Date of Degree: May 25, 1953

ame: Richard S. Logan Position: Student

nstitution: Oklahoma A. and M. Location: Stillwater, Oklahoma

itle of Study: STRUCTURAL GROUP ANALYSIS OF SELECTED LUBE OIL FRACTIONS.

umber of Pages in Study: 58 Candidate for What Degree: Master of Science

nder Direction of What Department: Chemical Engineering

cope and Method Study: A basis objective of this work was to gain some knowledge about the constitution of refined lubricating oils produced at the Kansas City Refinery of Phillips Petroleum Company. A secondary objective, but one which has received major attention in this work, was the examination of the extremely viscous lube stocks. The experimental approach used in this work involved application of the n-d-m method of ring analysis to commercially prepared plant oils as well as to laboratory fractions of plant oils.

'indings and Conclusions: Molecular distillations of the finished oils show that the heavier the grade of oil, the more heterogenous are its components with respect to molecular weight, viscosity, viscosity index, and the mean number of rings per molecule.

It appears that the deleterious effect of aromatics on viscosity index diminishes as the molecule becomes larger, with the percentage of carbon in aromatic structure remaining constant.

While the generalization that aromatic hydrocarbons are the major contributors to low viscosity index is undoubtedly valid, this work definitely shows that there is no direct correlation between the absolute value of aromatic carbon content and viscosity index. Thus, West Texas oil with the same viscosity index and paraffinic carbon content as a Mid Continent oil was found to have approximately twice the aromatic carbon content.

The separations processes used effected separations in the following ways when applied to finished 250 stock.

1. Propane Fractionation - Mainly according to molecular weight and to a lesser degree by molecular type.
2. Phenol Extraction - Mainly according to molecular type and to a lesser degree by molecular weight.
3. Molecular Distillation - Mainly according to vapor pressure and partly by molecular weight.
4. Silica Gel Chromatography - selectively removed aromatics from paraffins and naphthenes. Separation by molecular type.

DVISOR'S APPROVAL Loren L. Nickolls

STRUCTURAL GROUP ANALYSIS OF SELECTED LUBE OIL FRACTIONS

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Bachelor of Science

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1947

Submitted to the Faculty of the Graduate School
of the Oklahoma Agricultural and Mechanical
College in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
1953

STRUCTURAL GROUP ANALYSIS OF SELECTED
LUBE OIL FRACTIONS

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PREFACE

The composition of finished lubricating oils produced at the Kansas City Refinery of Phillips Petroleum Company has been investigated. The method used was structural group analysis. This method enables the composition of an oil fraction to be expressed in terms of ring content and the distribution of carbon with reference to aromatic, naphthenic and paraffinic hydrocarbon types. The oils subjected to the analysis were as follows:

1. Finished SAE 10 stock
2. Finished SAE 20 stock
3. "Special extract oil" - An oil rejected from the phenolic extract of 20 stock by the addition of water.
4. Finished SAE 50 stock
5. Finished SAE 250 stock
6. An extra heavy finished oil (590 SUS @ 210° F)

Each of these oils except the SAE 10 stock and the "special extract oil" was fractionated by molecular distillation. The SAE 250 stock was also fractionated by solvent extraction with both phenol and propane. The molecular distillation fractions of this stock were further fractionated by silica gel chromatography.

Several samples of finished oils were prepared from a raw West Texas 20 stock and represent varying degrees of solvent refining.

All the above fractions of oils were analyzed to determine pertinent physical properties and their structual characteristics calculated.

The author wishes to express appreciation to the Phillips Petroleum Company for permission to publish this paper and to Dr. W. N. Axe of Phillips Petroleum Company for his helpful comments and constructive criticisms.

Appreciation is also expressed to Dr. C. L. Nickolls of the Graduate School for his suggestions and assistance in the completion of this paper.

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I. INTRODUCTION

During the past 30 years considerable progress has been made toward elucidation of the composition of petroleum hydrocarbons distilling below the lubricating oil range. With the development of new techniques of separation and analysis, work of this nature is being extended into the heavy oil range by most petroleum laboratories and certain universities. It would appear to be a truism that the more that is known about the composition of petroleum, the more progress is made toward conversion of petroleum to useful products. Thus, in the field of light hydrocarbons, where the knowledge of composition is most firmly established, conversion and separation techniques have developed phenomenally. In this respect, progress in lube oil refining has been something less than sensational with no new developments during the last decade or so.

Considering the present state of affairs in the field of petroleum lubricants refining, a basic objective of the present work was to gain some knowledge about the constitution of refined lubricating oils produced at the Kansas City Refinery of Phillips Petroleum Company. There are at least two points of interest in this plant that could render its lube stocks constitutionally different from the products of other plants. Thus, lube stocks heavier than SAE 20 are prepared by propane fractionation, namely: SAE 50 and a fraction having a nominal viscosity of about 205 SUS @ 210°F referred to in this report as SAE 250 stock. The crude supply to the lube plant comprises a blend of West Texas and a typical Mid-continent oil. The former lube crude is of interest because of its high natural viscosity index, low wax content coupled with physical properties indicative of a low grade lube stock.

A secondary objective, but one which has received major attention in this work, was the examination of the extremely viscous lube stocks. Because of viscosity considerations these so-called bright stocks have limited usefulness as lubricants as such and are primarily used as blending stocks with oils of lower viscosity. In addition to providing obviously viscous protection against high cylinder and bearing temperatures, bright stocks have a salutary effect on oxidation stability. Constitutional studies may throw some light on this subject. In many refineries and Kansas City particularly oils of high viscosity (ca 600 SUS @ 210°F) are currently being disposed of as asphaltic products. Constitutional studies here may be useful in up-grading potential fractions as lubricants or chemical raw materials.

While the lube refining art has been substantially static, service requirements for lubricants have progressed rapidly in recent years. Fulfillment of modern performance standards has been by the additive route which in turn poses problems that may ultimately be explained by a more thorough knowledge of constitution of base oils. For example the response of a given base oil to a given additive is at present unpredictable. This in effect means that conventional parameters such as viscosity, viscosity index, VGC and the like do not adequately characterize the lubricant from a chemical standpoint.

The experimental approach used in this work involved application of the n-d-m method of ring analysis to commercially prepared plant oils as well as to laboratory fractions of plant oils. Fractionation techniques employed were: molecular distillation, propane fractionation, phenol extraction and silica gel chromatography. No effort was made to achieve exhaustive fractionation in this work, but rather reliance was placed on ring analysis data to indicate the type of separation and the general trend in chemical composition of the various fractions.

II. THE STRUCTURE OF LUBRICATING OILS

The Complex Structure of Oils

The portion of petroleum commonly called the lubricating oil fraction is of extremely complex character. Numerous investigators in the past have reported work concerning the constitution of lubricating oils. None of this work however has led to the isolation of a single pure compound. Up to the early 1930's, results of various types of analyses of lube oils were reported by means of empirical formulas. Mabery(9,10) obtained high boiling fractions of Pennsylvania, Canada, and California oils and found them to have empirical formulas ranging from about $C_n H_{2n}$ to about C_nH_{2n-8}, the proportion of hydrogen decreasing with rise in boiling point. Later Mabery (11,12) fractionated, by extraction, various crude oil residues not volatile at 300°C and 30 millimeters of mercury pressure. He obtained some fractions very low in hydrogen (C_nH_{2n-20}) and reported molecular weights as high as 1700. Smith(17) subjected topped, dewaxed, and steam distilled crude oil to successive extractions with acetone and determined the physical properties of the fractions. He found that the fractions poorer in hydrogen were more soluble as were those of low molecular weight. Molecular weights varied from 300 to 900 and empirical formulas from C_nH_{2n-2} to C_nH_{2n-8}.

A great deal of work has been done in the last twenty years at the Bureau of Standards under API Project 6 (Director: F. D. Rossini). A part of this project was concerned with the chemical constitution of the lube fraction of a mid-continent (Ponca City) petroleum. This oil was separated into a great number of fractions by distillation, extraction, adsorption, and crystallization. Several of these fractions were analyzed completely with respect to both size and type of molecules present. Rossini points out that, in terms of significant amounts, every hydrocarbon in the dewaxed and deasphalted fractions contains one or more naphthene rings. This is to say that there are no purely paraffinic hydrocarbons in these portions.

Kapff, Bowman, and Lowy (8) carried out an extensive investigation of a Pennsylvania lube oil stock. Fractionation was effected by distillation and extraction. The physical properties of the fractions and their chemical constitution as calculated by Waterman's method are reported. This work again brings out the complexity of the molecules in the lube oil range. All the fractions contained paraffinic, naphthenic, and aromatic carbon atoms.

The investigations of the chemical constitution of lube oils reported to date indicate the apparent hopelessness of splitting the heavier petroleum fractions into individual components. Since the identification of pure compounds in lube oil fractions is practically impossible, the next best method of expressing composition is in terms of aromatic rings, naphthene rings, and paraffin chains. Several methods for this type of analysis have been developed, a few of which are mentioned in the following section.

III. METHODS OF DETERMINATION OF STRUCTURE

One of the basic ideas underlying structural group analysis is the conception of an oil molecule being complex in structure and hence complex in properties. Heavy hydrocarbon molecules may contain (frequently do contain) aromatic as well as naphthenic rings and paraffinic side chains. This is reflected in their physical and chemical properties. For instance, the viscosity and viscosity index of such hydrocarbons will to a large extent be determined by the relative quantity of each structural element. The same is trude for the behavior of these hydrocarbons in physical separation processes such as solvent extraction and adsorptive percolation. Since these complex molecules cannot be described as either aromatics, naphthenes, or paraffins it is logical that their composition should be expressed in terms of structural fragments. A complete structural analysis consists of the following data:

R_T	Mean total No. of rings per molecule
R_A	Mean No. of aromatic rings per molecule
R_N	Mean No. of naphthenic rings per molecule
$\%C_R$	Percentage of total carbon in ring structure
$\%C_A$	Percentage of total carbon in aromatic ring structure
$\%C_N$	Percentage of total carbon in naphthenic ring structure
$\%C_P$	Percentage of total carbon in paraffinic structure

This section on "Methods of Determination of Structure" is taken in part from the book "Aspects of the Constitution of Mineral Oils" by K. van Nes and H. A. van Westen$^{(18)}$. The nomenclature used by those authors has also been employed in this report.

A. The Direct Method

The most fundamental structural group analysis is that made with the "Direct Method". This method is based on molecular weight determination and ultimate analysis of the oil fractions before and after hydrogenation. This allows the direct determination of R_T and $\%C_A$ without employing any correlations between physical constants and chemical composition. This procedure serves as a basis for all existing methods of structural group analysis. The precision of the direct method is as follows:

TABLE I

PRECISION OF THE DIRECT METHOD (2)

$\%C_A$ ± 1.0	R_A ± 0.04
$\%C_N$ ± 1.7	R_N ± 0.07
$\%C_P$ ± 1.3	R_T ± 0.05

Because of the fundamental importance of the direct method it is discussed herewith in some detail. The method consists of determination of the number of rings, R_T, and percentage of carbon in aromatic structure, $\%C_A$, by means of ultimate analysis and molecular weight determination before and after hydrogenation. This procedure must be supplemented by the assumptions (1) that olefins are absent and (2) that a mean ring type describes the ring structure.

Upon straight hydrogenation of an olefin-free oil fraction, the increase in hydrogen content is an exact measure of the total amount of aromatic carbon atoms present. Each aromatic carbon atom takes up one hydrogen atom. Assume that the empirical formula of the hypothetical "mean molecule" of the original oil fraction is C_cH_h and after hydrogenation $C_cH_{h'}$. These formulas are derived from ultimate analysis and molecular weight determination before and after hydrogenation. Then $h' - h$ hydrogen atoms are taken up per molecule, which equals the number of aromatic carbon atoms per molecule in the original oil fraction. Thus for the percentage carbon atoms in aromatic structure we have:

$$\%C_A = \frac{h'-h}{c}(100) \tag{1}$$

Now let C = % carbon and H = % hydrogen and assume that no foreign atoms are present. Then $C = 100 - H$

Since $c = \frac{MC}{1201}$, $h = \frac{MH}{100.8}$, and $h' = \frac{M'H'}{100.8}$ where M is the mean molecular weight and the prime indicates the hydrogenated state, it follows that:

$$\%C_A = \frac{1201}{100.8}(100)\frac{M'H'-MH}{M(100-H)} \tag{2}$$

This formula holds good only in the ideal case when the oil does not contain foreign elements and when no cracking or ring opening takes place during hydrogenation.

Now let us assume a hydrocarbon with h hydrogen atoms and c carbon atoms having the formula C_cH_h. If the molecule is a paraffin (noncyclic and saturated) we know that:

$$h = 2c + 2$$

A hydrogen deficiency in the absence of unsaturated bonds can only be caused by the presence of rings. Now the deficiency in hydrogen is defined as the factor 2p so that

$$h = 2c + 2 - 2p \tag{3}$$

For the molecular weight we may write generally:

$$M = 12.010c + 1.008h \tag{4}$$

and for the percentage hydrogen (H) in the compound:

$$H = 1.008h\frac{100}{M} \tag{5}$$

After eliminating c and h from (3), (4), and (5) we find for the hydrogen content of the compound:

$$H = 14.37 - 172.6\frac{p-1}{M} \tag{6}$$

This relation is not only applicable to the hydrogen content of individual hydrocarbons but also holds good for the hypothetical "mean molecule" of a mixture of hydrocarbons, as encountered in oil fractions.

For a saturated hydrocarbon the hydrogen content is an exact measure of the number of rings, because each ring involves a reduction by two hydrogen atoms. This is true regardless of the number of caron atoms per ring, and whether or not the rings are condensed. For any saturated hydrocarbon with the overall formula C_cH_h containing R_N rings, the relation, $h = 2c + 2 - 2R_N$, holds good because each ring closure gives rise to the loss of two hydrogen atoms. This means that p in equation (3) equals R_N, so that equation (6) can be rewritten to give equation (7).

$$H = 14.37 - 172.6 \frac{R_N - 1}{M} \tag{7}$$

As the hydrogenated sample is supposed to consist of only saturated hydrocarbons, we can calculate the mean number of naphthene rings (R_N) present in the hypothetical "mean molecule" of the hydrogenated oil fraction from equation (7). Thus the exact mean number of naphthene rings per molecule in the hydrogenated oil can be found from the average molecular weight (M') and the percentage hydrogen (H') in the hydrogenated oil fraction. This ring number is the sum of the mean number of aromatic and naphthene rings per molecule in the original oil fraction which can be expressed as R_T, the mean total number of rings. Rewriting the above formula (7) we have:

$$R_T = 1 + \frac{M' (14.37 - H')}{172.6} \tag{8}$$

The above procedure is a fairly simple and exact way of determining the percentage of carbon in aromatic rings ($\%C_A$) and the mean total number of rings per molecule (R_T). From these two data the analysis of an oil sample may be deduced, namely:

(a) Determination of carbon distribution ($\%C_A$, $\%C_N$, and $\%Cp$).

Conversion of ring number (R_T) into percentage carbon in ring structure ($\%C_R$) requires an assumption on the type of rings present: condensed or non-condensed, and the number of carbon atoms in a naphthene ring.

(b) Determination of ring content (R_T, R_A, and R_N). Conversion of the percentage carbon in ring structure into the mean number of aromatic rings per molecule (R_A) also requires an assumption on the type of rings present, in particular as regards the extent to which rings are condensed.

The choice of the kata-condensed six-membered rings as a basis for calculation, although somewhat arbitrary, is the most obvious as long as methods affording a better insight into the real character of the rings are lacking. The supposition seems reasonable as the kata-condensed six-membered rings can be seen as average in mixtures containing different types of polycyclic series. The assumption essentially means that two groups of molecules are supposed to counterbalance each other, that is the molecules with more and the molecules with less than the number of ring carbon atoms in corresponding molecules having condensed six-membered rings. Thus, concerning the aromatic molecules the assumption means that peri-condensed molecules (containing fewer carbon atoms per ring) and polycyclic non-condensed molecules (containing on an average more carbon atoms per molecule) are supposed to counterbalance each other.

Let us distinguish "substantial" rings, which contain six carbon atoms per ring, and "additional" condensed rings, which are supposed to contribute four carbon atoms per ring. We define R as the average total number of rings per molecule and R_S as the average number of substantial rings per molecule. If an individual hydrocarbon contains only six-membered kata-condensed or non-condensed rings the number of ring carbon atoms per molecule c_R is given by the equation:

$$c_R = 4R + 2R_S$$

The percentage of carbon in ring structure, $\%C_R$, can be found from the equation:

$$\%C_R = \frac{100\ (4R + 2R_S)}{c} = 240200\ \frac{2R + R_S}{M\ (100-H)} \tag{9}$$

where c is the number of carbon atoms per molecule. For mixtures (such as oil fractions) we start from the two cases where R_S follows directly from R. In the case of mixtures of non-cyclic and mono-cyclic hydrocarbons we may state: $R \leq 1$ and $R_S = R$. In the case of mixtures of cyclic compounds (provided that in each of the polycyclic components all rings are kata-condensed to each other) we may state $R \geq 1$ and $R_S = 1$. For these two cases equation (9) is transformed into:

$$\begin{aligned} &\text{If } R \leq 1 \qquad R = \%C_R\ \frac{M\ (100-H)}{720600} \\ &\text{If } R \geq 1 \qquad R = \%C_R\ \frac{M\ (100-H)}{480400} - 1/2 \end{aligned} \tag{10}$$

The above relations hold good for both naphthene and aromatic rings. Moreover, they may also be applied to mixtures containing these two types of rings in kata-condensed six-membered arrangement side by side. Thus, for the mean number of aromatic rings per molecule, R_A, we have:

$$\begin{aligned} &\text{for } R \leq 1 \qquad R_A = \%C_A\ \frac{M\ (100-H)}{720600} \\ &\text{for } R \geq 1 \qquad R_A = \%C_A\ \frac{M\ (100-H)}{480400} - 1/2 \end{aligned} \tag{11}$$

The value of the mean number of naphthene rings, R_N, can now be calculated from the relation

$$R_T = R_A + R_N$$

The values of the percentage of carbon in naphthenic ring structure, $\%C_N$, and the percentage of carbon in paraffinic structure, $\%C_P$, calculated from the following relations:

$$\%C_R = \%C_A + \%C_N$$

and

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

The ideal case described above is not wholly realized in practice because some cracking may take place during hydrogenation and because experimental errors are involved in the measurement of H, H', M, and M'. These errors may find expression in a decrease of the mean number of carbon atoms on hydrogenation (c'> c), so that the increase in hydrogen content is not reflected by an increase in molecular weight as required by the following equation:

$$M'-M = (h'-h)\ 1.008 = \frac{M'H'-MH}{100} \qquad (12)$$

A relatively simple correction in the formulas is possible by assuming that the molecular weight decrease during hydrogenation is caused by splitting off CH_2 groups. Instead of equation (1) we get in that case:

$$\%C_A = \frac{(h'-h) + 2(c'-c)}{c}\ (100) \qquad (13)$$

Thus, formulas (2) and (11) for the calculation of $\%C_A$ and R_A respectively may be corrected by replacing

$$\frac{M'H' - MH}{1.008} \text{ with } \frac{M'H' - MH}{1.008} - 2\ \frac{C'M'-CM}{12.01}$$

An additional correction is necessary because of the presence of a small percentage of foreign elements in the original oil fraction. Errors due to the presence of these foreign elements are suitably suppressed by measuring, as well as H and H', the percentage carbon before hydrogenation C and after hydrogenation C'.

B. The Waterman Analysis

The "Waterman ring analysis" was one of the first of the simplified methods (19,20). This method requires only the determination of molecular weight, aniline point, and specific refraction. The structural group analysis is arrived at through the use of experimentally derived correlations and the determined properties.

C. The n-d-n Method

The "n-d-m" method of structural group analysis is one of the most recent developments. The method is completely described and discussed by van Nes and van Westen in their book "Aspects of the Constitution of Mineral Oils"(18). This method requires the determination of refractive index (n), density (d), and molecular weight (m). The carbon distribution and ring content are calculated directly from these constants by the use of formulas or nomographs. The n-d-m method was selected for use in this investigation for two reasons, (1) the relative ease of obtaining the necessary data, and (2) demonstrated reliability when checked against the so-called "direct method". The oils used in the development of this method were obtained from five crude sources:

1. Borneo - aromatic naphthenic
2. Venezuela - medium grade
3. Oklahoma - Nowata
4. Caucasian - paraffinic
5. Pennsylvania - paraffinic

Thirty-four oil samples were carefully prepared and subjected to the rigorous direct method. The molecular weights of these samples ranged from 194 upwards. This provided correlation data for the rapid n-d-m method. The method has been validated for solvent extracted samples, distillation samples, thermal diffusion samples, and mixtures of widely variable crudes.

TABLE II

DEVIATION OF n-d-m (70°C) DATA FROM THE "DIRECT METHOD" DATA(18)

$\%C_A \pm 1.2$

$\%C_N \pm 2.0$

$\%C_R$ and $\%C_P \pm 1.7$

$R_A \pm 0.05$

$R_N \pm 0.12$

$R_T \pm 0.11$

TABLE III

REPRODUCIBILITY OF THE n-d-m METHOD(18)

$\%C_A = 0.8$

$\%C_N = 1.8$

$\%C_R$ and $\%C_P = 1.6$

$R_A = 0.06$

$R_N = 0.14$

$R_T = 0.12$

The validity of the method has been proved(18) for oil fractions with up to 75 per cent carbon in ring structure, insofar as the percentage of carbon in aromatic structure does not exceed 1.5 times that in naphthenic ring structure. The validity has also been proved for oil fractions containing up to four rings per molecule with not more than half of them aromatic. Application to paraffin waxes gives accurate results. As far as is known the method is also suitable for application to residual oils. The method can also be used for samples containing up to 2 per cent sulfur, 0.5 per cent nitrogen, and 0.5 per cent oxygen.

The effect of these elements has been neglected in this work. Available data, shown in Table IV, show them to be present in less than critical amounts in the finished oils.

TABLE IV

SULFUR, NITROGEN, AND OXYGEN CONTENTS OF SOME OILS

STOCK	% S	% N	% O
SAE 50	0.15	0.01	-
SAE 250	0.25	0.05	0.27
Extra heavy	0.28	0.15	-

IV. THE CONSTITUTION OF KANSAS CITY OILS

A. General Influence of Refining Procedure:

The refining procedure used to prepare a series of finished lubricating oils from topped crude has an effect on the constitution of these oils. At the Kansas City Refinery the following procedure is employed to obtain the various grades of oil from topped crude: Topped crude is charged to a vacuum distillation unit and the gas oil, raw SAE 10, and raw SAE 20 stocks are removed as overhead product. This overhead product is charged to a second vacuum distillation unit and the gas oil removed as overhead product, the raw SAE 10 removed as a side stream, and the raw SAE 20 as the bottoms product. The bottoms from the first vacuum distillation unit are designated as Vacuum Reduced Crude and contain raw SAE 50, raw SAE 250, raw oil heavier than SAE 250, and asphalt. These bottoms are subjected to two successive counter-current extractions with liquid propane. Raw SAE 50 is obtained as overhead product from the first extraction and raw SAE 250 is obtained as overhead product from the second extraction. The bottoms (propane insolubles) from the second extraction are made up of heavy oil and asphalt. The raw SAE 10, 20, 50 and 250 oils are each extracted with phenol in a counter-current column to improve viscosity index and color stability. These phenol extracted raffinates are then each solvent dewaxed by use of liquid propane. These dewaxed oils are called finished oils and the term "SAE" has been applied to them in this report. "SAE" as used in this report does not refer to commercial blended oils.

The extra heavy oil (heavier than SAE 250) which is included in this report was prepared at the Lube Oil Pilot Plant in Bartlesville from the bottoms from the second propane extraction of Vacuum Reduced Crude at the Kansas City Refinery. Processing consisted of the following: propane extraction yielding raw extra heavy oil as overhead product and asphalt as the bottoms; phenol extraction of the raw extra heavy oil; and solvent (methyl isobutyl ketone) dewaxing of the raffinate from the phenol column. This dewaxed oil is called finished extra heavy oil.

The above mentioned refining processes effect separations in the following ways:

Vacuum Distillation

Separation by vacuum distillation takes place according to volatility. A narrow boiling fraction may contain compounds having a wide variety of molecular weights. In a given fraction the higher molecular weight molecules will be of a paraffinic nature and the lower molecular weight molecules will be of a more aromatic character. Thus, the refining procedure causes the raw oil fractions to be in order of increasing volatility, gas oil, SAE 10 stock, and SAE 20 stock. Other properties of these oils that in general increase along with volatility are: viscosity, molecular weight, and specific gravity.

Propane Fractionation

Evidence has been presented(15) indicating that propane fractionation separates with respect to both molecular weight and molecular type and that the sharpest separation is with respect to viscosity. Propane tends to be selective for paraffinic molecules of low molecular weight. However, if aromatic molecules of lower molecular weight are present they will also dissolve in the propane. Thus, it would be expected that of the three stocks obtained by propane fractionation of vacuum reduced crude the raw SAE 50 would have the lowest molecular weight, the lowest viscosity, and would be the most paraffinic. The aromatic molecules will tend to be found in the raw SAE 250 and even more so in the raw extra heavy stock.

Phenol Extraction

The function of phenol extraction of the raw oil stocks is to improve their quality by removing the low viscosity index aromatic constituents. These constituents are selectively dissolved by phenol under proper conditions. This separation is also influenced somewhat by molecular weight as after the low molecular weight aromatics have been dissolved, some of the lower molecular weight paraffins will begin to dissolve along with higher molecular weight aromatics. The selectivity of phenol also decreases somewhat as the molecular weight of the oil stock increases.

Solvent Dewaxing

The dewaxing process effects removal of high melting constituents to a degree such that the pour point of the dewaxed oil is about 0°F. The wax removed is of a highly paraffinic nature. This slack wax however is not oil free and may contain as much as 20 per cent or more of oil which is essentially the same as the dewaxed oil.

B. General Influence of Crude Source:

The various grades of finished oils produced at the Kansas City Refinery have been subjected to structural group analysis. An important point which should be kept in mind is that these oil samples were not all taken from the Lube Plant at the same time and therefore are not all derived from the same crude mixture. The following table shows these differences of crude source.

TABLE V

CRUDE MIXTURES FROM WHICH THE LUBE STOCKS STUDIED IN THIS REPORT WERE OBTAINED

Lube Stock	Crude Mixture, % Vol.		
	Mid Continent "A"	Mid Continent "B"	West Texas
SAE 20 (#2)	50	50	0
"Special extract oil"	50	50	0
SAE 20 (#1)	27	27	46
SAE 50	27	27	46
Extra Heavy	25	25*	50
SAE 10	20	20*	60
SAE 250 (A)	20	20*	60
SAE 250 (B)	20	20*	60
SAE 250 (C)	20	20*	60

* Mid Continent "C"

These data show that the SAE 20 (#2) and the "special extract oil" are from a substantially different crude mixture than the other stocks. Analytical data on the SAE 20 (#2) and the "special extract oil" (see Table VII) show the latter to contain about three times the amount of aromatic carbon as SAE 20 (#2). The "special extract oil" contains less paraffinic carbon and about the same amount of naphthenic carbon. This "special extract oil" represents about 30 per cent of the oil contained in the phenolic extract solution obtained by phenol extraction of raw SAE 20 stock. It is evident that the extract oil is much more aromatic than the SAE 20 stock, and that phenol acts as a selective solvent primarily for aromatic molecules.

A comparison of SAE 20 (#1) and SAE 20 (#2) (see Table VII) shows that the former has a higher density, viscosity-gravity constant, and refractive index, but that both have about the same viscosity index. This would indicate that SAE 20 (#1) has a higher percentage of ring carbon. The structural group analysis is in agreement with this conclusion. This means that the addition of Ellenberger topped crude to the Kansas City Lube Plant charge stock caused an increase in the aromaticity of finished

SAE 20 stock (and probably the other stocks as well).

The transition from an all Mid Continent crude blend (1:1 Mid Continent "A" - Mid Continent "B") to an all West Texas crude is reflected in the abridged ring-analysis data given in Table VI for finished 20 stocks.

TABLE VI

EFFECT OF FINISHED 20 STOCK OF BLENDING WEST TEXAS CRUDE WITH MID CONTINENT CRUDE

% West Texas in Crude Mixture	VI* of finished 20 stock	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
0	97	1.94	0.25	1.69	34.0	7.5	26.5	66.0
46	96	2.00	0.43	1.57	36.0	10.1	25.9	64.0
100	91	2.30	0.94	1.36	35.0	17.8	17.2	65.0
100	104	2.06	0.57	1.49	31.9	11.1	20.8	68.1

* Kinematic Viscosity Index, ASTM Designation D 567-41 (reference 1)

Further study of the data contained in Table VII shows that as oil viscosity increases, the molecular weight and the mean number of rings per molecule (R_T) also increase. The percentage of carbon in ring structure ($\%C_R$) follows a somewhat difference pattern. It is essentially constant at about 35 per cent for the distillate oils (SAE 10 and SAE 20), drops to 26 per cent for the SAE 50 stock, increases to about 30 per cent for the SAE 250 stock and to 34 per cent for the extra heavy oil. The percentage of aromatic carbon ($\%C_A$) also follows this pattern. This means that the SAE 50 stock is the most paraffinic oil produced at the Kansas City Lube Plant.

Bowman(8) fractionated a Pennsylvania lube stock (comparable to topped crude) by distillation and reported results of the following nature: As the molecular weight (and viscosity) increases, the percentage of carbon in ring structure ($\%C_R$) decreases slightly and the percentage of aromatic carbon ($\%C_A$) increases. This difference between the pattern of ($\%C_A$) for the Kansas City oils and the Pennsylvania oil is probably a result of the propane fractionation process employed in refining the Kansas City oils. Propane exhibits some selectivity as to molecular type while distillation separates by volatility. This would cause an SAE 50 stock prepared by propane fractionation of a distillation residue to be more paraffinic than an SAE 50 stock prepared entirely by distillation.

C. Molecular Distillation and Structural Analysis:

The following finished oils were each separated into three approximately equal fractions by molecular distillation: SAE 20 (#1), SAE 50, SAE 250 (A), and the "extra heavy" oil. Laboratory inspection data and the structural group analysis were determined on each fraction. These data are presented in TABLE VIII. It should be mentioned here that molecular distillation does not separate with respect to volatility as in all other distillation procedures but separates with respect to the ratio of the vapor pressure to the square root of the molecular weight. The separation is not sharp since no reflux can be applied to the apparatus. The information contained in Table VIII points to the following conclusions:

(1) As was previously noted, the 20 stock (#1) has a higher percentage of carbon in ring structure, $\%C_R$, than do the heavier oils. This may be attributed to the presence of West Texas crude which is more aromatic than the Mid Continent crudes and also contains less bright stock.

(2) As the viscosity of the finished oils increases, the oils become more heterogeneous with respect to molecular weight, viscosity, viscosity index, and the mean number of rings per molecule (R_T). In other words the lighter oils are more closely cut fractions than the heavy oils.

(3) There is appreciable overlapping of many of the properties of the oil fractions. This is particularly true in the case of viscosity and molecular weight.

(4) It appears that the deleterious effect of aromatics on viscosity index is decreased as the molecule becomes larger while the percentage of carbon in aromatic structure ($\%C_A$) remains constant.

The molecular still was also utilized to separate SAE 250 (A) into ten approximately equal fractions and the "extra heavy" stock into eleven approximately equal fractions. The distillation of SAE 250 (A) was carried out to investigate the structural effects resulting from propane fractionation and to obtain a series of fractions for further fractionation. The "extra heavy" oil was distilled to obtain information for the first time on the constitution of a bright stock beyond the range of ordinary commercial oils. Table IX presents inspection data and structural group analyses on the fractions resulting from these distillations. A study of these data reveals some interesting points.

(1) Molecular distillation of the "extra heavy" oil proved that oil having a molecular weight above 1000 can be distilled with the molecular still.

(2) The most striking difference in the properties of these two sets of fractions is in the specific gravity and refractive index. For the fractions of SAE 250 stock, the values of both properties increase for each succeeding distillate portion and reach a maximum in the residue. (This is also true for fractions of SAE 20 and SAE 50 stocks.) However, for the fractions of "extra heavy" oil, the values of both properties decrease for each succeeding distillate portion

and reach a minimum in the residue. The specific gravities and refractive indices of both residues are very nearly the same. The results of the structural group analysis are in agreement with the above difference. For the fractions of 250 stock, the increase of specific gravity and refractive index is associated with a small increase in $\%C_A$ which is accentuated by a decrease in $\%C_N$. For the fractions of heavy stock the decrease of specific gravity and refractive index is in agreement with the notable decrease in $\%C_A$ and slight increase of $\%C_N$.

This difference is quite possibly a result of a refining procedure in that these stocks are prepared by successive propane fractionations. For both the SAE 50 and SAE 250 raw stock separations the propane tends to reject some aromatics. For the "extra heavy oil" separation however, an oil is being separated from an asphalt rather than from an oil. Under these conditions all of the oil molecules dissolve in the propane including those aromatics which were not soluble during the 50 and 250 stock separations. Phenol treatment is not too efficient because of the high molecular weight of the oil and thus, phenol does not remove as large a proportion of aromatics from the heavy as it would from a light oil. Molecular distillation then separates mainly by vapor pressures (and to a lesser extent by molecular weight) which causes the fractions of the heavy stock to become progressively poorer in aromatics.

(3) The two sets of fractions showed considerable overlap of viscosity, viscosity index, and molecular weight. The fractions of heavy stock covered a broader range of viscosity index than

did those of the 250 stock. These data are in agreement with the higher aromaticity of the heavy stock.

(4) It is not possible to determine from these data whether viscosity index is a function of the percentage of carbon in ring structure or the percentage of some type of ring carbon.

D. Structural Analysis of SAE 250 Stock After Fractionation by Molecular Distillation and Silica Gel Adsorption:

The ten fractions of 250 stock obtained by molecular distillation were each further fractionated by silica gel. Physical properties and structural group analyses were determined on each fraction. Complete data on these fractions are reported in Table X. Portions of these data are presented graphically in the following Figures:

Figure 1 - R_T vs Weight percentage distilled or eluted
Figure 2 - $\%C_R$ and $\%C_A$ vs Weight percentage distilled or eluted
Figure 3 - V.I. vs Weight percentage distilled or eluted
Figure 4 - Molecular Weight vs Weight percentage distilled or eluted

Data from Table IX on the molecular distillation fractions are also included in the above Figures. A study of these data leads to the following generalizations:

(1) Molecular distillation of SAE 250 stock effected no separation with respect to molecular type (see Figures 1, 2 and 3). A fairly good separation was effected with respect to molecular weight until about 50 per cent of the oil was distilled. Beyond the 50 per cent point the fractions began to exhibit considerable overlap. It should be mentioned that the first six fractions were each obtained with one pass through the molecular still while the last three overhead fractions each required two

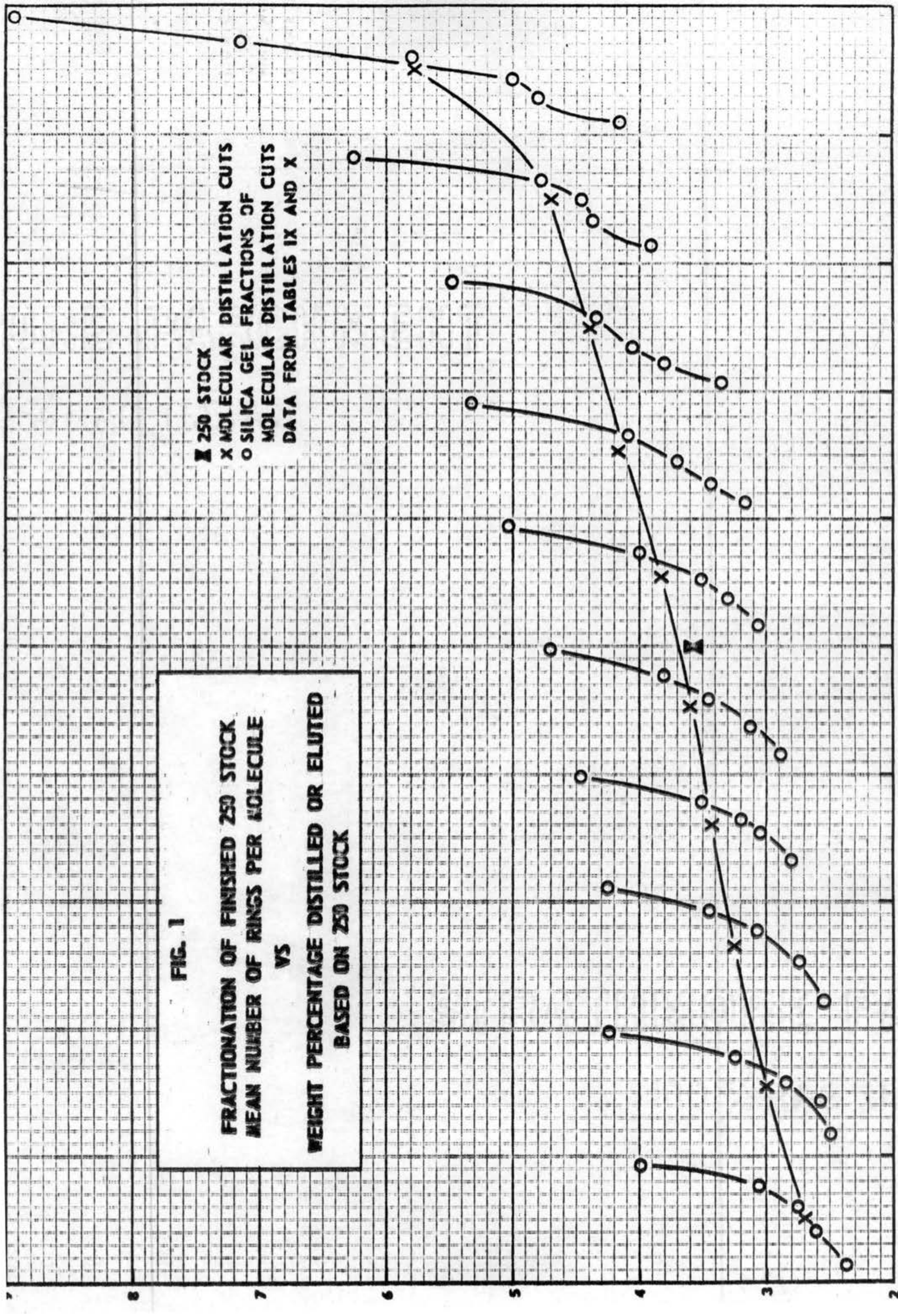

FIG. 1

FRACTIONATION OF FINISHED 250 STOCK
MEAN NUMBER OF RINGS PER MOLECULE
VS
WEIGHT PERCENTAGE DISTILLED OR ELUTED
BASED ON 250 STOCK

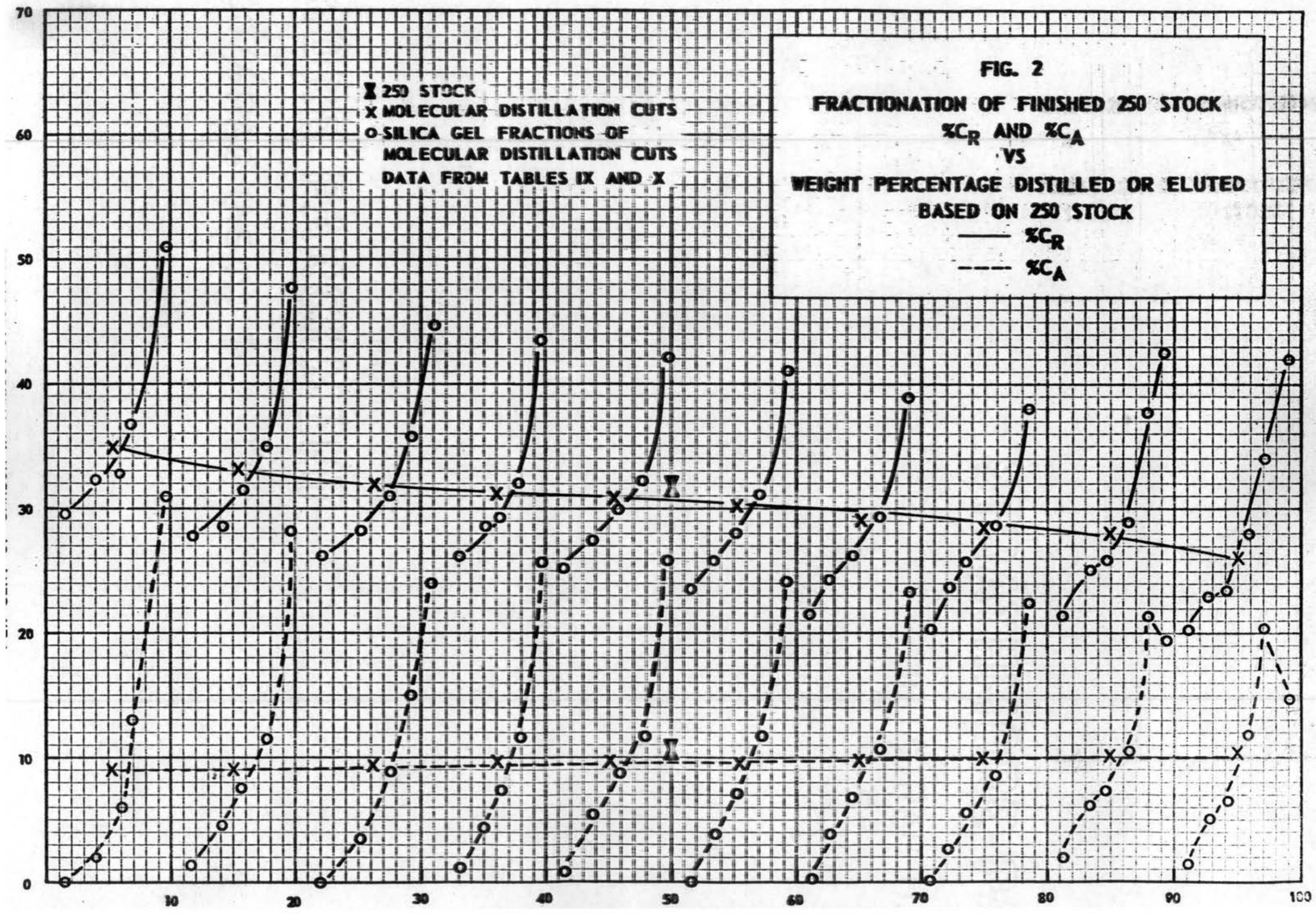

FIG. 2

FRACTIONATION OF FINISHED 250 STOCK
$\%C_R$ AND $\%C_A$
VS
WEIGHT PERCENTAGE DISTILLED OR ELUTED
BASED ON 250 STOCK

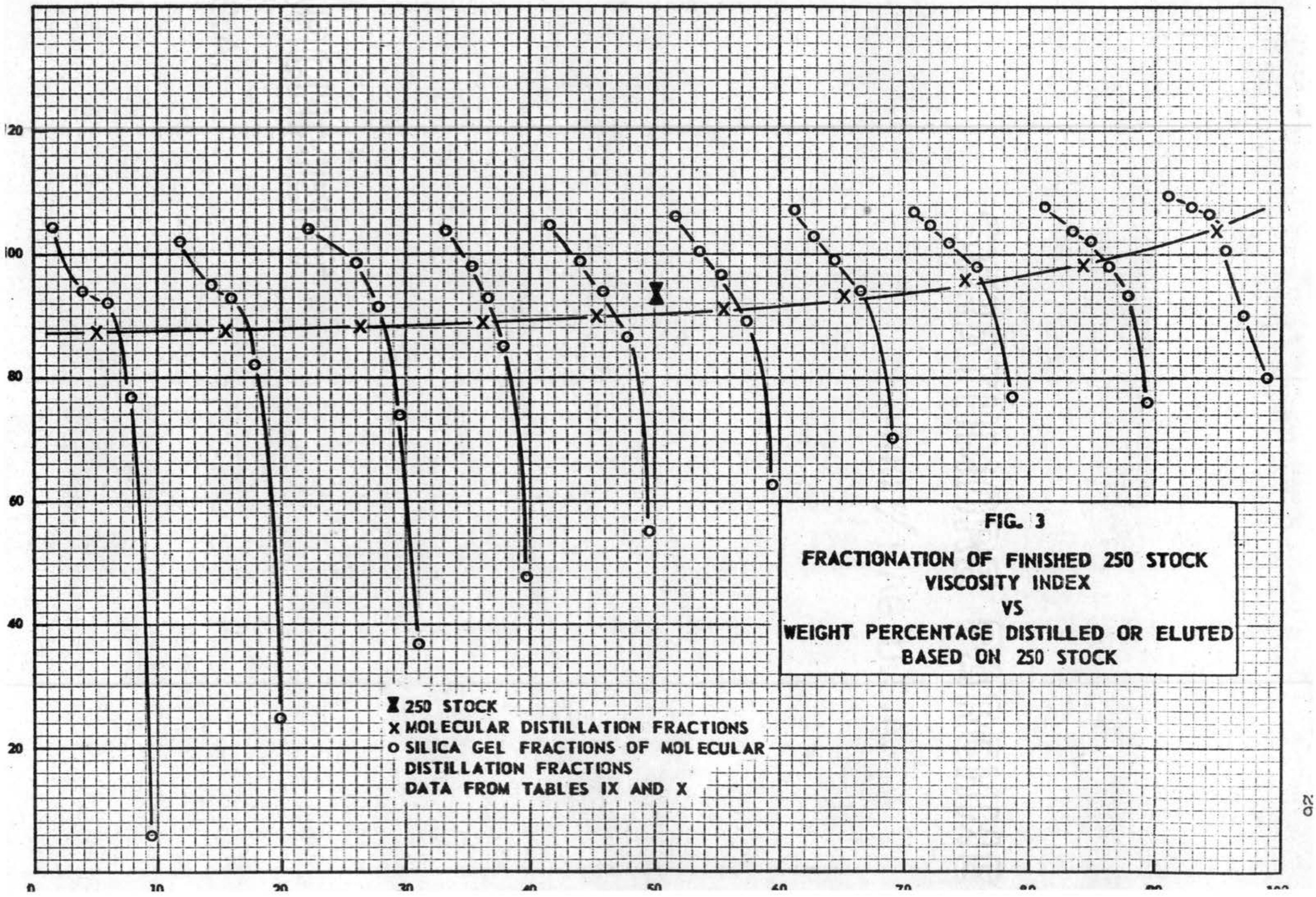

FIG. 3

FRACTIONATION OF FINISHED 250 STOCK
VISCOSITY INDEX
VS
WEIGHT PERCENTAGE DISTILLED OR ELUTED
BASED ON 250 STOCK

passes. The first five distillate fractions were each essentially homogenous with respect to molecular weight except that each contained about 15 per cent of low molecular weight highly aromatic material (see Figures 1, 2, 3, and 4). In each case this material is found in the fraction following the one it belongs in according to molecular weight. This apparent anomaly can be explained by the well known fact that aromatic hydrocarbons have lower vapor pressures than paraffinic or naphthenic hydrocarbons of the same molecular weight.

(2) Silica gel separates aromatics from paraffins and naphthenes in the low molecular weight range only slightly better than in the high molecular weight range. In no case was a sharp separation effected. This can be ascribed to the complexity of the molecules (see Figure 2).

(3) Confirming facts well known in light hydrocarbon separations, silica gel differentiates very little between paraffins and naphthenes in heavy lube stocks and does not separate with respect to molecular weight (see Table X and Figure 4).

(4) A high concentration of aromatic carbon in high molecular weight fractions does not result in such low viscosity indices as does a high concentration of aromatic carbon in low molecular weight fractions (see Figures 2 and 3).

E. Solvent Extraction of SAE 250 Stock:

Finished SAE 250 stock was also separated into three fractions by solvent extraction. Two solvents were employed (phenol and propane) in order to obtain different types of separation. Propane fractionation yielded fractions representing 30 per cent, 33.4 per cent, and 36.6

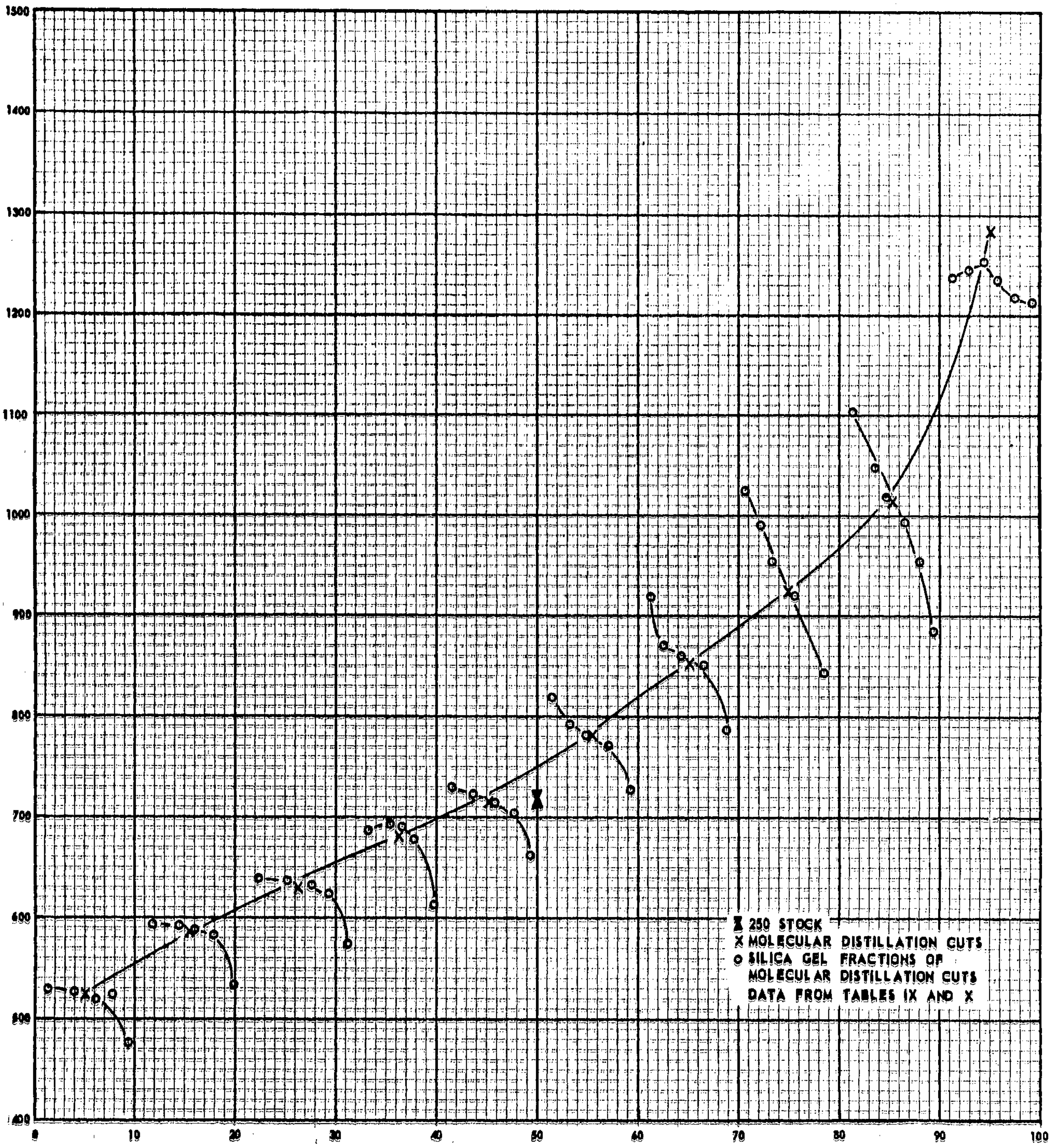

FIG. 4

FRACTIONATION OF FINISHED 250 STOCK
MOLECULAR WEIGHT
VS
WEIGHT PERCENTAGE DISTILLED OR ELUTED
BASED ON 250 STOCK

per cent of SAE 250 stock (B). Phenol extraction yielded fractions representing 30 per cent, 22.2 per cent and 47.8 per cent of SAE 250 stock (C). Operating conditions for these extraction runs are presented in Table XI and XII. Table XIII contains laboratory inspection data and structural group analyses on the fractions obtained by extraction with propane. Table XIV presents similar data on the fractions obtained by extraction with phenol. Pertinent data from the two latter tables are presented graphically in Figure 5. Figure 5 also shows comparable data from Table VIII on fractions of 250 stock obtained by molecular distillation. The data shown in Figure 5 allows a comparison to be made as to how the three methods of separation function on finished 250 stock. The results of this comparison are given below:

(1) Liquid propane exhibits selective solvent power for compounds having the following characteristics: low R_T, R_A, molecular weight, specific gravity, and viscosity. Since the percentages of the various types of carbon in the fractions do not vary notably, it is indicated that propane tends to separate mainly by molecular weight and to a lesser degree by molecular type.

(2) Anhydrous phenol exhibits selective solvent power for compounds having the following characteristics: high $\%C_A$, R_A, specific gravity and low molecular weight and viscosity index. Since the fractions vary widely in aromatic carbon content and viscosity index, it is indicated that phenol tends to separate mainly with respect to molecular type and to a lesser degree by molecular weight. It would be expected that as an oil becomes more homogenous as to molecular type, the molecular weights of the components will affect the separation to a great degree.

(3) The materials distilling most readily by molecular distillation

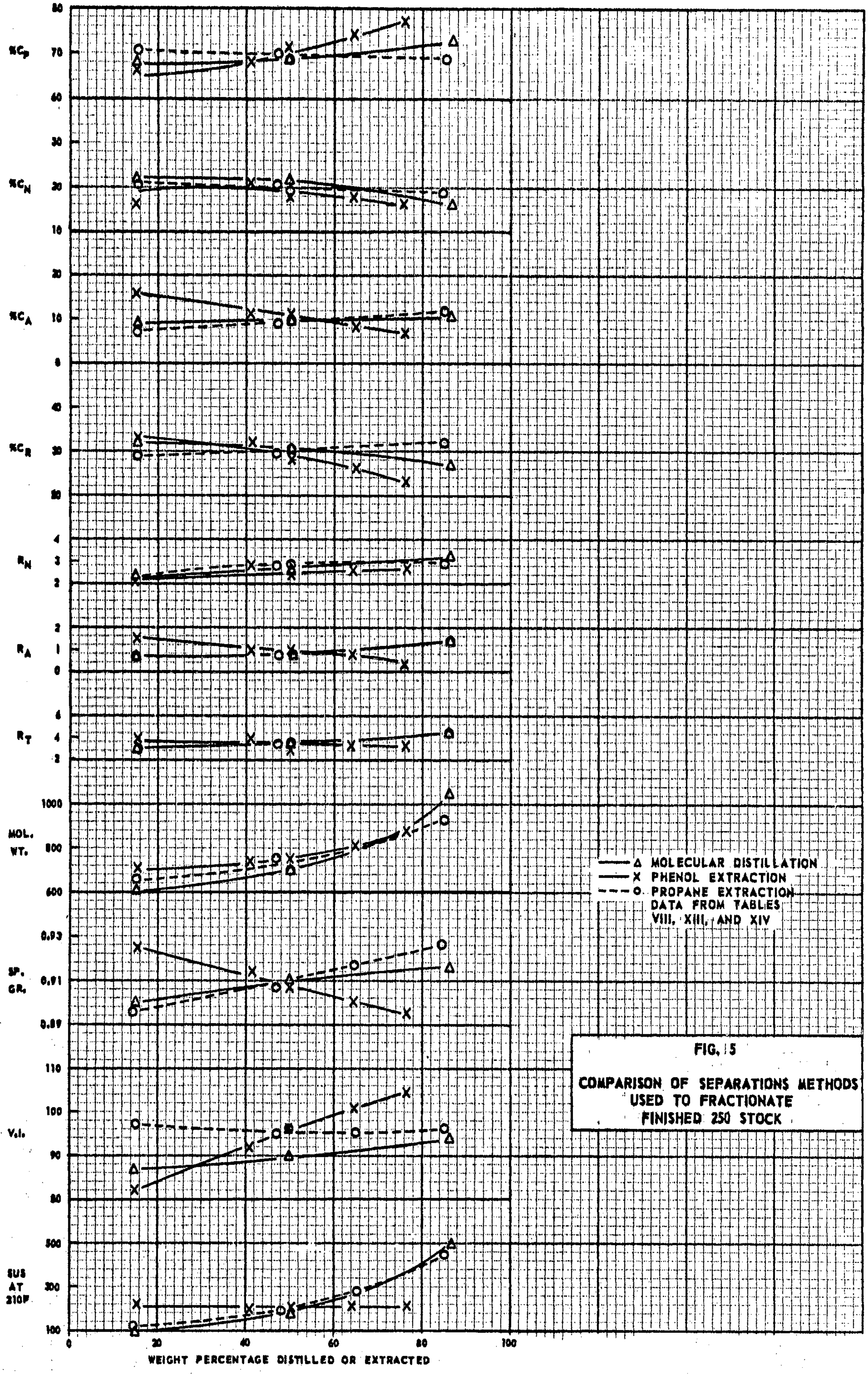

FIG. 5

COMPARISON OF SEPARATIONS METHODS USED TO FRACTIONATE FINISHED 250 STOCK exhibit the following characteristics: low molecular weight, specific gravity, viscosity, viscosity index, R_T, R_A, R_N, $\%C_A$, and high $\%C_R$, and $\%C_N$. This indicates that molecular distillation separates both with respect to molecular weight and molecular type. The apparent separation as to type is the result of the strong effect of vapor pressure on the separation. For any fraction the effect of vapor pressure causes the low molecular weight portion to be made up mainly of aromatics. As a result the fractions are not so homogeneous with respect to molecular weight as they might be otherwise.

F. Effect of the Phenol Extraction Process on Finished Oil:

The process of phenol extraction was further investigated by extracting a raw West Texas SAE 20 stock at several solvent to oil ratios. Laboratory inspection data and structural group analyses were determined on the raw SAE 20 stock, the dewaxed raw stock (0°F pour point) and each of the raffinates (dewaxed of 0°F pour point). The nominal solvent to oil ratios employed were 1.5, 2.0, 2.5, and 3.5. All data concerning these runs and analyses of the products are presented in Table XV. Figure 6 shows a graphical representation of the relations of ring content, carbon distribution, yield, and viscosity index with solvent to oil ratio.

The data contained in Table XV and Figure 6 show the effect on the structure of finished oil caused by increasing the severity of the solvent extraction process. Increased depth of extraction results in an oil having a higher viscosity index, higher percentages of both paraffinic and naphthenic carbon and a lower content of aromatic carbon. The yield, of course, decreases as the solvent to oil ratio is increased and apparently has not reached a minimum at the highest ratio employed. The other

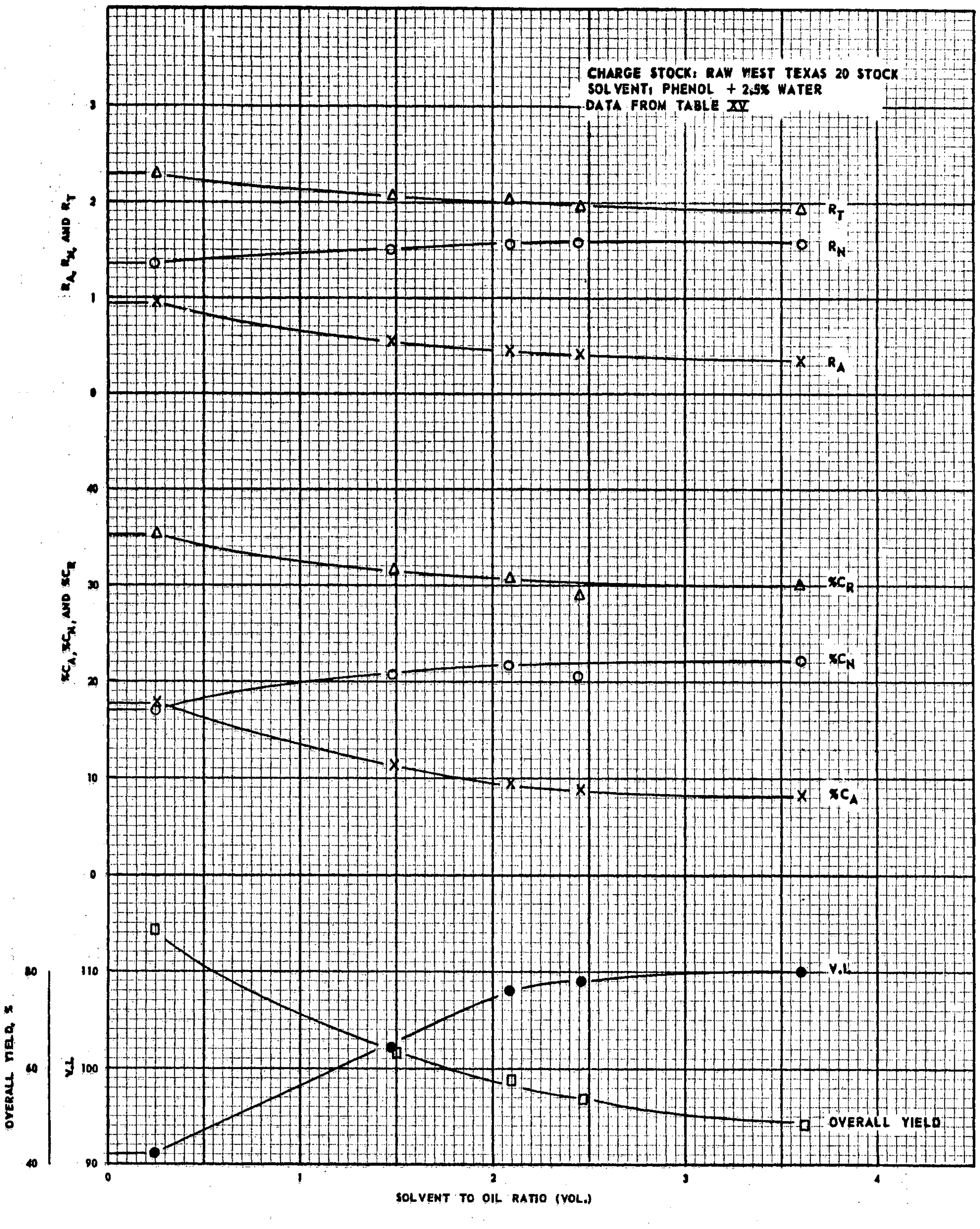

FIG. 6

COMPARISON OF FINISHED 20 STOCKS REFINED
AT VARIOUS SOLVENT TO OIL RATIOS
VI, YIELD, $\%C_A$, $\%C_N$, $\%C_R$, R_A, R_N, AND R_T
OF DEWAXED (0F POUR) RAFFINATES
VS
SOLVENT TO OIL RATIO

properties mentioned appear to have reached essentially constant values at the 3.5 to 1 ratio. This in effect means that above the 3.5 to 1 ratio phenol is no longer selective as to molecular type. Thus further extraction would yield a product having essentially the same properties as that produced at 3.5 to 1 ratio except the yield would be lower. The molecular weight of the finished oil showed only slight increases as a result of increased depth of extraction.

The above remarks indicate that phenol separates primarily with respect to molecular type. To be more specific it is a solvent for the more aromatic molecules. It appears to exhibit little affinity for the naphthenic structures.

V. SUMMARY

The composition of finished lubricating oils recently produced at the Kansas City Refinery has been investigated. The method used was structural group analysis. This method enables the composition of an oil fraction to be expressed in terms of ring content and the distribution of carbon with reference to aromatic, naphthenic and paraffinic hydrocarbon types. The oils subjected to the analysis were as follows:

1. Finished SAE 10 stock
2. Finished SAE 20 stock
3. "Special extract oil" - An oil rejected from the phenolic extract of 20 stock by the addition of water.
4. Finished SAE 50 stock
5. Finished SAE 25 stock
6. An extra heavy finished oil (690 SUS at 210°F)

Each of these oils except the SAE 10 stock and the "special extract oil" was fractionated by molecular distillation. The SAE 250 stock was also fractionated by solvent extraction with both phenol and propane. The molecular distillation fractions of this stock were further fractionated by adsorption on silica gel.

Several samples of finished oil were prepared from raw West Texas 20 stock and represent varying degrees of solvent refining.

All the above fractions of oils were analyzed to determine pertinent physical properties and structural characteristics. From these data the following abridged conclusions concerning the structure of finished oils and the methods of separation were reached:

1. The addition of West Texas crude to the Kansas City Plant charge stock caused an increase in the aromaticity of finished SAE 20 stock. It is to be expected that the other stocks were affected in a like manner.

2. The regular finished oils produced at the Kansas City Refinery are, in order of increasing paraffinicity: SAE 250 stock, SAE 20 stock, SAE 10 stock, and SAE 50 stock. The 590-second oil was less paraffinic than the SAE 250 stock.

3. Molecular distillations of the finished oils show that the heavier the grade of oil, the more heterogenous are its components with respect to molecular weight, viscosity, viscosity index, and the mean number of rings per molecule. This is partly a result of the natural complexity of heavy oils and partly caused by the refining procedures.

4. It appears that the deleterious effect of aromatics on viscosity index diminishes as the molecule becomes larger, with the percentage of carbon in aromatic structure remaining constant.

5. The extra heavy (590 SUS @ 210°F) oil showed a notable difference from other stocks in that the low molecular weight fractions of the heavy oil were <u>much</u> more aromatic than the high molecular weight fractions. This apparent anomaly is attributed to the various propane fractions employed to obtain this heavy stock.

6. While the generalization that aromatic hydrocarbons are the major contributors to low viscosity index is undoubtedly valid, this work definitely shows that there is no direct correlation between the absolute value of aromatic carbon content and V.I. thus, West Texas oil with the same V.I. and paraffinic carbon content as a Mid Continent oil was found to have approximately twice the aromatic carbon content.

7. Silica gel separates aromatics from naphthenes and paraffins in the low molecular weight range only slightly better than in the high molecular weight range. In no case was a sharp separation

effected.

8. Propane fractionation of finished 250 stock effects a separation mainly according to molecular weight and to a lesser degree by molecular type.

9. Phenol extraction of finished 250 stock effects a separation mainly according to molecular type and to a lesser degree by molecular weight.

10. The main effect on finished 20 stock of increasing the depth of phenol extraction is to increase the viscosity index and decrease the aromatic carbon content with an attendant decrease if yield. Increasing the depth of extraction beyond a certain point results in only very slight structural changes although the decrease in yield remains appreciable.

The n-d-m method of structural group analysis provides a tool which can be utilized to study separations processes when applied to petroleum. Investigations of this nature should result in a better understanding of the separations processes and of this complex mixture of hydrocarbons we call petroleum. Needless to say, as more becomes known about the composition of petroleum fractions and separations processes, these processes will operate more efficiently and economically. More work of this nature concerning the structural group analysis of heavy hydrocarbons is needed. Better correlations of physical properties might then be possible and indeed it may be possible to correlate particular structures with viscosity index, response to a particular additive, or the behavior of the oil in an automotive engine.

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NOMENCLATURE

c	Number of carbon atoms per molecule
c'	Number of carbon atoms per molecule after hydrogenation
C	Percentage carbon in molecule
C'	Percentage carbon in molecule after hydrogenation
c_R	Number of ring carbon atoms per molecule
$\%C_R$	Percentage of total carbon in ring structure
$\%C_A$	Percentage of total carbon in aromatic ring structure
$\%C_N$	Percentage of total carbon in naphthenic ring structure
$\%C_p$	Percentage of total carbon in paraffinic structure
d	Density
h	Number of hydrogen atoms per molecule
h'	Number of hydrogen atoms per molecule after hydrogenation
H	Percentage hydrogen in molecule
H'	Percentage hydrogen in molecule after hydrogenation
m, M	Molecular weight
M'	Molecular weight after hydrogenation
n	Refractive index
R_T, R	Mean total number of rings per molecule
R_A	Mean number of aromatic rings per molecule
R_N	Mean number of naphthenic rings per molecule
R_S	Average number of substantial rings per molecule
R.I.	Refractive index
SUS	Saybolt Universal Seconds
Vis.	Viscosity
V.I.	Kinematic viscosity index
V.G.C.	Viscosity-Gravity Constant

APPENDIX

A. MATERIALS

Lube Oil Fractions

1. Finished SAE 10 stock - This oil was obtained at the Kansas City Plant from a mixed crude containing 20 per cent Mid Continent "A", 20 per cent Mid Continent "B", and 60 per cent West Texas. Finished 10 stock was obtained from the crude mixture in the following manner: Distillation at atmospheric pressure was employed to remove that portion of the crude lighter than gas oil. From this bottoms product (topped crude) the gas oil, raw 10 stock, and raw 20 stock were distilled under reduced pressure. The bottoms product is called vacuum reduced crude. The overhead product was again subjected to vacuum distillation removing gas oil as overhead product, raw 10 stock as a side stream, and leaving the raw 20 stock as bottoms. The raw 10 stock was then solvent refined by solvent extraction with phenol and subsequent solvent dewaxing (to 0°F pour point) with liquid propane.

2. Finished SAE 20 stock #1 - This oil was obtained at the Kansas City Lube Plant from a mixed crude made up of 27 per cent Mid Continent "A", 27 per cent Mid Continent "B", and 46 per cent West Texas. The finished 20 stock was obtained from the crude in the manner described above (see finished SAE 10 stock).

3. Finished SAE 20 stock #2 - This oil was obtained at the Kansas City Lube Plant from a mixed crude containing 50 per cent Mid Continent "A" and 50 per cent Mid Continent "B". Its refining was essentially the same as finished SAE 20 stock #1.

4. Special Extract Oil - This is oil that was rejected from the phenolic extract of 20 stock by the addition of water. The oil was then

dewaxed to 0°F pour point. This product represents about 30 per cent of the total oil contained in the extract solution. The phenolic extract represents essentially the extract obtained during the refining of finished 20 stock #2. Additional processing was done at the Lube Oil Pilot Plant in Bartlesville.

5. Finished SAE 50 stock - This oil was obtained at the Kansas City Lube Plant from a mixed crude containing 27 per cent Mid Continent "A", 27 per cent Mid Continent "B" and 46 per cent West Texas. Vacuum reduced crude was obtained from this mixture in the manner described under SAE 10 stock. Raw 50 stock was obtained as overhead product by fractionation of the vacuum reduced crude with liquid propane. This raw 50 stock was refined by solvent extraction with phenol and subsequent solvent dewaxing with liquid propane.

6. Finished SAE 250 Stocks (A), (B), and (C) - These oils were obtained at the Kansas City Lube Plant from a mixed crude consisting of 20 per cent Mid Continent "A", 20 per cent Mid Continent "C", and 60 per cent West Texas. Raw 250 stock was obtained from the bottoms product of the 50 stock separation by propane fractionation of that bottoms product. Raw 250 stock was the overhead product and was refined by solvent extraction with phenol and solvent dewaxing with propane.

7. Extra Heavy Oil (590 SUS at 210°F) - This oil is from a mixed crude containing 25 per cent Mid Continent "A", 25 per cent Mid Continent "C" and 50 per cent West Texas. It was produced from the bottoms product resulting from the propane fractionation yielding 250 stock as overhead product. This bottoms product was obtained from the Kansas City Plant and the following refining was done at the Lube Oil Pilot Plant in Bartlesville. The bottoms product was propane fractionated yielding the heavy oil as overhead product. This raw heavy oil was refined by solvent

extraction with phenol and subsequent solvent dewaxing with methyl isobutyl ketone.

8. Raw West Texas 20 Stock - A sample of West Texas Crude obtained from the Shell pipeline at Yale, Oklahoma was processed at the Philtex Experiment Station in December, 1951. The crude was subjected to three flash distillations. The first, at atmospheric pressure, removed light products; the second, at reduced pressure, removed the remaining light ends and the 10 stock fraction; the third, at reduced pressure, removed the raw 20 stock as overhead product.

Adsorbent

1. Silica gel - Activated silica gel, mesh size through 200. 25 pound cans from Davidson Chemical Corp.

Solvents

1. Benzene and Methanol - Bakers Analyzed, meets ACS specifications, 5 lb. bottles.
2. n-Pentane - Phillips Petroleum Company, C. P. grade, 55 gallon drum.
3. Propane - Phillips Petroleum Company.
4. Phenol - Dow Chemical Co., 450 pound drums.
5. Methyl Isobutyl Ketone - Shell 55 gallon drums, commercial grade.

B. APPARATUS

Molecular Distillation

A CMS-5 Centrifugal Cyclic Batch Molecular Still made by the Vacuum Equipment Division of Distillation Products Inc., Rochester, New York was used. This still had capacity for a one liter charge and was capable of operating at pressures down to one micron.

Silica Gel Fractionation

A two liter glass burette having a nominal inside diameter of two inches was used as a column.

Propane Fractionation

This equipment consisted of supply tanks, charge pumps, preheaters for oil and propane, the fractionation column, flow meters for propane streams, and miscellaneous heaters and control instruments. All vessels and piping were fabricated from stainless steel and were tested with 1000 pounds per square inch of water pressure. The column was a vertical tower 25 feet tall and 3 inches inside diameter equipped with sampling valves at various points. The column contained horizontal half baffles staggered 2 inches apart. The bottom 3 feet of the column was contained in a constant temperature water bath, while the remainder was electrically heated. Oil was introduced into the column about the middle and propane about 3½ feet above the bottom. The interface was maintained about 2 feet from the bottom of the column. This was accomplished by a control instrument actuated by specific gravity differences at the interface. This device operated a motor valve in the bottoms product line. The maximum flow rates possible were about 14 gallons per hour of liquid propane and 2.5 gallons per hour of oil.

Phenol Extraction

This equipment consisted of supply tanks, charge pumps, preheaters for oil and phenol, the extraction column, and miscellaneous heaters and control instruments. The column was fabricated of glass and was 8 feet high, 2 inches inside diameter, and was equipped with a spinning band to obtain more efficient contacting. Temperature control was effected by enclosing the column in a heated box. The interface was maintained about 10 inches from the bottom by an instrument actuated by differences in conductivity of the two phases in the column. This instrument controlled a motor valve in the bottoms product line. Oil was fed to the column just above the interface and phenol about 3 inches from the top of the column. Feed rates to the column were of the order of 0.75 gallons per hour of oil.

C. SEPARATIONS PROCEDURES

Molecular Distillation

Nine molecular distillations were made with the centrifugal type molecular still. The following distillations were performed: finished SAE 20, SAE 50, SAE 250, and extra heavy oil were each cut into three fractions of approximately equal size; four batches of finished SAE 250 stock were cut into nominal 10 per cent fractions and the corresponding fractions blended together; one batch of extra heavy oil was cut into eleven fractions of approximately equal size.

To perform a distillation, the still was charged with about 900 ml of oil and the pressure reduced to about 20 microns. The rotor was heated to about 130 C and the oil completely cycled over the rotor. This degassed the oil. The rotor temperature was then raised until overhead was produced at the desired rate. The rate at which overhead product evolved was determined by the rotor temperature and the feed rate to the rotor. A complete pass was then made yielding an overhead cut of about 10 per cent. The rotor temperature was raised and the cycle repeated. This was continued until the desired number of fractions had been obtained or until the pressure rose above about 25 microns indicating incipient cracking.

To obtain the three fractions of SAE 20 stock it was necessary to make two complete passes to obtain each of the two overhead fractions. The two passes made for each fraction were both made at the same conditions of temperature and pumping rate. The same was true for the separation of SAE 50 stock into three fractions. For the separation of 250 stock into three fractions, three passes were necessary to obtain the first fraction, and five passes to obtain the second overhead fraction. The separation of extra heavy oil into eleven nominally equal cuts was accomplished by making only one pass for each of the first eight fractions, two for the ninth, and four for the tenth overhead fraction.

Silica Gel Fractionation

Each of the ten fractions of SAE 250 stock was fractionated into five or six cuts by adsorptive percolation through silica gel. Columns of gel two inches in diameter and thirty four inches high were used, each column containing approximately two and one half pounds of gel. The procedure was essentially the same for all runs. 200 ml of pentane were added to the column to wet the gel. About 300 g. of oil were mixed with an equal volume of pentane (to reduce viscosity) and this mixture was added to the top of the column. When all this had passed into the silica gel additional pentane was added until the effluent from the bottom of the column was essentially oil free. Benzene was then added until the benzene effluent was essentially oil free. Finally methyl alcohol was added to desorb the last of the oil. The effluent from the bottom of the column was collected in a number of fractions, the solvents removed by heating and laboratory test data obtained on the oil contained in each fraction.

Propane Fractionation

Finished SAE 250 stock (B) was fractionated into three parts with propane in the pilot plant column. Two runs were made; the first (H32) taking about 30 per cent of the 250 stock overhead and the second (H33) taking about 50 per cent overhead of the bottoms from the first run. The column temperature and propane to oil ratio were adjusted so as to give the desired yields for each run (see Table XI).

Phenol Extraction

Finished SAE 250 stock (C) was separated into three parts with anhydrous phenol in the pilot plant column. Two runs were made; the first (A-390) taking about 70 per cent of the 250 stock overhead and the second (A-391) taking about 69 per cent overhead of the overhead from the first run. The column temperatures and phenol to oil ratio were adjusted so as to give the desired yields for each run (see Table XII).

Raw West Texas 20 stock was also solvent extracted to several V.I. levels with aqueous phenol (2.5 per cent water). These raffinates and the raw stock itself were dewaxed to approximately 0°F pour point and thus, represent finished 20 stocks of different V.I. levels (see Table XV).

D. SUMMARY OF THE PROCEDURE FOR THE n-d-m METHOD

(FROM REFERENCE (18))

Procedure

Refractive index (n), density (d), and molecular weight (m) of the oil sample are determined first. Density and refractive index must be determined at the same temperature. Since a large number of the samples were very viscous and others showed separation of paraffin wax at 20°C, a temperature of 70°C was selected. Refractive indices were obtained with an Abbe refractometer and the results reported to four decimal places. Densities were determined at 70°C using pycnometers. These results were also reported to four decimal places. Molecular weights were determined by the ebullioscopic method using benzene as the solvent. Molecular weights determined in this manner are accurate to ± 2 per cent or better.

From these data the percentage carbon in aromatic structure ($\%C_A$) and the mean number of rings (aromatic + naphthenic) per molecule (R_T) are calculated by means of simple equations. The percentage of cyclic carbon ($\%C_R$) and the mean number of aromatic rings per molecule can be calculated by similar equations. In these latter equations the assumption is incorporated that all rings are six membered and condensed (if polycyclic) in such a way that each additional ring adds four carbon atoms. The percentages of carbon in paraffinic and naphthenic structures ($\%C_p$ and $\%C_N$) and the mean number of naphthene rings per molecule (R_N) are obtained by difference.

Regarding the formulas used the following can be noted. Calculations are made by means of simple relations between the molecular weight M, the factor Δ d which is the difference between the density of the sample itself and the density of the limiting normal paraffin, (this hypothetical normal paraffin has an infinite number of CH_2 groups and is in the liquid state) and finally the factor Δn which means the same difference for the refractive index. For the limiting paraffin the following constants have been chosen:

$$n\frac{70}{D} = 1.4600 \qquad d^{70} = 0.8280$$

In deriving the formulas it was found that two different equations were necessary for each magnitude because it was not possible to give one sufficiently accurate equation for the entire range. Most probably this is caused by the fact that the mean number of carbon atoms per ring decreases when the number of rings increases. For each quantity two equations are given, the first for the "low range", the second for "high range" values.

Calculation of Carbon Distribution and Ring Contest

Only the formulas utilizing measurements at 70°C are presented here: for those requiring measurements at 20°C the reader is referred to reference (18) page 340.

For observed values of density and refractive index at 70°C the factors X and Y are calculated by means of the following equations:

$$X = 2.42\ (n^{70} - 1.4600) - (d^{70} - 0.8280)$$

$$Y = (d^{70} - 0.8280) - 1.11\ (n^{70} - 1.4600)$$

Carbon distribution:

The percentage aromatic carbon $\%C_A$ is calculated from X and the molecular weight by means of one of the following equations:

if X is positive: $\%C_A = 410X + \frac{3660}{M}$

if X is negative: $\%C_A = 720X + \frac{3660}{M}$

The percentage cyclic (aromatic + naphthenic) carbon $\%C_R$ can be calculated from Y and the molecular weight:

$$\text{if Y is positive:} \quad \%C_R = 775Y - 3S + \frac{11500}{M}$$

$$\text{if Y is negative:} \quad \%C_R = 1400Y - 3S + \frac{12100}{M}$$

Where S is the sulfur content in weight per cent.

The percentage naphthenic carbon $\%C_N$ and the percentage paraffinic carbon are calculated as follows:

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

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

Ring Content

The mean number of aromatic rings per molecule R_A is calculated from X and the molecular weight by means of one of the following equations:

$$\text{if X is positive:} \quad R_A = 0.41 + 0.055\ MX$$

$$\text{if X is negative:} \quad R_A = 0.41 + 0.080\ MX$$

The mean total number of rings (aromatic + naphthenic) per molecule R_T can be calculated from Y and the molecular weight:

$$\text{if Y is positive:} \quad R_T = 1.55 + 0.146\ M\ (Y-0.005S)$$

$$\text{if Y is negative:} \quad R_T = 1.55 + 0.180\ M\ (Y-0.005S)$$

The mean number of naphthene rings per molecule R_N is found by difference as follows:

$$R_N = R_T - R_A$$

All data on carbon distribution and ring content in this report were calculated from nomographic forms of the above formulas.

TABLE VII

ANALYTICAL DATA AND STRUCTURAL GROUP ANALYSIS

OF SOME LUBE OILS

Lube Stock	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.G.C.*** 210°F	Density 70°C	R.I. 70°C	Mol. Wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Finished 10H Stock	123.7	41.30	99	.8603	.799	0.8240	1.4537	357	1.57	0.10	1.47	35.0	2.0	33.0	65.0
Finished 20H Stock (#1)	352.4	55.20	96	.8811	.811	0.8453	1.4679	390*	2.00	0.43	1.57	36.0	10.1	25.9	64.0
Finished 20H Stock (#2)	343.4	54.73	97	.8724	.800	0.8365	1.4617	390	1.94	0.25	1.69	34.0	7.5	26.5	66.0
Special Extract Oil**	1340	74.77	9	.9400	.880	0.9053	1.5062	410	3.10	1.22	1.98	47.8	22.7	25.1	52.2
Finished 50 Stock	1329	101.5	93	.8855	.802	0.8499	1.4710	647	2.68	0.58	2.10	26.0	6.5	19.5	74.0
Finished 250 Stock (A)	4278	205.5	93.5	.9094	.822	0.8744	1.4840	715	3.62	0.89	2.58	31.2	10.0	21.2	68.8
Finished 250 Stock (B)	4206	207.6	96	.9095	.822	0.8745	1.4845	715*	3.72	0.95	2.77	31.0	10.4	20.6	69.0
Finished 250 Stock (C)	4158	208.5	96	.9079	.820	0.8728	1.4844	741	3.43	1.00	2.43	29.0	11.0	18.0	71.0
Finished Extra Heavy Stock	27050	590	90	.9380	.845	0.9032	0.5040	912	5.10	2.00	3.10	34.0	17.5	16.5	66.0

* Estimated.

** Oil rejected from phenolic extract of 20 stock by water addition and dewaxed to 0°F pour.

*** Viscosity-gravity Constant (see reference 6 and 7).

TABLE VIII

MOLECULAR DISTILLATION OF SOME LUBE OILS INTO THREE FRACTIONS AND DATA ON THE FRACTIONS

Fraction	Pressure microns	Temp C	Wt. % of charge	Mid % wt.	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.G.C. 210°F	Density 70°F	R.I. 70°C	Mol. wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Charge (20 Stock #1)			100	50.0	352.4	55.20	96	.8811	.811	.8453	1.4679	390	2.00	0.43	1.57	36.0	10.1	25.9	64.0
1	7	120	32.5	16.2	208.7	46.77	95	.8782	.815	.8421	1.4654	350	1.95	0.35	1.60	39.0	10.6	28.4	61.0
2	1.5	140	33.4	49.2	344.1	54.63	96+	.8800	.811	.8440	1.4675	350	1.91	0.43	1.48	38.0	11.5	26.5	62.0
Btms			34.1	82.9	613.4	68.82	94	.8853	.811	.8495	1.4707	536	2.27	0.54	1.73	28.5	8.9	19.6	71.5
Charge (50 Stock)			100	50.0	1329	101.5	93	.8855	.802	.8499	1.4710	647	2.68	0.58	2.10	26.0	6.5	19.5	74.0
1	8	166	32.7	16.3	647	69.23	90	.8824	.806	.8469	1.4668	514	2.40	2.28	2.12	30.7	6.1	24.6	69.3
2	2.5	194	32.8	49.1	1227	96.45	92	.8838	.800	.8478	1.4693	695	2.52	0.54	1.98	23.3	6.6	16.7	76.7
Btms			34.5	82.7	3168	171.3	94	.8925	.801	.8573	1.4738	797	3.14	0.56	2.58	25.0	6.4	19.6	75.0
Charge (250 Stock (A))			100	50.0	4278	205.5	93.5	.9094	.822	.8744	1.4840	715	3.62	0.89	2.58	31.2	10.0	21.2	68.8
1	7	196	33.3	16.6	1369	99.6	87	.9013	.823	.8661	1.4793	600	2.98	0.69	2.29	32.0	9.7	22.3	68.0
2	1.5	238	34.5	50.5	4278	194.5	90	.9088	.822	.8736	1.4833	700	3.56	0.83	2.73	31.5	10.0	21.5	68.5
Btms			32.2	83.9	16670	504	94	.9159	.817	.8809	1.4890	1040	4.65	1.39	3.26	27.0	10.5	16.5	73.0
Charge (Heavy oil)			100	50.0	27050	590	90	.9380	.845	.9032	1.5040	912	5.10	2.00	3.10	34.0	17.5	16.5	66.0
1	1.5	225	31.6	15.8			61*	.9507		.9160	1.5140	658	4.25	1.93	2.32	39.0	23.0	16.0	61.0
2	2.4	278	31.6	47.4			86*	.9367		.9020	1.5031	975	5.30	2.00	3.30	32.0	16.0	16.0	68.0
Btms			36.8	81.6			102*	.9272		.8923	1.4956	1326	6.30	1.94	4.36	28.0	11.5	16.5	72.0

* Estimated from data in Table IX.

TABLE IX

MOLECULAR DISTILLATION OF 250 AND EXTRA HEAVY STOCKS INTO TEN FRACTIONS AND DATA ON THE FRACTIONS

Fraction	Pressure micron	Temp °C	Wt. % of charge	Mid.% wt.	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.O.C. 210°F	Color* NPA	Density 70°C	R.I. 70°C	Mol. wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Charge (250 Stock A)			100.0	50.0	4278	205.5	93.5	.9094	.822	Above 8	.8744	1.4840	715	3.62	0.89	2.58	31.2	10.0	21.2	68.8
1	10	168	10.1	5.1	800	75.40	87	.8983	.825	2 1/2	.8630	1.4763	524	2.72	0.55	2.17	34.9	9.1	25.8	65.1
2	3.5	183	10.6	15.4	1369	99.60	87	.9017	.824	2 1/2	.8665	1.4788	588	3.00	0.64	2.36	33.0	9.1	23.9	67.0
3	3.1	191	11.2	26.3	1923	121.5	88	.9041	.824	3 1/2	.8689	1.4804	633	3.23	0.70	2.53	32.0	9.5	22.5	68.0
4	2.8	201	8.5	36.1	2703	149.0	89	.9062	.823	4 -	.8712	1.4820	684	3.45	0.77	2.68	31.2	9.5	21.7	68.8
5	3.1	215	10.1	45.2	3673	180.9	90	.9085	.823	4 1/2	.8734	1.4833	718	3.60	0.85	2.75	31.1	9.7	21.4	68.9
6	3.1	230	9.8	55.4	5091	222.9	91	.9103	.822	6 -	.8753	1.4845	783	3.86	0.91	2.95	30.2	9.6	20.6	69.8
7	3.1	248	9.8	65.2	6898	275.5	93.5	.9121	.821	7	.8771	1.4857	854	4.17	1.00	3.17	29.1	9.8	19.3	70.9
8	3.1	269	9.8	75.0	9836	352	96	.9128	.819	Above 8	.8778	1.4867	927	4.39	1.10	3.29	28.5	9.5	19.0	71.5
9	3.1	290	10.0	84.9	15200	473	98.5	.9155	.819	Above 8	.8805	1.4881	1019	4.70	1.27	3.43	28.0	10.0	18.0	72.0
Btms			10.1	94.9	36692	878	104	.9208	.816	Above 8	.8859	1.4914	1281	5.80	1.65	4.15	26.3	10.5	15.8	73.7
Charge (Heavy stock)			100	50.0	27050	590	90	.9380	.845		.9032	1.5040	912	5.10	2.0	3.10	34.0	17.5	16.5	66.0
1	2.3	181	6.5	3.2	8000	195.1	29	.9612	.891		.9272	1.5238	514	3.70	1.94	1.76	44.0	29.5	14.5	56.0
2	1.1	199	8.4	10.7	12390	272.4	49	.9563	.880		.9215	1.5184								
3	1.5	219	10.1	19.9	16313	356	68	.9483	.865		.9135	1.5120								
4	1.3	234	9.4	29.7	19420	425	77	.9430	.856		.9091	1.5087								
5	1.7	249	9.6	39.2	22550	492	83.5	.9404	.850		.9054	1.5066								
6	2.4	265	7.2	47.6	24906	560	86	.9367	.844		.9020	1.5030	899	5.03	1.86	3.17	33.0	16.2	16.8	67.0
7	3.3	280	10.0	56.2	27817	621	87.5	.9336	.838		.8988	1.5010								
8	7.5	294	9.3	65.8	31600	693	95.5	.9318	.835		.8970	1.4995	1075	5.33	1.91	3.42	30.0	14.1	15.9	70.0
9	18.5	317	9.6	75.3		786		.9285	.829		.8935	1.4974								
10	25	339	9.9	85.0	34448	831	103	.9260	.825		.8911	1.4956	1202	5.70	1.90	3.80	28.0	12.3	15.7	72.0
Btms			10.0	95.0	58000	1290	109	.9216	.813		.8876	1.4918	1435	6.60	1.72	4.88	26.3	9.5	16.8	73.7

* ASTM designation D 155-45T (reference 1).

TABLE X

SILICA GEL PERCOLATION OF FRACTIONS OF SAE 250 OIL (A) OBTAINED BY MOLECULAR DISTILLATION AND DATA ON THE FRACTIONS

Dist Cut No.	Sil gel Cut No.	Based on Dist. Cut		Based on SAE 250		100 F°Vis SUS	210 F°Vis SUS	VI	Color NPA	R. I. 70°C	Density 70°C	Mol. Wt.
		Wt. %	Mid % Wt.	Wt. %	Cum Mid % Wt.							
1	1	28.1	14.1	2.84	1.42	497.1	64.79	104.5	0	1.4609	.8395	531
1	2	22.2	39.3	2.24	3.96	618.2	68.94	94	0	1.4658	.8486	527
1	3	17.4	59.0	1.76	5.96	675.0	71.16	92	1-	1.4694	.8528	522
1	4	18.6	77.0	1.88	7.78	1069	83.40	77	1 1/2	1.4865	.8769	524
1	5	13.7	93.0	1.38	9.41	6720	163.1	6	7	1.5292	.9396	476
2	1	31.2	15.6	3.31	11.75	793.7	81.20	102.5	0	1.4637	.8437	594*
2	2	16.8	39.6	1.78	14.30	1008	88.42	95	0	1.4678	.8486*	592*
2	3	14.1	55.1	1.49	15.93	1128	92.83	93	1	1.4728	.8576*	588*
2	4	23.2	73.7	2.46	17.91	1627	106.2	82	2-	1.4850	.8772*	584*
2	5	14.7	92.6	1.56	19.92	12270	240.2	25	8	1.5262	.9358	535*
3	1	26.0	13.0	2.92	22.16	978.5	92.13	104	0	1.4628	.8424	640*
3	2	27.0	39.5	3.02	25.13	1190	98.93	99	0	1.4674	.8497*	638*
3	3	17.0	61.5	1.90	27.59	1707	116.0	91.5	1 1/2	1.4787	.8660*	633*
3	4	13.2	76.6	1.48	29.28	3410	153.7	74	2-	1.4943	.8886*	625*
3	5	16.8	91.6	1.88	30.96	16500	297.9	37	Above 8	1.5240	.9316	575*
4	1	31.2	15.6	2.66	33.23	1312*	109.3*	104*	0	1.4643	.8453	687
4	2	16.7	39.5	1.42	35.27	1720*	122.4*	98*	1	1.4707	.8552	694
4	3	12.3	54.1	1.04	36.50	2280*	139.2*	93*	1 1/2	1.4780	.8646	692
4	4	20.7	70.6	1.76	37.90	3275*	162.1*	85*	2	1.4863	.8764	680
4	5	19.1	90.4	1.62	39.59	21480*	365*	48*	Above 8	1.5210	.9280	613
5	1	23.5	11.7	2.37	41.58	1735*	130.8*	105*	1-	1.4650	.8462	730*
5	2	21.2	34.1	2.14	43.84	2290*	147.2*	99*	1 1/2	1.4720	.8566*	725*
5	3	17.8	53.6	1.80	45.81	3170*	171.6*	94*	2	1.4802	.8686*	717*
5	4	19.8	72.4	2.00	47.71	4650*	203.4*	87*	3 1/2	1.4889	.8812*	705*
5	5	17.7	91.2	1.79	49.61	36500*	507*	55*	Above 8	1.5222	.9296	663*
6	1	22.6	11.3	2.21	51.60	2140	150.5	106	1-	1.4653	.8469	820*
6	2	14.5	29.8	1.42	53.42	2870	171.7	100.5	1	1.4708	.8550*	793*
6	3	21.0	47.6	2.06	55.16	3760	196.0	97	2 1/2	1.4778	.8653*	782*
6	4	21.2	68.7	2.08	57.23	6040	242.5	89	3 1/2	1.4897	.8827	772*
6	5	20.7	89.6	2.03	59.28	44900	597	62.5	Above 8	1.5210	.9283	727*
7	1	16.6	8.3	1.62	61.11	2750*	180.7*	107*	1-	1.4656	.8465	920*
7	2	16.2	24.7	1.59	62.71	3490*	199.7*	103*	1 1/2	1.4708	.8549*	870*
7	3	18.7	42.1	1.84	64.43	4710*	232.1*	99*	2 1/2	1.4780	.8653	860*
7	4	25.5	64.2	2.50	66.60	10450*	283*	94*	4	1.4872	.8788*	850*
7	5	23.9	88.5	2.25	68.97	61780*	753*	70*	Above 8	1.5199	.9273	785*
8	1	14.8	7.4	1.46	70.83	3670*	219.1*	107*	1-	1.4660	.8474	1026
8	2	12.5	21.0	1.22	72.17	4460	242.3*	105*	1 1/2	1.4708	.8560	990
8	3	14.6	34.6	1.44	73.50	5720*	272.4*	102*	3-	1.4752	.8641	955
8	4	31.3	57.5	3.06	75.75	8310*	326*	98*	4-	1.4840	.8753	920
8	5	26.8	86.6	2.62	78.59	81000*	927*	77*	Above 8	1.5182	.9250	843
9	1	28.0	14.0	2.80	81.30	5520	290	107.5	2-	1.4691	.8529	1105*
9	2	14.2	35.1	1.42	83.41	8940	368	103.5	4-	1.4788	.8675	1050*
9	3	13.2	48.8	1.32	84.78	10500	397	102	5-	1.4817	.8715	1020*
9	4	19.3	65.1	1.93	86.40	14520	465	98.5	6	1.4893	.8828	994*
9	5	12.4	80.9	1.24	87.99	123000	1234	83	Above 8	1.5187	.9270	955*
9	6	12.9	93.5	1.29	89.25	215500	1685	76	Above 8	1.5174	.9302	885*
Btms	1	21.8	10.9	2.20	91.10	9600	436	109.5	2-	1.4692	.8528	1239
Btms	2	13.6	29.4	1.54	92.87	15200	558	107.5	4 1/2	1.4774	.8656	1245*
Btms	3	15.2	43.8	1.37	94.32	17730	602	106.5	4	1.4805	.8695*	1253
Btms	4	11.8	56.5	1.19	95.60	44400*	919	100.5*	Above 8	1.4943	.8900	1235*
Btms	5	17.1	70.9	1.73	97.06	292000*	2135	90*	Above 8	1.5167	.9231	1319
Btms	6	20.5	89.7	2.08	98.96	542000*	2595	80*	Above 8	1.5140	.9302	1213

* Obtained by interpolation

TABLE X (Continued)

Dist Cut No.	Sil gel Cut No.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$	Through** with	Sp. Gr. 60/60°F	V.G.C. 210°F
1	1	2.39	0	2.39	29.4	0	29.4	70.6	P	.8754	.799
1	2	2.63	0.10	2.53	32.2	2.1	30.1	67.8	P	.8843	.809
1	3	2.66	0.31	2.35	32.8	6.0	26.8	67.2	P	.8883	.814
1	4	3.06	0.85	2.21	36.8	13.0	23.8	63.2	P	.9119	.840
1	5	4.00	1.90	2.10	51.0	31.0	20.0	49.0	B,A	.9741	.911
2	1	2.50	0.07	2.43	27.8	1.4	26.4	72.2	P	.8796	.799
2	2	2.57	0.30	2.27	28.4	4.5	23.9	71.6	P	.8845	.804
2	3	2.85	0.44	2.41	31.1	7.9	23.2	68.9	P	.8930	.814
2	4	3.23	0.80	2.43	34.9	11.5	23.4	65.1	P	.9102	.834
2	5	4.22	1.93	2.29	47.5	28.3	19.2	52.5	B,A	.9703	.900
3	1	2.55	0.16	2.39	26.1	0	26.1	73.0	P	.8784	.795
3	2	2.75	0.24	2.51	28.1	3.3	24.8	71.9	P	.8854	.802
3	3	3.08	0.65	2.43	31.0	9.0	22.0	69.0	P	.9013	.820
3	4	3.45	1.17	2.28	35.7	15.0	20.7	64.3	P	.9262	.849
3	5	4.24	2.01	2.23	44.6	24.0	20.6	55.4	B,A	.9662	.891
4	1	2.80	0.02	2.78	26.1	1.0	25.1	73.9	P	.8811	.795
4	2	3.05	0.30	2.75	28.5	4.1	24.4	71.5	P	.8903	.806
4	3	3.20	0.65	2.55	29.2	8.1	21.1	70.8	P	.8999	.816
4	4	3.50	0.97	2.53	31.8	11.5	20.3	68.2	P	.9114	.827
4	5	4.45	2.00	2.45	43.5	25.4	18.1	56.5	B,A	.9626	.885
5	1	2.88	0.02	2.86	25.2	0.6	24.6	74.8	P	.8820	.794
5	2	3.12	0.40	2.72	27.4	5.4	22.0	72.6	P	.8921	.805
5	3	3.45	0.73	2.72	30.0	8.7	21.3	70.0	P	.9038	.817
5	4	3.80	1.04	2.76	32.0	11.7	20.3	68.0	P	.9162	.831
5	5	4.70	2.20	2.50	42.0	25.6	16.4	58.0	B,A	.9643	.881
6	1	3.05	0	3.05	23.5	0.2	23.3	76.5	P	.8826	.791
6	2	3.30	0.33	2.97	25.8	4.0	21.8	74.2	P	.8910	.800
6	3	3.50	0.64	2.86	28.0	7.0	21.0	72.0	P	.9006	.811
6	4	4.00	1.11	2.89	31.1	11.6	19.5	68.9	P	.9205	.835
6	5	5.02	2.11	2.91	41.0	24.0	17.0	59.0	B,A	.9630	.878
7	1	3.17	0	3.17	21.5	0.2	21.3	78.5	P	.8823	.787
7	2	3.43	0.33	3.10	24.3	3.8	20.5	75.7	P	.8904	.797
7	3	3.70	0.68	3.02	26.3	6.9	19.4	73.7	P	.9006	.809
7	4	4.10	1.12	2.98	29.4	10.5	18.9	70.6	P	.9138	.830
7	5	5.32	2.35	2.97	39.0	23.1	15.9	61.0	B,A	.9619	.874
8	1	3.37	0	3.37	20.3	0	20.3	79.7	P	.8813	.793
8	2	3.80	0.23	3.57	23.8	2.4	21.3	76.2	P	.8915	.796
8	3	4.07	0.56	3.51	25.8	5.2	20.6	74.2	P	.8995	.805
8	4	4.34	0.94	3.40	28.6	8.5	20.1	71.4	P	.9103	.816
8	5	5.38	2.43	3.05	38.1	22.2	15.9	61.9	B,A	.9597	.867
9	1	3.90	0.13	3.77	21.5	1.8	19.7	78.5	P	.8884	.787
9	2	4.37	0.72	3.65	25.1	6.0	19.1	74.9	P	.9028	.805
9	3	4.45	0.87	3.58	26.0	7.1	18.9	74.0	P	.9065	.809
9	4	4.78	1.24	3.54	29.0	10.2	18.8	71.0	P	.9178	.821
9	5	6.25	2.70	3.55	37.8	21.2	16.6	62.2	B	.9613	.865
9	6	6.50	2.18	4.32	42.5	19.3	23.2	57.5	B,A	.9048	.866
Btms	1	4.15	0.13	4.02	20.4	1.3	19.1	79.6	P	.8884	.783
Btms	2	4.80	0.73	4.07	23.0	5.0	18.0	77.0	P	.9009	.796
Btms	3	5.00	0.97	4.03	23.5	6.5	17.0	76.5	P	.9046	.800
Btms	4	5.82	1.83	3.99	28.0	11.7	16.3	72.0	P	.9248	.821
Btms	5	7.17	3.26	3.91	34.3	20.2	14.0	65.8	B	.9577	.854
Btms	6	8.95	2.29	6.66	42.0	14.6	27.4	58.0	B,A	.9648	.860

** P = Pentane, B = Benzene, A = Methanol

TABLE XI

PROPANE FRACTIONATION OF 250 STOCK (X-166)

OPERATING CONDITIONS

Run No.	H 32	H 33
Charge Stock	250 Stock	H 32 Bottoms
Top Column temp., F	186	169
Oil feed temp., F	178	162
Propane feed temp., F	171	156
Bottom column temp., F	171	155
Column pressure, psig.	650	650
Oil charge rate, gph 60 F	1.476	1.610
Propane to Oil ratio, vol.	8.84	7.79
Yield based on 250 stock		
Wt. % ohp	30.0	33.4
Wt. % btms	70.0	36.6

TABLE XII

ANHYDROUS PHENOL FRACTIONATION OF 250 STOCK (X-182)

OPERATING CONDITIONS

Run No.	A390	A391
Charge stock	X182	A390 ohp
Top column temp., F	224	248
Btm column temp., F	204	224
Oil charge rate, gph 60 F	0.73	0.59
Phenol to oil ratio, vol.	3.6	5.1
Yield base on 250 stock		
Wt. % ohp	70	47.8
Wt. % btms	30	22.2

TABLE XIII

PROPANE FRACTIONATION OF 250 STOCK (B)

ANALYTICAL DATA AND STRUCTURAL GROUP ANALYSIS ON PRODUCTS

	Based on 250 Stock																
Fraction	Wt. %	Mid % Wt.	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.G.C. 210°F	Density 70°C	R.I. 70°C	Mol. Wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Charge (250 Stock B)	100.0	50.0	4206	207.6	96	.9095	.822	.8745	1.4845	715*	3.72	0.95	2.77	31.0	10.4	20.6	69.0
Primary (H32) ohp	30.0	15.0	1404	107.8	97	.8944	.813	.8590	1.4747	650	2.91	0.56	2.35	28.8	7.5	21.3	71.2
Primary (H32) btms	70.0	65.0	7159	286	95	.9161	.825	.8812									
Secondary (H33) ohp	33.4	46.7	3538	185.4	95	.9065	.820	.8715	1.4820	752	3.66	0.80	2.86	30.0	9.0	21.0	70.0
Secondary (H33) btms	36.6	84.7	15021	450.6	96	.9251	.831	.8902	1.4920	920	4.32	1.38	2.94	31.0	11.8	19.2	69.0

* Estimated

TABLE XIV

ANHYDROUS PHENOL FRACTIONATION OF 250 STOCK (C)

ANALYTICAL DATA AND STRUCTURAL GROUP ANALYSIS ON PRODUCTS

	Based on 250 Stock																
Fraction	Wt. %	Mid % Wt.	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.G.C. 210°F	Density 70°C	R.I. 70°C	Mol. Wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Charge (250 Stock C)	100	50.0	4158	208.5	96	.9079	.820	.8728	1.4844	741	3.43	1.00	2.43	29.0	11.0	18.0	71.0
Primary (A390) Btms	30.0	15.0	6147	230.9	82.5	.9259	.842	.8910	1.4974	699	3.72	1.45	2.27	33.1	16.4	16.7	66.9
Primary (390) ohp	70.0	65.0	3753	205.2	101	.8999	.810	.8645	1.4788	806	3.38	0.80	2.58	26.0	8.1	17.9	74.0
Secondary (A391) Btms	22.2	41.1	4256	201.8	92	.9138	.828	.8788	1.4870	735	3.80	0.96	2.84	31.6	10.6	21.0	68.4
Secondary (A391) ohp	47.8	76.1	3652	211.0	104.5	.8937	.800	.8583	1.4750	870	3.28	0.68	2.60	23.1	6.8	16.3	76.9

TABLE XV

ANALYTICAL AND STRUCTURAL DATA ON SAMPLES OF 20 STOCK THAT REPRESENT DIFFERENT DEGREES OF REFINING

Sample	Phenol to Oil Ratio	Extraction Yield Vol.%	Dewaxing Yield Vol.%	Yield Based on Raw Stock Vol.%	100°F Vis SUS	210°F Vis SUS	VI	Sp. Gr. 60/60°F	V.G.C. 210°F	Density 70°C	R.I. 70°C	Mol. Wt.	R_T	R_A	R_N	$\%C_R$	$\%C_A$	$\%C_N$	$\%C_P$
Raw 20 stock, X-169	-	-	-	100	-	52.74	-	.8983	.836	.8630	1.4835	425	2.08	0.91	1.17	33.5	17.5	16.0	66.5
Dewaxed raw stock	0	100	88.5	88.5	365.0	55.14	91	.9040	.841	.8688	1.4863	431	2.30	0.94	1.36	35.0	17.8	17.2	65.0
Extr. and dewax. raw stock	1.49	80.9	78.0	63.2	312.8	53.73	104	.8849	.818	.8493	1.4718	446	2.06	0.57	1.49	31.9	11.1	20.8	68.1
Extr. and dewax. raw stock	2.08	73.3	78.2	57.3	292.2	53.36	108	.8793	.810	.8434	1.4673	453	2.01	0.45	1.56	30.8	9.1	21.7	69.2
Extr. and dewax. raw stock	2.46	71.8	74.2	53.3	289.7	53.22	109	.8771	.808	.8412	1.4660	468	1.96	0.40	1.56	29.0	8.5	20.5	71.0
Extr. and dewax. raw stock	3.62	63.3	75.7	48.0	289.9	53.39	110	.8752	.805	.8393	1.5655	451	1.94	0.36	1.58	20.0	8.0	22.0	70.0
Slack wax* from dewaxing of raw stock	-	-	11.5	11.5	-	46.76	-	.8574	.787	.8214	1.4584	400**	1.20	0.45	0.75	24.7	10.1	14.6	75.3

* Melting point = 125°F

** Estimated

VITA

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