{O}{C}$ -scale is twice as large as the $\frac{H}{C}$ -scale. Methane is on the $\frac{H}{C}$ -axis at $\frac{H}{C} = 4$ (indicated by B), carbon is at the origin (indicated by D), carbon dioxide is on the $\frac{O}{C}$ -axis at $\frac{O}{C} = 2$ (indicated by E) and water at infinity ($\frac{H}{C} = \infty; \frac{O}{C} = \infty$) in the direction DA. The use of the diagram is not restricted to the triangle given, though this triangle covers most of the practical cases

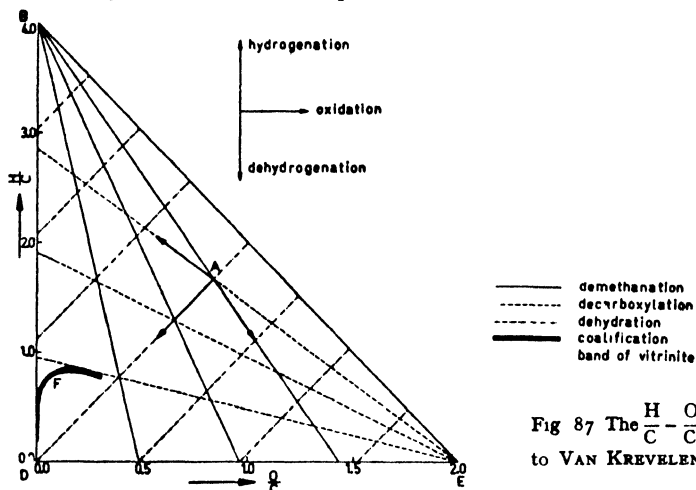


Fig 87 The $\frac{H}{C} - \frac{O}{C}$ diagram according to VAN KREVELEN

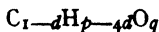
In this diagram any product composed of carbon, hydrogen and oxygen can be indicated if the molecular formula is known from ultimate analysis.

Pure cellulose $(C_6H_{10}O_5)_n$, for example, is indicated by point A in the diagram ($\frac{H}{C} = \frac{5}{3}, \frac{O}{C} = \frac{5}{6}$). If methane (CH_4) or carbon dioxide (CO_2) or water (H_2O) are expelled from cellulose, the compositions of the resulting products move along straight lines, connecting point B with A, if methane is split off, along EA, if carbon dioxide is split off and along AD, if H_2O is split off, all in the direction of the indicated arrows.

In the $\frac{H}{C} - \frac{O}{C}$ diagram several sets of straight lines are constructed, one set for the demethanation (the various lines diverging from B), one set for the decarboxylation (the various lines diverging from E), and one for the dehydration, the various lines running parallel. The equations for these sets can be derived as follows, assuming the molecular formula CH_pO_q for the starting material (coal, lignine, cellulose).

I. DEMETHANATION

If d is the fraction of carbon atoms that is transformed into CH_4 , then $4d$ hydrogen atoms are split off. The molecular formula for the resulting product is:



If the set of straight lines for the demethanation is represented by the equation

$$\frac{H}{C} = a \frac{O}{C} + b \quad \dots \dots \dots (81)$$

then the following equation holds

$$p = aq + b \quad \dots \dots \dots (82)$$

and

$$\frac{p-4d}{1-d} = a \frac{q}{1-d} + b \quad \dots \dots \dots (83)$$

a and b can be solved from these equations by first subtracting eqn. (83) from eqn. (82)

$$p - \frac{p-4d}{1-d} = a \left(q - \frac{q}{1-d} \right)$$

or

$$a = \frac{p-4}{q}$$

Substituting this value of a in equation (82) gives

$$p = \frac{p-4}{q} \cdot q + b$$

$$b = 4$$

Consequently equation (81) for the set of straight lines for the demethanation becomes

$$\frac{H}{C} = \frac{p-4}{q} \cdot \frac{O}{C} + 4 \quad \dots \dots \dots (84)$$

It follows from equation (84) that the lines for the demethanation intersect the $\frac{H}{C}$ -axis in $\frac{H}{C} = 4$, independent of the elementary composition of the starting material. Furthermore the tangent a of the slope of the lines is equal to $\frac{p-4}{q}$ and consequently varies with the elementary composition of the starting material. These facts are shown in Fig. 87.

2. DEHYDRATION

The equation for the set of lines for the dehydration can be derived in the same way as has been discussed for the demethanation. The result is

$$\frac{H}{C} = 2 \cdot \frac{O}{C} + (p-2q) \quad \dots \dots \dots (85)$$

It can be concluded from this equation that the tangent of the slope of the lines for the dehydration is constant and equal to 2. This means that the lines for the dehydration are parallel in the $\left[\frac{H}{C} - \frac{O}{C} \right]$ -diagram, which is shown in Fig. 87. The lines intersect the $\frac{H}{C}$ -axis in $\frac{H}{C} = (p-2q)$, the point of intersection being dependent on the elementary composition of the starting material.

3. DECARBOXYLATION

The following equation for the set of lines for the decarboxylation can be derived:

$$\frac{H}{C} = \frac{p}{q-2} \cdot \frac{O}{C} - \frac{2p}{q-2} \dots \dots \dots (86)$$

It follows from this equation that the tangent of the slope of the decarboxylation lines is dependent on the elementary composition of the starting material and is equal to $\frac{p}{q-2}$. All the lines intersect the $\frac{O}{C}$ -axis in $\frac{O}{C} = 2$, which is shown in Fig. 87.

In Fig. 87 a coalification band F for vitrinites is also represented. From the straight lines in the $\frac{H}{C}$ - $\frac{O}{C}$ -diagram for the demethanation, the dehydration and the decarboxylation it follows that initially CO_2 is split off during the coalification process and that in the final stages mainly CH_4 is split off.

Recently it has proved possible to convert cellulose by catalytic hydrogenation under mild conditions into ring-containing hydrocarbons⁸⁸. If we assume HAWORTH's concept of oxygen-containing rings in cellulose to be correct, it is certain that, on the removal of the oxygen, rings containing carbon only, are formed from products with rings containing oxygen as well as carbon.

For a discussion regarding the constitution of coal we refer to the book of VAN KREVELEN AND SCHUYER⁸².

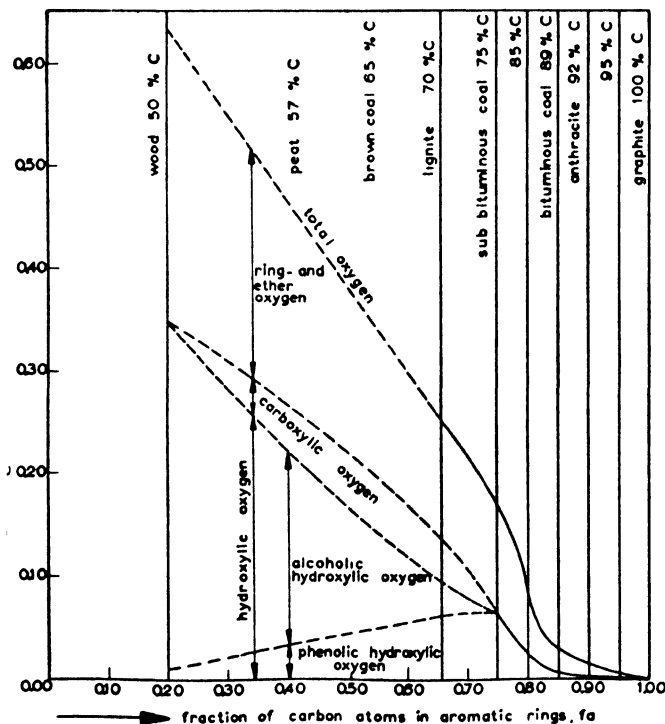


Fig 88a The conversion of the various oxygen-containing compounds during the coalification process, according to MEIJIS.



If the set of straight lines for the demethanation is represented by the equation

$$\frac{H}{C} = a \frac{O}{C} + b \quad \dots \dots \dots (81)$$

then the following equation holds

$$p = a q + b \quad \dots \dots \dots (82)$$

and

$$\frac{p-4d}{1-d} = a \frac{q}{1-d} + b \quad \dots \dots \dots (83)$$

a and b can be solved from these equations by first subtracting eqn. (83) from eqn. (82)

$$p - \frac{p-4d}{1-d} = a \left(q - \frac{q}{1-d} \right)$$

or

$$a = \frac{p-4}{q}$$

Substituting this value of a in equation (82) gives

$$p = \frac{p-4}{q} \cdot q + b$$

$$b = 4$$

Consequently equation (81) for the set of straight lines for the demethanation becomes

$$\frac{H}{C} = \frac{p-4}{q} \cdot \frac{O}{C} + 4 \quad \dots \dots \dots (84)$$

It follows from equation (84) that the lines for the demethanation intersect the $\frac{H}{C}$ -axis in $\frac{H}{C} = 4$, independent of the elementary composition of the starting material. Furthermore the tangent a of the slope of the lines is equal to $\frac{p-4}{q}$ and consequently varies with the elementary composition of the starting material. These facts are shown in Fig. 87.

2. DEHYDRATION

The equation for the set of lines for the dehydration can be derived in the same way as has been discussed for the demethanation. The result is

$$\frac{H}{C} = 2 \cdot \frac{O}{C} + (p-2q) \quad \dots \dots \dots (85)$$

It can be concluded from this equation that the tangent of the slope of the lines for the dehydration is constant and equal to 2. This means that the lines for the dehydration are parallel in the $\left[\frac{H}{C} - \frac{O}{C} \right]$ -diagram; which is shown in Fig. 87. The lines intersect the $\frac{H}{C}$ -axis in $\frac{H}{C} = (p-2q)$, the point of intersection being dependent on the elementary composition of the starting material.

3. DECARBOXYLATION

The following equation for the set of lines for the decarboxylation can be derived

$$\frac{H}{C} = \frac{p}{q-2} \cdot \frac{O}{C} - \frac{2p}{q-2} \dots \dots \dots (86)$$

It follows from this equation that the tangent of the slope of the decarboxylation lines is dependent on the elementary composition of the starting material and is equal to $\frac{p}{q-2}$. All the lines intersect the $\frac{O}{C}$ -axis in $\frac{O}{C} = 2$, which is shown in Fig. 87.

In Fig. 87 a coalification band F for vitrinites is also represented. From the straight lines in the $\frac{H}{C} - \frac{O}{C}$ -diagram for the demethanation, the dehydration and the decarboxylation it follows that initially CO_2 is split off during the coalification process and that in the final stages mainly CH_4 is split off.

Recently it has proved possible to convert cellulose by catalytic hydrogenation under mild conditions into ring-containing hydrocarbons⁸⁸. If we assume HAWORTH's concept of oxygen-containing rings in cellulose to be correct, it is certain that, on the removal of the oxygen, rings containing carbon only, are formed from products with rings containing oxygen as well as carbon.

For a discussion regarding the constitution of coal we refer to the book of VAN KREVELEN AND SCHUYER⁸⁸.

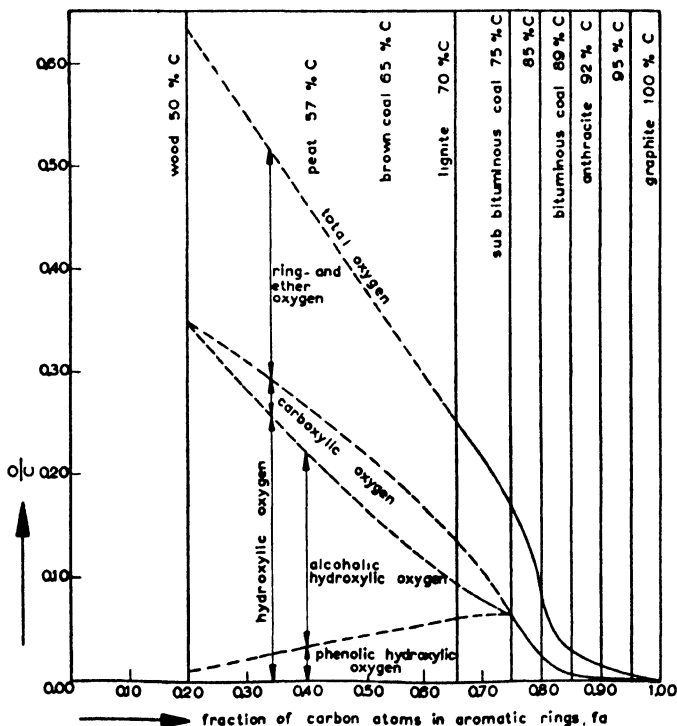


Fig 88a The conversion of the various oxygen-containing compounds during the coalification process, according to MEIJIS.

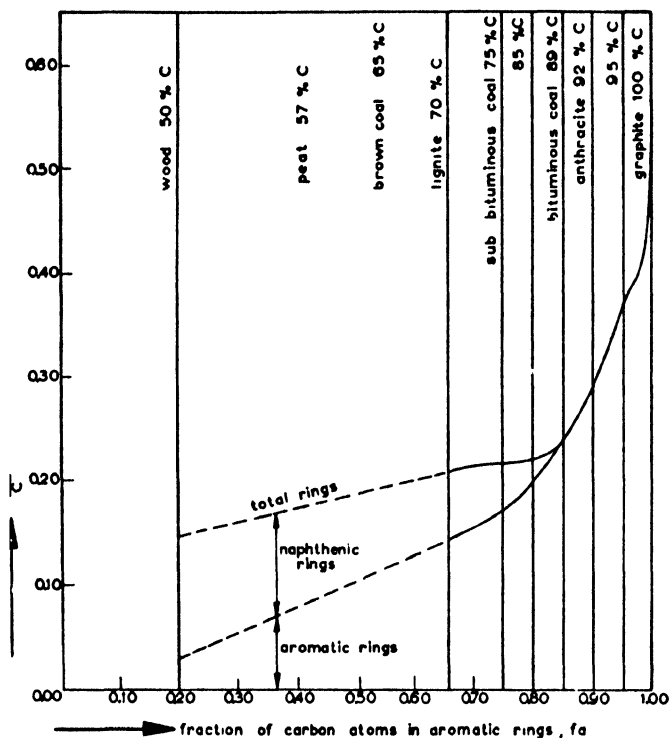


Fig. 88b The change of naphthenic and aromatic rings during the coalification process, according to MEIJIS R/C = number of rings per carbon atom

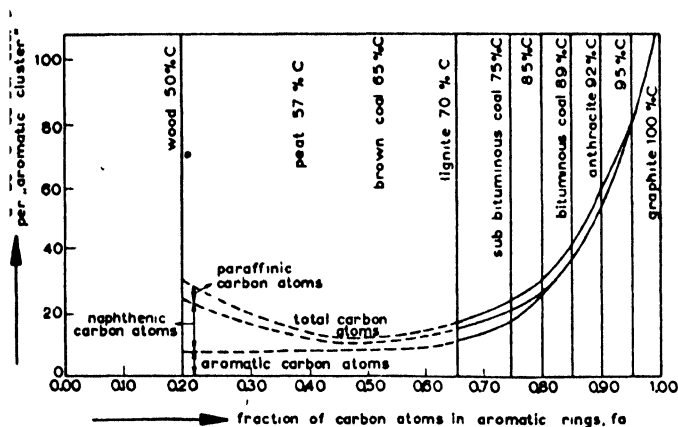


Fig. 88c The change of the number of carbon atoms in naphthenic, aromatic and paraffinic structure during the coalification process, according to MEIJIS

Investigations of VAN KREVELEN and further studies of MEIJIS⁸⁴ have led to the construction of various graphs, representing the changes in chemical structure during the coalification process, the conversion of the various oxygen-containing compounds and the formation of aromatic clusters. The graphs are represented in Figs. 88a, 88b and 88c.

VI. GRAPHICAL STATISTICAL METHODS FOR STUDYING CATALYTIC PROCESSES. CHARACTERIZATION OF CATALYSTS BY PARAMETERS

I. INTRODUCTION

Chemical reactions are generally connected with a change in chemical composition. A graphical representation of the reactions often facilitates a better understanding of the nature of the chemical transformations (Fig 89). The change in various physical

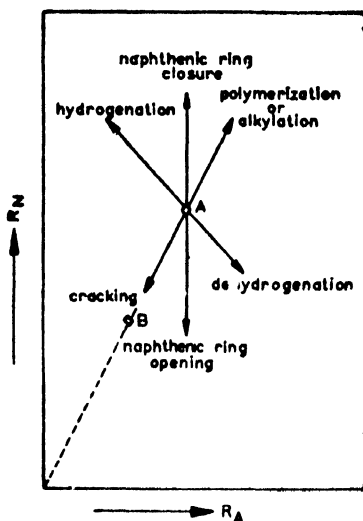


Fig 89 Graphical tracing of reactions of hydrocarbon mixtures⁸⁵

constants during the process can often be taken as an indication of the occurrence of changes in the chemical composition of the reactants (Figs. 1a and 1b).

The use of physical constants is, however, limited in the case of more complicated chemical processes the more complex the chemical change, the larger the number of physical properties necessary to investigate completely the chemical transformations. This especially holds when catalysts are involved in the reactions. When studying catalytic reactions we are dealing with catalysts as mixtures of a far more complicated nature than is the case, for example, in the structural analysis of hydrocarbon mixtures. The latter can be described, as was shown in the preceding sections, by means of a limited number of physical constants, from which either the chemical composition of the mixture or a series of other physical constants can easily be derived. For the characterization of catalysts completely different principles have to be applied even in simple cases, because in the case of a catalyst it is not chiefly its chemical composition that is important, but its chemical activity, which determines the result obtained by its chemical action.

In recent years the investigation of catalytic processes has led to better knowledge of the properties of catalysts and of the reaction kinetics. The complexity of the phenomena has, however, greatly hampered a real elucidation of the problems involved.

Recent work by WEBER^{86,87} has shown that it is possible to determine the activity of catalysts from a completely practical point of view by correlating the more important actions of the catalyst as a function of the process variables (temperature, pressure, nature of catalyst) by means of simple equations, the validity of which has been proved for a large number of catalytic processes. These equations are especially useful in the study of simultaneous chemical reactions in which selectivity problems play a part. They are of great value for more systematical research on catalysts

2 CHARACTERIZATION OF CATALYSTS

In the method of WEBER for the characterization of catalytical chemical reactions use is made of a very simple principle of *graphical tracing*, in which the most important actions of the catalyst, viz. *the conversion of the starting material, the formation of the desired products and the formation of by-products* are considered

According to this principle a chemical process in which selectivity problems are involved, can be represented graphically as a *pseudo-ternary system*. The unconverted starting material (A), the desired product (B) and the byproducts (C) can be chosen as the "components" of this system, the course of the reactions can be plotted in a triangular diagram.

WEBER stated that *the change in concentration of the three components chosen, resulting from the variation of one reaction variable, can be represented by an equation of the second order.*

$$y = \frac{x(1-x)}{a+bx} \quad \dots \dots \dots (87)$$

in which y and x represent the two co-ordinate lines of the diagram, while a and b are constants.

Equation (87) represents a *hyperbola* (Fig. 90); the equations of the asymptotes are

$$x = -\frac{a}{b}$$

$$bx + b^2y = a + b$$

It should be emphasized that only the part of the hyperbola within the triangle (Fig. 90) has practical significance

If the starting material consists of two or more different substances, e.g., A and A' , the reaction products therefrom can still be regarded as three component systems, if unconverted A , unconverted A' , and the combined products obtained from A and A' , are represented as the three components. For these cases the following holds

$$y = x + \frac{x(1-x)}{a+bx} \quad \dots \dots \dots (88)$$

in which y and x represent the retention of A and A' , respectively, expressed as A/A_0 and A'/A'_0 (in these ratios A and A' represent the concentrations of A and A' , respectively, A_0 and A'_0 being the concentrations of A and A' in the starting material), cf. Fig. 91.

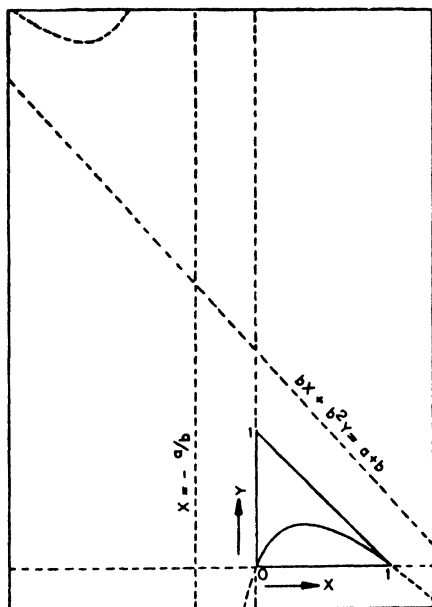


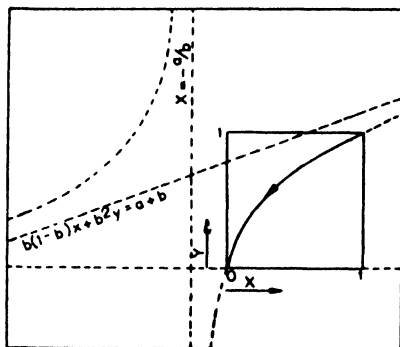
Fig 90 Graphical representation of the hyperbola

$$y = \frac{x(1-x)}{a+bx} \quad (a = 0.4, b = 0.9)$$

y = fraction of A transformed into B,
 x = fraction of A transformed into C

Fig 91 Graphical representation of the hyperbola

$$y = x + \frac{x(1-x)}{a+bx} \quad (a = 0.4, b = 1.6)$$



3. APPLICATIONS

The applicability of the hyperbolic equations will be demonstrated for the following processes (*cf.* Figs. 92-98).

a. Catalytic hydrogenation of linoleic esters^{70,88}

This reaction is an example of a consecutive first order reaction⁸⁸:



Series of experiments carried out at a relatively high temperature (180°C) and at

relatively low temperatures (20–90°C) with different catalysts and at different hydro pressures are represented in the triangular diagrams of Figs. 92 and 93, respectively. The course of each experiment can be represented by a hyperbola in accordance with equation (87), the values of a and b for the different experiments are collected in Table XVII.

TABLE XVII
CATALYTIC HYDROGENATION OF LINOLEIC ESTERS
REACTION COURSES ACCORDING TO THE HYPERBOLIC FORMULA

$$y = \frac{x(1-x)}{a + bx}$$

Reaction conditions			a	b
High temperature hydrogenations (cf Fig 92)	2% Ni-guhr, 180°C, 1 atm		0.0065	0.94
	30% Ni-guhr, 180°C, 1 atm		0.0272	0.88
	10% Pt-carbon, 180°C, 1 atm		0.0481	0.87
	2% Ni-guhr, 180°C, 100 atm		0.0950	0.97
Low temperature hydrogenations (cf Fig 93)	2.5% Ni-guhr, 90°C, 1 atm		0.117	0.71
	10% Pt-carbon, 30°C, 1 atm		0.340	0.35
	3% Ni-guhr, 50°C, 100 atm		0.340	0.35
	10% Pt-carbon, 30°C, 0.1 atm		0.340	0.35
	10% Pt-carbon, 20°C, 100 atm		0.747	0.12
	10% Pt-carbon, 50–65°C, 100 atm		1.660	2.21

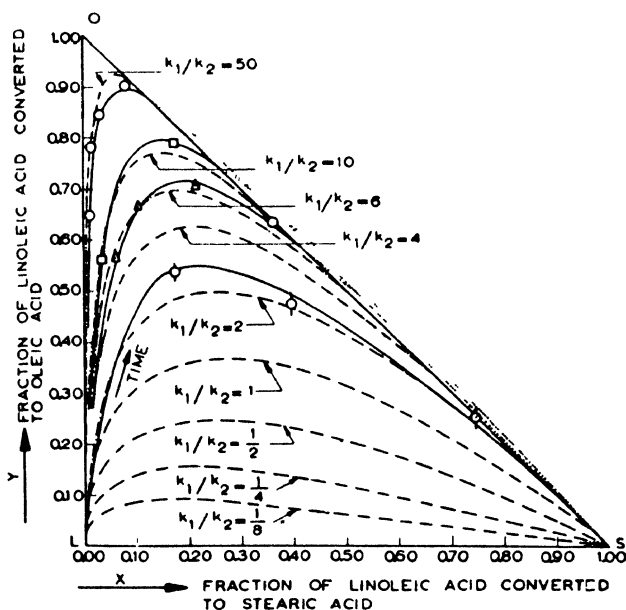


Fig 92 Hydrogenation of linoleic esters at a relatively high temperature (180°C).

- 2% Ni-guhr, 180°C, 1 atm
- 30% Ni-guhr, 180°C, 1 atm
- ▲ 10% Pt-carbon, 180°C, 1 atm
- ◆ 2% Ni-guhr, 180°C, 100 atm

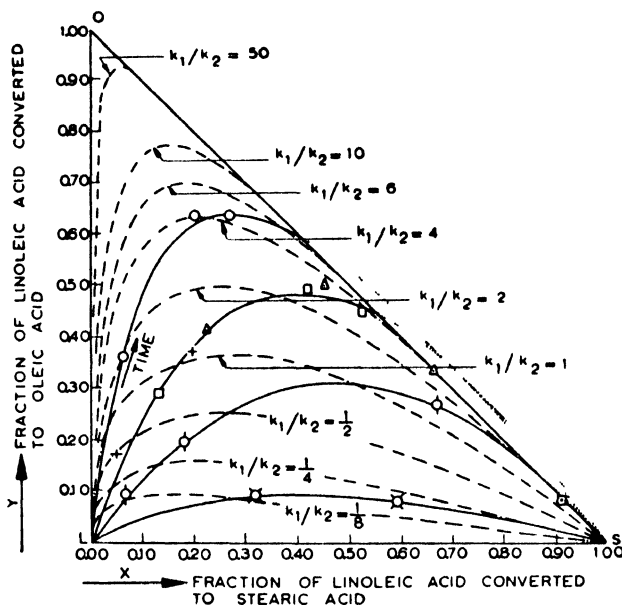


Fig 93 Hydrogenation of linoleic esters at relatively low temperatures (20-90°C)

- 2.5% Ni-guhr, 90°C, 1 atm
- 10% Pt-carbon, 30°C, 1 atm
- ▲ 3% Ni-guhr, 50°C, 100 atm
- + 10% Pt-carbon, 30°C, 0.1 atm
- ◆ 10% Pt-carbon, 20°C, 100 atm
- ⋈ 10% Pt-carbon, 50-65°C, 100 atm

The catalytic hydrogenation of linoleic esters has also been treated kinetically by BOELHOUWER *et al*⁸⁸. If the velocity constants of the consecutive reactions are represented by k_1 and k_2 and first order kinetics are assumed, the following equations hold:

$$\begin{aligned}
 -\frac{dL}{dt} &= k_1 L \\
 \frac{dO}{dt} &= k_1 L - k_2 O \\
 \frac{dS}{dt} &= k_2 O
 \end{aligned}$$

in which L , O and S represent the molar concentrations of linoleic, oleic and stearic esters, respectively. With the aid of these equations it is possible to calculate the course of hydrogenation reactions for distinct constant values of the ratio r

$$r = \frac{k_1}{k_2}$$

and to represent them also in the triangular diagrams of Figs. 92 and 93. It is remark-

able that for the high temperature experiments the reaction proceeds according to the theoretical assumptions (*cf.* Fig. 92). the calculated curves coincide with the experimentally determined ones. The low temperature hydrogenations, however, deviate considerably from the theoretical curves. apparently the assumption of a simple first order reaction mechanism is in this case not in accordance with the experimental results.

These data clearly demonstrate the practical significance of the hyperbolic equation of WEBER: *the equation holds for both the high temperature and the low temperature experiments*, whereas the kinetic considerations are valid for the high temperature hydrogenations only.

b. The hydro-isomerization of paraffin wax⁸⁹

In a number of hydro-isomerization experiments paraffin wax (average molecular weight 375) was vaporized with hydrogen and treated with different catalysts (W.H.-S.V. 0.89-1.04, temperature 410-450°C, hydrogen pressure 32-102 atm., molar ratio hydrogen : wax = 61 : 183). The reaction products were distilled at atmospheric pressure

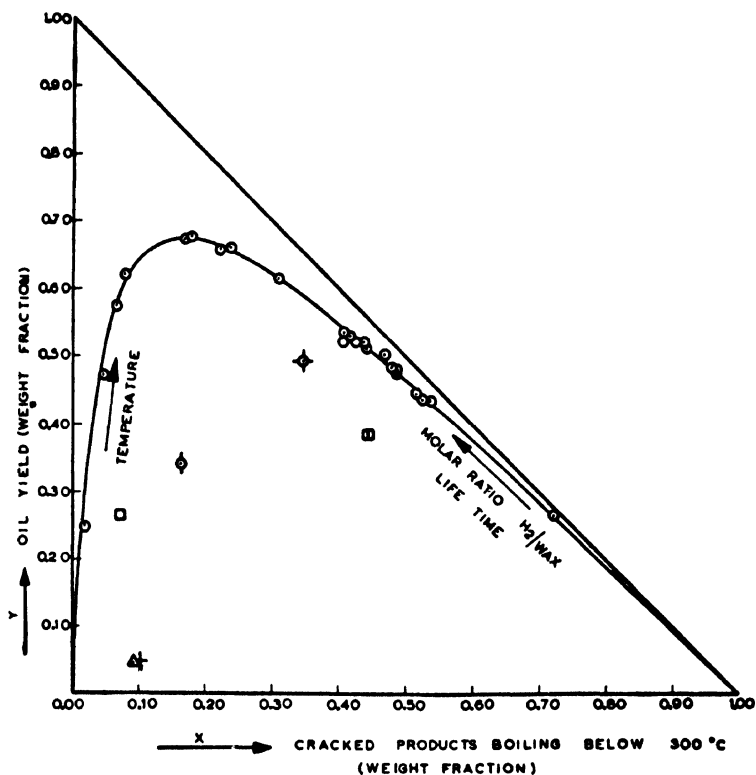


Fig 94 Hydro-isomerization of paraffin wax.

● Experiments with a platforming catalyst.
 ▲ + ◻ ♦ ◆ ◼ Experiments with other catalysts.

up to 300°C and the residues subjected to a dewaxing treatment at -20°C.

To follow the reactions in a triangular diagram the following "components" were considered:

- (1) unconverted wax, the wt. fraction of wax obtained in the dewaxing treatment;
- (2) isomerized oil (the desired product), the wt. fraction of oil obtained after dewaxing;
- (3) cracked products (by-products), the wt. fraction of low-boiling products obtained by distillation of the reaction products.

Fig. 94 shows the experimental results.

It appears that the experiments carried out with a platforming catalyst under different reaction conditions are all represented by *one* hyperbola (the values of a and b being: $a = 0.040$, $b = 0.9950$) in accordance with eqn. (87); the performance of the catalyst under the conditions mentioned above can thus be characterized by *two* constants, a and b . The use of other catalysts leads to other hyperbolas, some experiments with a few other catalysts are indicated in the diagram.

In this case it is a remarkable fact that experiments at different pressures and temperatures can be represented by *one* hyperbola. Fig. 94 immediately shows in which direction the product distribution will change when one of the process variables (the temperature, the molar ratio hydrogen · wax, the life-time of the catalyst) increases.

c. The chlorination of benzene⁹⁰

This reaction was studied by MACMULLIN with anhydrous ferric chloride as a catalyst at 55°C; in the experiments the amount of chlorine introduced was varied with the change in reaction time.

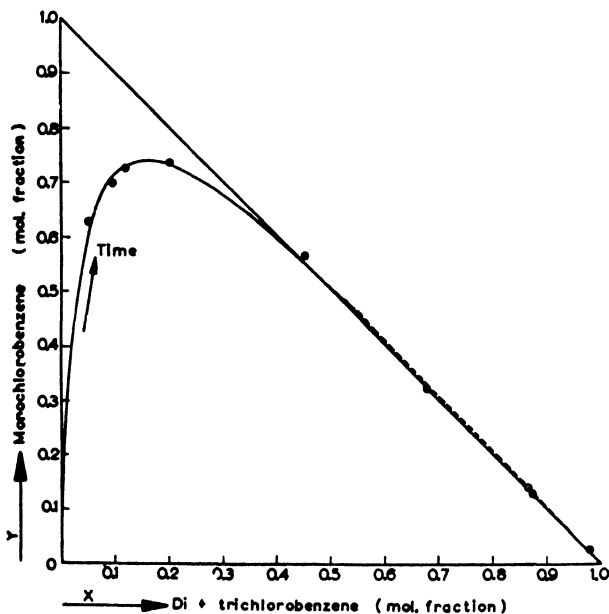


Fig 95. Chlorination of benzene.

Fig. 95 gives the change in concentration of the components·
 unconverted benzene,
 monochlorobenzene,
 (di + tri)chlorobenzene.

The curve can be represented by equation (87), in which $a = 0.0340$ and $b = 0.922$.

d Selective hydrotreating of shale gasoline⁹¹

The simultaneous hydrogenation of olefins and thiophens in shale gasoline was studied by BERTIL HAMMAR⁹¹. The selectivity of the process under different conditions was judged by determining bromine numbers (Br) and sulphur contents (S) of the reaction products.

In Figs 96, 97 and 98 reaction courses according to equation (88) are given for different temperatures, S_0 and Br_0 are the sulphur content and bromine number, respectively, in the starting materials.

4 SELECTION OF CATALYSTS

The experimental fact that the change of a reaction variable in a chemical process is connected with a change in the product distribution of the reactants according to eqn. (87) or eqn. (88) has an interesting consequence.

When only *one* experiment has been carried out with a certain catalyst, if eqn. (87)

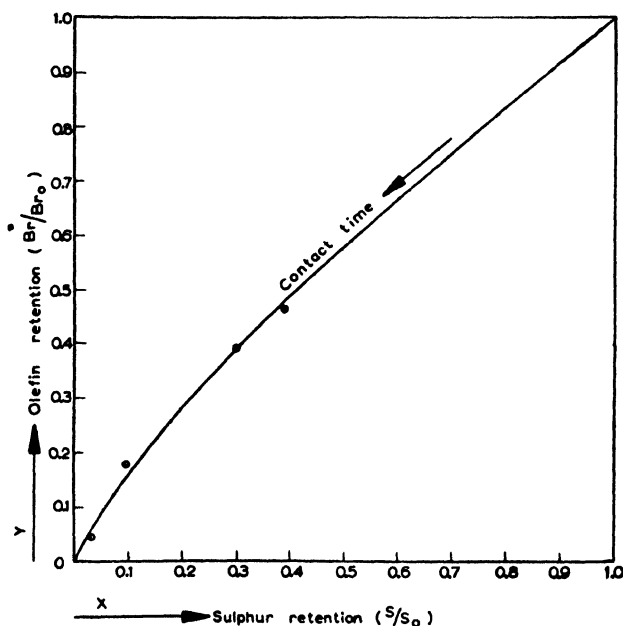


Fig 96 Hydrotreating of shale gasoline (300°C) $S_0 = 0.340$, $Br_0 = 41.4$.

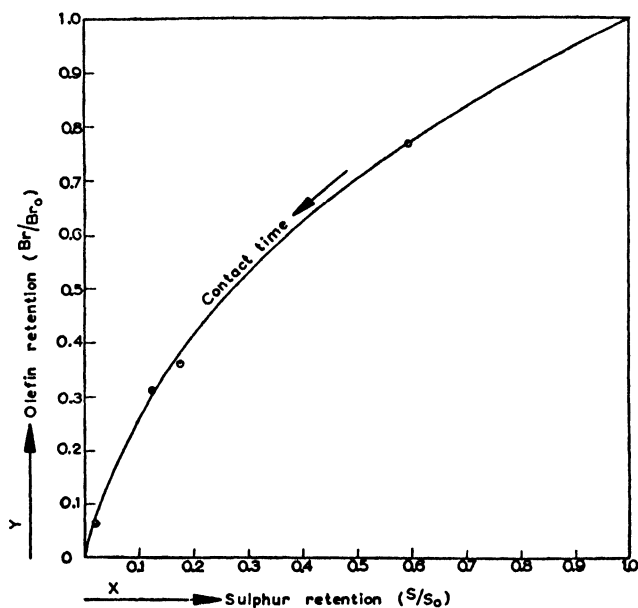


Fig 97 Hydrotreating of shale gasoline (325°C) $S_0 = 0.190$, $Br_0 = 32.0$

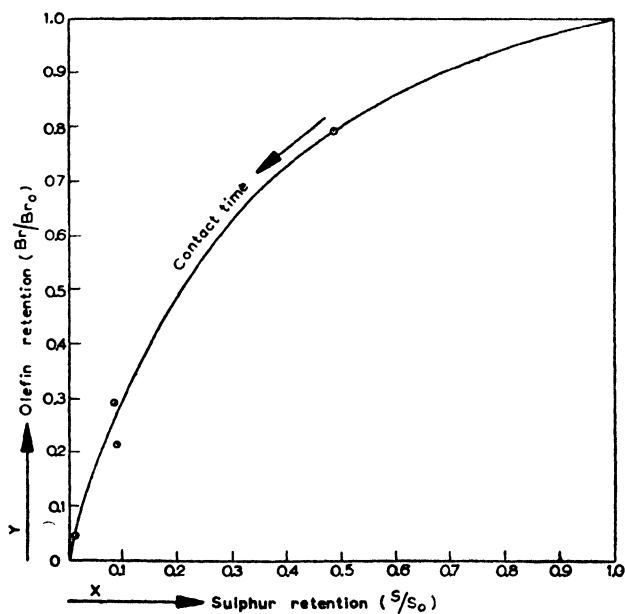


Fig 98 Hydrotreating of shale gasoline (375°C) $S_0 = 0.0678$, $Br_0 = 17.7$.

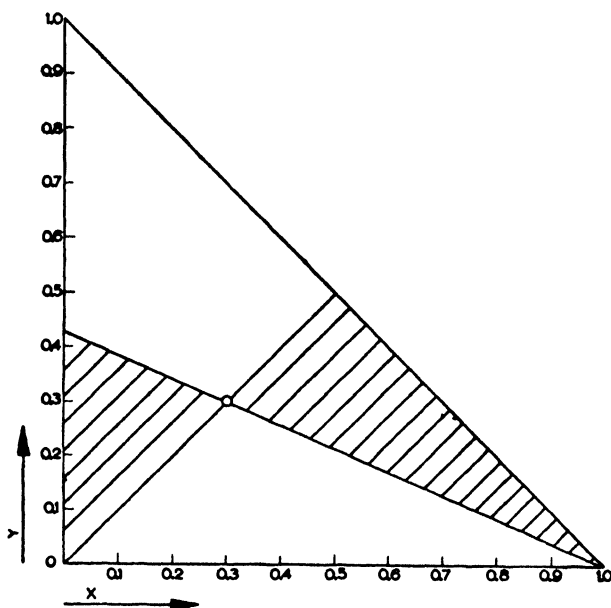


Fig. 99 Construction of the area which includes all hyperbolas according to eqn. (87), going through one experimental point and the angular points ($x = 0, y = 0$) and ($x = 1, y = 0$)

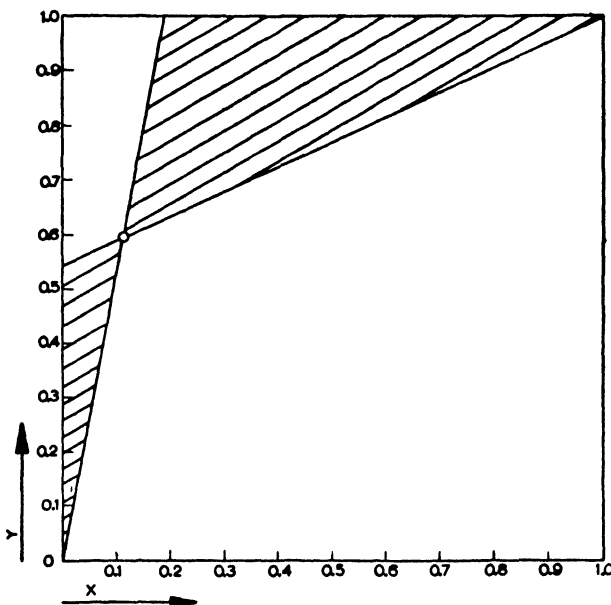


Fig. 100 Construction of the area which includes all hyperbolas according to eqn. (88) going through one experimental point and the angular points ($x = 0, y = 0$) and ($x = 1, y = 1$)

is valid, the hyperbola is not yet determined, infinite hyperbolas are possible, all going through the angular points ($x = 0, y = 0$), ($x = 1, y = 0$), and the experimental point. However, the limiting cases are given by straight lines drawn from the angular points ($x = 0, y = 0$) and ($x = 1, y = 0$) through the experimental point; these two straight lines enclose an area which represents all possible product distributions with the catalyst under investigation (*cf.* Fig. 99) when one reaction variable is changed with respect to the conditions of the experimental point.

The same considerations hold if eqn. (88) is valid, *cf.* Fig. 100.

When trying to find catalysts for chemical reactions of these types there is a convenient method of screening that can be used, if a proper choice of the components for the process under investigation has been made and the analysis of the reaction products has been directed accordingly. With each of the catalysts a single standard experiment is carried out and the results are plotted in the appropriate diagrams. The limiting reaction courses that are possible with the investigated catalysts can be directly compared and the most promising ones selected. A second experiment with each of these makes it possible to determine the values of a and b and construct the hyperbolas for a more precise comparison.

With this scheme a considerable saving of time and money may be achieved in the process research of complex reactions.

ADDENDUM

1 The correction for sulphur amounts to -3% C_N for each percent of S present, and a proportional correction of R_N should be made. No corrections are necessary for $\%C_A$ and R_A (see page 33)

2 For the nomograms the same corrections for the presence of sulphur hold as for the cross-sections -3% C_N for each percent of S present, and a proportional correction of R_N , no corrections are necessary for $\%C_A$ and R_A (see page 36)

3 A quantitative relationship has been found to exist⁹⁴ between the ultrasonic sound velocity u and the surface tension σ (both at 20°C) for pure saturated hydrocarbons and saturated mineral oil fractions

$$\sigma = 0.0354 u - 20.6 \quad (44a)$$

It appears that this equation can also be applied to straight run (non-hydrogenated) mineral oil fractions, especially in those cases where the fractions have been distilled freshly and, moreover, have a relatively low aromatic content (see page 50)

REFERENCES

- ¹ H I WATERMAN AND H A VAN WESTEN *J Soc Chem Ind (London)*, 55 (1936) 225T, S T SIE AND H I WATERMAN, *Chim & ind*, 81 (1959) 204, 357
- ² H BOER, *Rec trav chim*, 67 (1948) 217, 70 (1951) 1020, H BOER AND E C KOOYMAN, *Anal Chim Acta*, 5 (1951) 550, H BOER, *Thesis*, Amsterdam, 1949
- ³ K VAN NES AND H A VAN WESTEN, *Aspects of the Constitution of Mineral Oils*, Elsevier Publ Co, Inc, Amsterdam, 1951
- ⁴ H I WATERMAN, A B R WEBER AND C ZWEEKHORST, *J Inst Petrol*, 42 (1956) 349
- ⁵ J C VLUGTER, H I WATERMAN AND H A VAN WESTEN, *J Inst Petrol Technologists*, 18 (1932) 735, 19 (1933) 1035, 21 (1935) 661, *Chem Weekblad*, 29 (1932) 226
- ⁶ H A LORENTZ, *Ann Physik u Chem*, 9 (1880) 641, L LORENZ, *Ann Physik u Chem*, 11 (1880) 70
- ⁷ F EISENLOHR, *Z physik Chem*, 75 (1911) 585
- ⁸ H GEELLEN, *Thesis*, Delft, 1956, H GEELLEN, H I WATERMAN AND J B WESTERDIJK, *Riv. combustibili*, 10 (1956) 1
- ⁹ C BOELHOUWER AND H I WATERMAN, *Fuel*, 36 (1957) 481
- ¹⁰ H BOOY, *Thesis*, Delft, 1952, H I WATERMAN AND H BOOY, *J Inst Petrol*, 38 (1952) 526.
- ^{10a} G J F STIJNTJES, H I WATERMAN AND J B WESTERDIJK, *Riv combustibili*, 7 (1953) 271.
- ¹¹ H GEELLEN, *Thesis*, Delft, 1956, H GEELLEN, H I WATERMAN AND J B WESTERDIJK, *J Inst Petrol*, 43 (1957) 14
- ¹² J J LEENDERTSE, H J TADEMA, J SMITTENBERG, J C VLUGTER, H I WATERMAN, H A VAN WESTEN AND K VAN NES, *Meeting Am Chem Soc*, Houston, Tex, 23 March 1950, *Chem Eng News*, (1950) 1192, *Erdöl u Kohle*, 6 (1953) 537
- ¹³ C BOELHOUWER, J VAN STEENIS AND H I WATERMAN, *Fuel*, 33 (1954) 60
- ¹⁴ C BOELHOUWER AND H I WATERMAN, *J Inst Petrol*, 40 (1954) 116, 118
- ¹⁵ J CORNELISSEN AND H I WATERMAN, *Chim & ind*, 76 (1956) 1019, *Brennstoff-Chem*, 37 (1956) 404
- ¹⁶ J CORNELISSEN AND H I WATERMAN, *Anal Chim Acta*, 15 (1956) 401, *J Inst Petrol*, 43 (1957) 47
- ¹⁷ J CORNELISSEN AND H I WATERMAN, *Chim & ind*, 79 (1958) 26 1
- ¹⁸ J CORNELISSEN AND H I WATERMAN, *Fuel*, 36 (1957) 130
- ¹⁹ J CORNELISSEN AND H I WATERMAN, *Fuel*, 36 (1957) 340
- ²⁰ J CORNELISSEN, O HARVA AND H I WATERMAN, *Chim & ind*, 77 (1957) 533
- ²¹ J CORNELISSEN, O HARVA AND H I WATERMAN, *Acta Chem Scand*, 10 (1956) 1497
- ²² J CORNELISSEN AND H I WATERMAN, *Rec trav chim*, 76 (1957) 101
- ²³ J CORNELISSEN, O HARVA AND H I WATERMAN, *Erdöl u Kohle*, 10 (1957) 80
- ²⁴ J CORNELISSEN AND H I WATERMAN, *Chem Eng Sci*, 4 (1955) 238
- ²⁵ J CORNELISSEN AND H I WATERMAN, *Fuel*, 35 (1956) 433
- ^{25a} J CORNELISSEN, *Thesis*, Delft, 1957
- ²⁶ J CORNELISSEN AND H I WATERMAN, *J Inst Petrol*, 42 (1956) 62, *Erdöl u Kohle*, 9 (1956) 456, *Chim & ind*, (*Génie chim*), 75 (1956) 116
- ²⁷ J CORNELISSEN AND H I WATERMAN, *Fuel*, 35 (1956) 291
- ²⁸ J J TH M GEERARDS AND H I WATERMAN, *Brennstoff-Chem*, 37 (1956) 267
- ²⁹ C L DE BOOIJ, *Thesis*, Delft, 1955
- ³⁰ H I WATERMAN, J B WESTERDIJK, H F O SPAN, H BOOIJ AND K VAN NES, *J Inst Petrol*, 36 (1950) 281
- ³¹ S BROERSMA, H I WATERMAN, J B WESTERDIJK AND E C WIERSMA, *Physica*, 10 (1943) 97.
- ³² S SUGDEN, *J Chem Soc*, 125 (1924) 1177, S SUGDEN, *The Parachor and Valency*, George Routledge & Sons Ltd, London, 1930
- ³³ S A MUMFORD AND J W C PHILLIPS, *J Chem Soc*, (1929) 2112
- ³⁴ J J LEENDERTSE, *Thesis*, Delft, 1938, H I WATERMAN AND J J LEENDERTSE, *J Inst Petrol Technologists*, 24 (1938) 16
- ³⁵ P SCHENK, A B H VERVOORN, H I WATERMAN AND A B R WEBER, *J Inst Petrol*, 42 (1956) 205
- ³⁶ F D ROSSINI, *Selected Values of Physical and Thermodynamical Properties of Hydrocarbons and Related Compounds*, A P I Project 44, Pittsburgh, 1953
- ³⁷ A DIAS SANTILHANO, C VAN VLODROP, H I WATERMAN AND J VAN WIJK, *Chem Weekblad*, 38 (1941) 111

- ³⁸ J J VERSTAPPEN, *Thesis*, Delft, 1953
- ³⁹ B J MAIR, A J SWEETMAN AND F D ROSSINI, *Ind Eng Chem*, 41 (1949) 2224, C. BOELHOUWER, A J VAN RIEMSDIJK, J VAN STEENIS AND H I WATERMAN, *Anal Chim Acta*, 6 (1952) 476
- ⁴⁰ K VAN NES AND H VAN WESTEN, *Aspects of the Constitution of Mineral oils*, Elsevier Publ Co., Inc., Amsterdam, 1951
- ⁴¹ H KRAMERS AND J J BROEDER, *Anal Chim Acta*, 2 (1948) 687, see also ref ⁴⁰, p 156.
- ⁴² See ref ⁴⁰, p 281
- ⁴³ *Am Petrol Inst Research Project*, 44, 48
- ⁴⁴ P T WHITE, D G BARNARD-SMITH AND F A FIDLER, *Ind Eng Chem*, 44 (1952) 1430
- ⁴⁵ W C VAN ZIJLL LANGHOUT AND H I WATERMAN, *Chem Eng Sci*, 2 (1953) 139, W C VAN ZIJLL LANGHOUT, *Thesis*, Delft, 1955
- ⁴⁶ D W VAN KREVELEN, *Fuel*, 29 (1950) 269
- ⁴⁷ H I WATERMAN AND W C VAN ZIJLL LANGHOUT, *Chim & ind*, 74 (1955) 161
- ⁴⁸ G A FAICK AND B FONOROFF, *J Opt Soc Am*, 34 (1944) 330
- ⁴⁹ J C H JACOBS, J M STEVELS AND H I WATERMAN, *XXVIIème Congr intern chim ind.*, Bruxelles, 1954
- ⁵⁰ R B SOSMAN cited in G W MOREY, *Properties of Glass*, 2nd Ed., Reinhold Publ Corp., New York, 1954, p 383
- ⁵¹ G HEITKAMP AND K ENDELL, *Glastech Ber*, 14 (1936) 89
- ⁵² L SHARTSIS, S SPINNER AND W CAPPS, *J Am Ceram Soc*, 35 (1952) 155
- ⁵³ H R LILLIE, *Proc Intern Comm Glass (London)*, 2 (1955) 16
- ⁵⁴ J HUNTER, J F HYDE, E L WARRICK AND H J FLETCHER, *J Am Chem Soc*, 68 (1946) 667.
- ⁵⁵ S H BERTRAM, *Z deut Öl- u Fett-Ind*, 45 (1952) 733, *Chem Weekblad*, 24 (1927) 226, S H. BERTRAM, *Thesis*, Delft, 1928
- ⁵⁶ H I WATERMAN, J N J PERQUIN AND H A VAN WESTEN, *J Soc Chem Ind (London)*, 47 (1928) 363T, W J C DE KOK, H I WATERMAN AND H A VAN WESTEN, *J Soc Chem Ind (London)*, 55 (1936) 225T, H A VAN WESTEN, *Thesis*, Delft, 1931
- ⁵⁷ H I WATERMAN AND D OOSTERHOF, *Rec trav chim*, 52 (1933) 895, H I WATERMAN AND C VAN VLODROP, *La distillation moléculaire*, Gauthier-Villars, Paris, 1940
- ⁵⁸ H BOOY, *Thesis*, Delft, 1952, W G ALDERSHOFF, H BOOY, S L LANGEDIJK, G TH PHILIPPI AND H I WATERMAN, *J Inst Petrol*, 39 (1953) 688, S T SIE AND H I WATERMAN, *Anal. Chim Acta*, 14 (1956) 228
- ⁵⁹ M TELS, C BOELHOUWER, A J KRUIDENIER AND H I WATERMAN, *J Am Oil Chemists' Soc*, 35 (1958) 163
- ⁶⁰ J P K VAN DER STEUR, *Rec trav chim*, 46 (1927) 278, 409, 414
- ⁶¹ H I WATERMAN, *Hydrogenation of Fatty Oils*, Elsevier Publ Co., Inc., Amsterdam, 1951
- ⁶² B B A HOSMAN, J VAN STEENIS AND H I WATERMAN, *Rec trav chim*, 68 (1949) 939
- ⁶³ H I WATERMAN, J P CORDIA AND B PENNEKAMP, *Research (London)*, 2 (1949) 483, C BOELHOUWER, *Thesis*, Delft, 1952
- ⁶⁴ C BOELHOUWER, A C JOL AND H I WATERMAN, *Research (London)*, 5 (1952) 317, C BOELHOUWER, W A KLAASSEN AND H I WATERMAN, *Research (London)*, 7 (1954) S 62
- ⁶⁵ C P A KAPPELMEIER, *Farben-Ztg*, 38 (1933) 1018, 1077
- ⁶⁶ C BOELHOUWER, J VAN STEENIS AND H I WATERMAN, *Rec trav chim*, 72 (1953) 716, C. BOELHOUWER, *Thesis*, Delft, 1952
- ⁶⁷ S T SIE AND H I WATERMAN, *J Appl Chem (London)*, 6 (1956) 197
- ⁶⁸ C BOELHOUWER, H I WATERMAN AND P H W WIJNANDS, *J Polymer Sci*, 17 (1955) 411
- ⁶⁹ K A WILLIAMS, *J Soc Chem Ind (London)*, 46 (1927) 444 T
- ⁷⁰ C VAN VLODROP, *Thesis*, Delft, 1938
- ⁷¹ A E BAILEY *Industrial Oil and Fat Products*, 1st Ed., Interscience Publ Inc., New York, 1945, p 611
- ⁷² H I WATERMAN, C VAN VLODROP AND M J PFAUTH, *Verfchroniek*, 13 (1940) 130, *Research (London)*, 1 (1948) 186
- ⁷³ C BOELHOUWER, E F BOON, W VAN KLAVEREN, A SIEDSMA, M C WAGEMAKER AND H I. WATERMAN, *Chem Eng Sci*, 1 (1952) 117
- ⁷⁴ H I WATERMAN, *Compt rend XIVème congr chim ind*, Paris, 1934, H I WATERMAN AND C VAN VLODROP, *Compt rend XVème congr chim ind*, Bruxelles, 1935
- ⁷⁵ H I WATERMAN, C VAN VLODROP AND W J TAAT, *Chim & ind*, 44 (1940) 285
- ^{76a} E A M F DAHMEN, *Thesis*, Delft, 1946
- ^{76b} S H BERTRAM, *Rec trav chim*, 59 (1940) 650
- ⁷⁷ S H BERTRAM, *Chem Weekblad*, 33 (1936) 3, 216, 255, 637, 700, *Seifen-Öle-Fette-Wachse*, (1938) No 7, *Österr Chemiker-Zig*, 44 (1941) 241
- ⁷⁸ C BOELHOUWER, F A DE ROOS AND H I WATERMAN, *Chem & Ind (London)*, (1953) 1287
- ⁷⁹ S T SIE AND H I WATERMAN, *Anal Chim Acta*, 14 (1956) 228

- ⁸⁰ C BOELHOUWER, S T TJOA AND H I WATERMAN *Anal Chim Acta*, 11 (1954) 74
- ⁸¹ D W VAN KREVELEN, *Ingénieur (Utrecht)*, 64 (1952) M5, 1
- ⁸² D W. VAN KREVELEN AND J SCHUYER, *Coal Science*, Elsevier Publ Co, Inc, Amsterdam, 1957.
- ⁸³ J J TH M GEERARDS, D W VAN KREVELEN AND H I WATERMAN, *Research (London)*, 10 (1957) 164, *Intern Conf Coal Sci*, Valkenburg, The Netherlands, May 1957, see *Brennstoff-Chem*, 39 (1958) 11, 332
- ⁸⁴ J A MEIJS, *Thesis*, Delft 1955
- ⁸⁵ H I WATERMAN AND H BOOIJ, *J Inst Petrol*, 38 (1952) 526
- ⁸⁶ F BREIMER, H I WATERMAN AND A B R WEBER, *J Inst Petrol*, 43 (1957) 297
- ⁸⁷ H I WATERMAN AND A B R WEBER, *J Inst Petrol*, 43 (1957) 408
- ⁸⁸ C BOELHOUWER, J SNELDERWAARD AND H I WATERMAN, *J Am Oil Chemists' Soc*, 33 (1956) 143
- ⁸⁹ P SCHENK, A B H VERVOORN, H I WATERMAN AND A B R WEBER, *J Inst Petrol*, 42 (1956) 205
- ⁹⁰ R B MACMULLIN, *Chem Eng Progr*, 44 (1948) 183
- ⁹¹ C G BERTIL HAMMAR, *Proc IIIrd World Petrol Congr, Sect IV*, (1951) 295, 301.
- ⁹² J CORNELISSEN, J VAN LEEUWEN AND H I WATERMAN, *Chim & ind*, 77 (1957) 69
- ⁹³ H I WATERMAN, W E R VAN HERWIJNEN AND H W DEN HARTOG, to be published in *J Appl. Chem (London)*, 8 (1958) 625
- ⁹⁴ J CORNELISSEN, J A WATERMAN AND H I WATERMAN, *Proc 5th World Petroleum Congress* Section V, No 29, New York, 1959

SUBJECT INDEX

- Activation of drying oils 95, 96
- Activity of catalysts, determination of 104
- Additive functions 2, 11, 61, 64
- Alkane-thiols 73
- Analysis, ultimate 1, 10, 21, 73
- Analytical hydrogenation of aromatic oil fractions 2, 4, 72
- Analytical hydrogenation of olefinic distillates 9
- Aniline point 19, 24
- Apparent ring numbers 59, 61, 66
- Aromatic clusters in coal 102
- Aromatic concentrates 68, 71
- Aromatic concentrates, analysis of 71
- Aromatic oil fractions, hydrogenation of 2, 4, 72
- Atomic hydrogen, polymerization with 90, 91
- Atomic parachor 61
- Atomic refraction 11
- Average molecule 3, 9

- Benzene, chlorination of 109
- Branching analysis of hydrogenated polymers 60, 68
- Branching analysis of isomerized paraffin wax 69
- Branching-analysis of mineral oil fractions 60
- Branching, degree of, of hydrocarbon mixtures 57
- Branched hydrocarbons, analysis of 57-69

- Carbon-type analysis of natural mineral oil fractions 21-38
- Carbon-type analysis of saturated mineral oil fractions 16-20
- Cascade fractionating molecular still 5
- Catalyst activity, determination of 104
- Catalysts, characterization of 3, 103-113
- Catalysts, chemical activity 103
- Catalysts, comparison of 3, 113
- Catalysts, selection of 110
- Catalytic processes, graphical statistical study of 103-113
- Catalytic properties, characterization of 3, 103-113
- Cellulose, hydrogenation of 101
- Chemical activity of catalysts 103
- Chlorination of benzene 109
- Chromatography 2, 4, 68, 70, 87
- Chromatographic analysis of aromatic mineral oil fractions 70, 72
- Cis-trans isomerization of fatty oils 88, 93, 97, 98
- Cis-trans isomerization of naphthenes 6, 7
- Cis-trans isomers in mineral oils 12
- Coal, composition of 99-102
- Coal, decarboxylation of 101
- Coal, dehydration of 100
- Coal, demethanation of 99
- Coalification 99, 101
- Coalification of vitrinites 101
- Concentrates, aromatic 68, 71
- Conjugation of drying oils 95-96
- Copolymerization of drying oils and styrene 98
- Copolymerization of methyl linoleate and styrene 91-92
- Correlation of physical constants of mineral oil fractions 38-56
- Correlation of physical constants of saturated mineral oil fractions 19, 28, 48-50
- Cottonseed oil, hydrogenation of 94
- Cracked distillates, constitution of 9
- Cracked distillates, selective hydrogenation of 9
- Critical demixing temperature 97
- Cross-sections of v - n - d space model 29-33, 41, 45-48
- Cyclohexane-thiols 73

- Decarboxylation of coal 101
- Degree of branching of hydrocarbon mixtures 57-68
- Degree of branching of isomerized paraffin wax 69
- Degree of branching of mineral oils 60, 66
- Degree of branching of saturated polymers 60
- Dehydration of coal 100
- Dehydrogenation of sulphur compounds 74
- Demethanation of coal 99
- Demixing temperature, critical 97
- Density of glass 75, 79, 80
- Density of glass, determination 75
- Density of mineral oil fractions 10, 16, 20, 24, 37, 40, 42-50
- Density of saturated mineral oil fractions, prediction of 24, 28
- Desoxidation of fatty oils 5, 89
- Desulphurization of mineral oils 72
- Di-aromatic rings, estimation of 68-72
- Di-aromatics in mineral oils 70-72
- Direct method 9, 21
- Dispersion 15
- Distillation 2, 4, 5
- Distillation, molecular 5, 87, 92
- Distillation of mineral oils 5
- Distillation of polymerized fatty oils 5
- Drying oils, activation of 95, 96
- Drying oils, conjugation of 95
- Drying oils, copolymerization with styrene 98
- Drying oils, hydrogenation of 96
- Drying oils, polymerization of 90, 95-96

- Elaidinization of fatty oils 97

Elements, structural 2, 4
Extraction 4

Faraday effect 57
Fatty oils 87-98
Fatty oils, cis-trans isomerization of 93, 97-98
Fatty oils, desoxidation of 89
Fatty oils, graphical representation 88
Fatty oils, hydrogenation 93-95
Fatty oils, selective hydrogenation of 93, 94
Fatty oils, polymerization of 90, 95-96
Five-membered rings in mineral oil fractions 9, 19
Fluorenone 92
Foreign elements in mineral oils 3, 4, 21, 72
Formaldehyde, polycondensation with phenols 92
Fractionation of mineral oils 4
Functions, additive 2, 64
Fundamental viscosity temperature index 54, 55
F.V.T.I. 54, 55
F.V.T.I. and structure of saturated mineral oil fractions 55
F.V.T.I. of lubricating oils 53, 54
F.V.T.I. of silicone oils 55, 85

Glass 75-82
Glass, composition of 77-82
Glass, homogeneity of 75
Glass, kinematic viscosity of 82, 83
Glass, preparation of homogeneous 75
Glass, thermal treatment of 1, 77-80
Glassy quartz 81
Graphical analysis of fatty oils 88
Graphical analysis of glass 77-83
Graphical analysis of hydrocarbon mixtures 9-74
Graphical analysis of styrenated linseed oil 98
Graphical analysis of sulphur compounds 73, 74
Graphical representation of C-H-O-compounds 99
Graphical representation of fatty oils 88
Graphical representation of saturated mineral oil fractions 11-20, 26-28, 62-65
Graphical representation of sulphur compounds 74
Graphical statistical methods 1
Graphic tracing 1, 3, 103
Graphic tracing of catalytic processes 104
Graphic tracing of coalification process 99-102
Graphic tracing of reactions of fatty oils 93-98
Graphic tracing of reactions of hydrocarbon mixtures 6, 7, 103
Groupings, structural 1, 4

Heterogeneous catalysts 3, 103
Homologous series of pure hydrocarbons 14, 62
Hydrocarbons from coal, by hydrogenation 55
Hydrogenation, analytical 2, 4, 9, 72

Hydrogenation of cellulose 101
Hydrogenation of fatty oils 93, 94
Hydrogenation of linoleic esters 94, 105
Hydrogenation, selective, of aromatic fractions 4, 72
Hydrogenation, selective, of linoleic esters 105
Hydrogenation, selective, of olefinic mineral oil fractions 7-9
Hydrogenation, selective, of shale gasoline 110
Hydrogen content 10, 11, 21
Hydrogen spectrum 15
Hydrogen value 3, 87, 89
Hydro-isomerization of paraffin wax 62, 68, 108
Hydro-treating of shale gasoline 110
Hyperbolic representation of catalytic reactions 104-113

Infrared spectra 2
Iodine value 89
Iodine value of hydrogenated fatty oils 95
Isomerization of naphthenes 6, 7
Isomerization of paraffin wax 62, 68, 108

Kata-condensed rings in mineral oils 17, 19, 22
Kerosine, selective hydrogenation of 9
Kinematic viscosity of mineral oil fractions 26-49
Kinematic viscosity of glass, temperature dependence of 82-84
Kinematic viscosity of lubricating oils, temperature dependence of 52-54
Kinematic viscosity of silicone oils, temperature dependence of 55, 85, 86

Linoleic esters, hydrogenation of 94, 105-108
Linoleic methyl ester, copolymerization with styrene 91, 92
Linseed oil, activation of 95-96
Linseed oil, conjugation of 95-96
Linseed oil, copolymerization with styrene 98
Linseed oil, polymerization of 90, 95-96
Lubricating oils, viscosity of 52-54

Magneto-optical rotation, molecular 59-61, 66
Margarine-industry 93
Mass spectrometry 2
Melting point of hydrogenated cottonseed oil 94
Methyl linoleate, copolymerization with styrene 91, 92
Mineral oil fractions, analytical hydrogenation 4
Mineral oil fractions, aniline point 19
Mineral oil fractions, branching analysis of 67
Mineral oil fractions, carbon-type analysis 9-37
Mineral oil fractions, cis-trans isomerism 6-7
Mineral oil fractions, correlation of physical constants 20, 28, 38-56
Mineral oil fractions, dispersion 15
Mineral oil fractions, kinematic viscosity 26-49
Mineral oil fractions, mono- and di-aromatics in 68-72

- Mineral oil fractions, ν - n - d space model 29-38
 Mineral oil fractions, ring analysis 9-37
 Mineral oil fractions, selective hydrogenation 4, 7-9, 72
 Mineral oil fractions, sulphur compounds in 72-74
 Mineral oil fractions, surface tension of 45-50
 Mineral oil fractions, temperature dependence of kinematic viscosity 50-56
 Mineral oil fractions, tri-aromatics in 70-71
 Mineral oil fractions, ultrasonic sound velocity of 39-44
 Molecular distillation 5, 87, 92
 Molecular magneto-optical rotation 59-61, 66
 Molecular parachor 61, 66
 Molecular refraction 11, 61
 Molecular weight, determination of 27, 29
 Molecular weight, prediction of 28, 29
 Molecule, average 3, 9
 Mono- and di-aromatics, selective hydrogenation of 72
 Mono- and di-aromatics in mineral oils 68, 71
 Mono-aromatic rings, estimation of 68-72
 Multiple ring systems in mineral oils 17, 19, 22, 68-72
- n - d - M -method 14, 24-26
 n - d - M -method, formulae of 25
 Nitrogen compounds in mineral oils 3, 4, 72
 ν - n - d -method 28
 ν - n - d -space model 29
 Nomograms of cross-sections of ν - n - d -space model 33-39
 Novolaks, analysis of 92
- Olefins in mineral oils 3, 21
 Olefins, selective hydrogenation of 9
 Olive oil, elaidimization of 97
 Oxygen compounds in mineral oils 3, 4, 72
 Ozone addition 3, 77, 89
- Parachor, atomic 61
 Parachor, molecular 61, 66
 Parachor, specific 14, 61-67
 Paraffin wax, analysis of 26, 68
 Paraffin-wax, hydro-isomerization of 62, 68, 108
 Parameters for the characterization of catalysts 3, 103-113
 Physical constants of mineral oil fractions, correlations of 19, 28, 38-56
 Polymerization of drying oils 95-96
 Polymers, saturated, branching analysis of 14, 60, 68
 Polymers, saturated, ring analysis of 14, 60, 68
 Prehydrogenation of aromatic fractions 4
 Process research 113
 Process variables of catalytic processes 104
 Pseudo-ternary systems, representation of chemical processes as 104
- Quartz 81
- Ramification, degree of 57
 Refraction, atomic 11
 Refraction, molecular 11, 61
 Refraction, specific, of fatty oils 88, 96
 Refraction, specific, of glass 77-81
 Refraction, specific, of mineral oil fractions 10-15, 17-20, 64-67
 Refraction, specific, of quartz 81
 Refraction, specific, of sulphur compounds 74
 Refractive index of glass, determination 76
 Refractive index of hydrogenated fatty oils 95
 Refractive index of mineral oil fractions 10, 16, 24-47
 Residual oils, analysis of 26
 Ring analysis applied to polymerized fatty oils 89-91
 Ring analysis of natural mineral oil fractions 21-38
 Ring analysis of saturated hydrocarbon polymers 14, 60, 68
 Ring analysis of saturated mineral oil fractions 9-15
 Ring number per average molecule 3, 4
 Ring numbers, apparent 59, 61, 66
 Ring type 9, 17, 19, 70
 Rotation, magneto-optical 59-61, 66
- Saponification value 89
 Saturated fatty acids, determination 87, 93
 Selection of catalysts 110
 Selective analytical hydrogenation of olefinic distillates 7-9
 Selective hydrogenation of fatty oils 93, 94
 Selective hydrogenation of linoleic esters 105
 Selective hydrogenation of mono- and di-aromatics 72
 Selective hydrogenation of shale gasoline 110
 Shale gasoline, selective hydrogenation of 110
 Silicone lubricants 85
 Silicones, cyclic 84-86
 Silicones, F V T I of 85, 86
 Silicones, kinematic viscosity of 85, 86
 Silicones, linear 86
 Silicones, structure of 83
 Six-membered rings in mineral oil fractions 9, 17, 19
 Sound velocity, specific 70
 Sound velocity, ultrasonic 39-44
 Space model, ν - n - d - 29-47
 Specific parachor 14, 61-67
 Specific refraction of fatty oils 88, 96
 Specific refraction of glass 77-81
 Specific refraction of mineral oil fractions 10-15, 17-20, 64-67
 Specific refraction of quartz 81
 Specific refraction of sulphur compounds 74
 Specific sound velocity 70
 Specific volume 70
 Spectra, infrared 2
 Spectra, mass 2
 Spectra, ultraviolet 2
 Statistical distribution 2
 Structural elements 1, 2, 4
 Structural group analysis 1, 3
 Styrenated oils, analysis of 98
 Styrene, copolymerization with drying oils 98

- Styrene, copolymerization with methyl
linoleate 91, 92
- Sulphur compounds, identification of 73
- Sulphur compounds in mineral oils 3, 4, 72-74
- Sulphur correction 26, 29, 71, 73
- Surface tension of mineral oil fractions 45-50
- Temperature dependence of kinematic viscosity of glass 82-84
- Temperature dependence of kinematic viscosity of mineral oils 26, 50-56
- Temperature dependence of kinematic viscosity of silicones 55, 85, 86
- Thermal treatment of glass 1, 77-80
- Thermodiffusion 2, 4, 68, 70
- Thio-alkanes 73
- Thiophen 73
- Tracing, graphic 1, 3, 103
- Tri-aromatics in mineral oils 70, 71
- Tung oil, polymerization of 90, 95-96
- Two-ring systems in mineral oils 19, 70
- Type concentrates 68, 71
- Ultimate analysis 1, 10, 21, 73
- Ultrasonic sound velocity of mineral oil fractions 39-45
- Ultrasonic sound velocity, specific 70
- Ultra-violet spectrometry 2, 96
- Verdet-constant 57, 58
- Viscosity, kinematic, of glass 82-84
- Viscosity, kinematic, of lubricating oils 52-54
- Viscosity, kinematic, of mineral oil fractions 26-49
- Viscosity, kinematic, of silicone oils 85, 86
- Viscosity, temperature dependence of 50-56
- Viscosity temperature index, fundamental 54
- Vitamins, concentration of 87
- Vitrinites, coalification of 101
- Volume, specific 70
- x, exponent 50-52, 82
- x, exponent, of glasses 82
- x, exponent, of lubricating oils 52
- x, exponent, of silicones 85
- x, exponent, relation with structure of mineral oil fractions 55, 56

