PHASE BEHAVIOR OF
PHENOL - LUBRICATING OIL SYSTEMS

BY

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ABSTRACT

Solvent extraction has played an increasingly important part in the petroleum industry in recent years. Phenol is one of the major solvents used by the petroleum industry.

Very few data are available in the literature for the system: phenol-lubricating oil. Even fewer data are available wherein the effect of water injection is taken into consideration. Therefore it was undertaken to investigate the phase behavior of several phenol-lube oil systems. Water injection was investigated.

The equilibrium data obtained are presented in the form of Ponchon type diagrams. Typical problem solutions are demonstrated and stage calculations for countercurrent extractions are made.

PHASE BEHAVIOR OF PHENOL-LUBRICATING OIL SYSTEMS

I. INTRODUCTION

The role of solvent extraction in petroleum refining is to bring about a separation of the undesirable compounds from the more desirable constituents of petroleum. The extraction is usually carried out on a petroleum fraction having a relatively narrow boiling point and molecular weight range, and hence is difficult to separate by distillation. Distillation accomplishes the first separation of the complex crude oil into fractions each having fewer chemical constituents than the original crude. In the lower boiling fractions of the crude, extremely pure compounds can be made by distillation, e.g., propane, butane, and pentane. As the boiling point and molecular weight of the fractions increase, further separation by distillation becomes increasingly difficult and requires very high temperatures. In the heavier fractions, such as the various SAE grades of lubricating oils, further separation by distillation would not entirely eliminate the undesirable constituents and therefore some other method of separation, such as solvent extraction, must be used.[1]

Whereas distillation employs difference in boiling points to bring about a separation, solvent extraction capitalizes on the difference in solubility of the compounds in the selective solvent to affect a separation. Under severe conditions of extraction, a point can be reached where more drastic treatment will produce no further improvement. This is comparable to the difficulty in separating a very narrow boiling fraction by distillation.

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[1] T. G. Hunter, The Science of Petroleum, Vol. III, pp. 1818, London, England, Oxford University Press, 1938.

However, for the solvent extraction of lubricating oils, the treatment is usually not severe and the separation is not difficult. In addition to the relative ease of separation by extraction, extraction has the attractive feature of being carried out at much lower temperatures than distillation.

Where solvent extraction is employed to separate the undesirable constituents from lube oils, the equilibria involved cannot be represented by any simple means. Exact representation could be achieved only if complete knowledge of the compounds in the lube oils was available. However, equilibria characterization of the type devised by Hunter and Nash leads to an approximate but useful solution.[1,5] The Ponchon type diagram, applied to solvent extraction, uses the same method of approach as Hunter but presents the data in a different manner.[2,3] The Ponchon diagram presents the data on rectangular coordinates and is a plot of solvent content of raffinate and extract phases versus an additive property of the solvent free oil. Refractive index is an additive property of the oil as shown by Figure 15 and is used exclusively throughout this report.

In this report the terms refractive index and quality of oil have been used to refer to the same property of the oil. In general, quality is understood to mean viscosity index. It has been found that a linear relationship exists between refractive index and viscosity index of raffinates from a given stock. Since most raffinate oils are dewaxed to approximately

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[1] Ibid., Vol. III, pp. 1818. Op. cit.

[5] R. E. Treybal, Liquid Extraction, pp. 34, First Edition, New York, N. Y., McGraw-Hill Book Company, 1951.

[2] J. O. Maloney and A. E. Schubert, "Transactions of the American Institute of Chemical Engineers", 36, 741 (1940).

[3] Ponchon, "Tech Moderne", Vol. 13, (1921), pp. 20.

$0^\circ F$ pour point, the viscosity index of the dewaxed raffinate is more significant than that of the waxy raffinate. A useful tool is the relationship between refractive index of waxy raffinate and viscosity index of dewaxed raffinate (Figure 16). If it is desired to produce a dewaxed oil of a certain viscosity index, the corresponding refractive index of waxy raffinate which must be made by solvent extraction can be read from the graph. By use of this relationship, quality of raffinate oil can be used on the phase diagram in the form of refractive index.

This paper presents the derivations of the basic equations for the Ponchon method as applied to phenol extraction, with water injection, of lube oils. The solutions of typical extraction problems are demonstrated. Equilibrium data for several oils and continuous countercurrent extraction data are presented. By use of equilibrium data and the continuous extraction data, the number of equilibrium stages was calculated.

II. DESCRIPTION OF PROCESS

The extraction apparatus used in this work was a spinning band type countercurrent extraction column. (Refer to Fig. 1). Oil is fed to the column near the bottom of the column just above the interface. Phenol is charged at the top of the column. Water is injected into the extract phase near the bottom of the column. The addition of water to the extract phase greatly alters the solvent properties of phenol. The solubility of the oil in phenol is reduced; thus an oil phase will separate from the extract phase and flow up the column.

A temperature gradient of 20-30°F is maintained over the column, with the top of the column being at the highest temperature. The purpose of the temperature gradient is to provide reflux by rejecting oil from the extract phase as it moves from a high temperature region to a low one. No external recycle is used in the phenol extraction process. The temperature gradient and water injection provide the reflux.

The water injection rate is usually 10 per cent of the phenol charge rate. Since the amount of phenol reaching the bottom of the column will vary, depending upon the amount that is dissolved in the raffinate, the water concentration will vary with operating conditions. The extract oil consists of compounds of varying degrees of aromaticity and it would be expected that the oil rejected by the addition of water would be less aromatic than that oil retained in solution. That this is the case is shown quite clearly by the equilibrium diagrams in this paper. (See Figures 10 and 12).

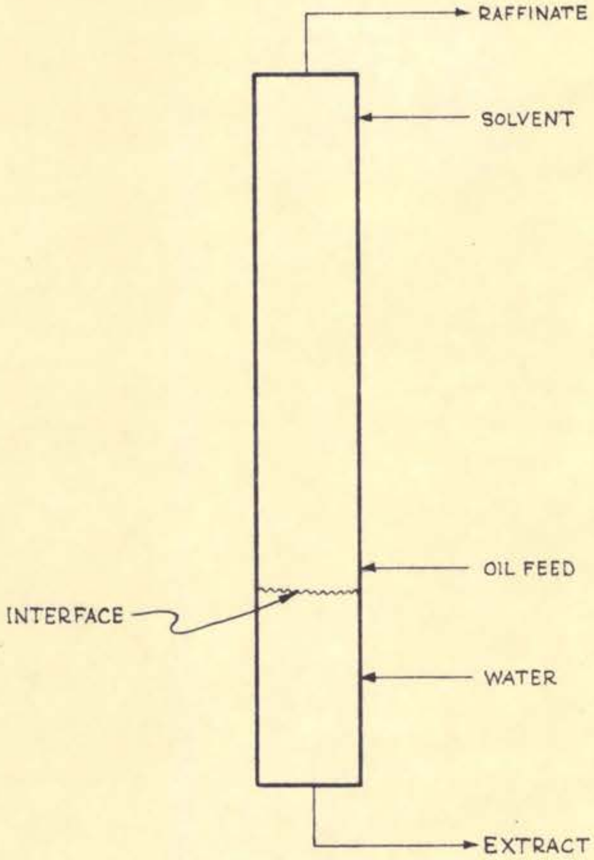

FIG. 1

SCHEMATIC DIAGRAM OF PHENOL EXTRACTION COLUMN

In the extraction of SAE 10 10 and 20 oils, phenol containing 2.5 per cent water by weight is often used as the solvent. Anhydrous phenol is employed almost exclusively for the extraction of the heavier stocks.

This brief description of the phenol extraction process was given in order to point out that the use of equilibrium data for calculations pertaining to the process is made difficult by four factors:

1. The use of two solvents for any given extraction. In the oil-continuous, or upper, section of the column, the solvent is anhydrous phenol or phenol containing 2.5% water, depending upon whether a light or heavy stock is being extracted. In the phenol-continuous, or bottom, section of the column, the solvent is phenol containing 12-20 per cent water, depending upon operating conditions. This difficulty is overcome by the use of two sets of equilibrium data plotted on the same diagram.

2. The oil used for reflux is not the same oil as that withdrawn as bottoms product; thus no reflux ratio can be calculated directly but must be done indirectly. With the use of two sets of data as previously mentioned, this problem is circumvented.

3. The column is not operated under isothermal conditions. In order to represent the process exactly, equilibrium data at several temperatures would be needed. Even if the data were available the graphical calculations would be reduced to a laborious trial and error process.

It has been found that an isothermal extraction, at the average temperature of the column when a gradient is used will give a raffinate of the same yield and quality as that produced when a gradient is employed. Therefore equilibrium data at the average temperature of the extraction process should prove accurate and at the same time the calculations would be easier and less time-consuming.

4. The application of stage calculations to continuous, countercurrent apparatus is valid only if the diffusion rates, and thus approach to equilibrium conditions is very rapid. In obtaining equilibrium data, contact time is sufficient for equilibrium conditions to prevail and hence unequal diffusion rates of the individual components do not affect the results. In the countercurrent extraction of materials with components of grossly unequal diffusion rates, analysis of the streams leaving the apparatus would not match the data obtained by batch extraction.

III. DERIVATION OF BASIC EQUATIONS

In the mathematical analysis of solvent extraction, the following nomenclature will be used:

F = oil feed rate, volume/unit time, solvent free basis

R = raffinate flow, volume/unit time, solvent free basis

E = extract flow, volume/unit time, solvent free basis

Y = yield of raffinate oil, volume fraction

Q = solvent flow, volume solvent/volume solvent free raffinate

P = solvent flow, volume solvent/volume solvent free charge oil = QY

W = water injection rate, volume water/volume solvent free extract

S = solvent content of indicated phase, volume solvent/volume solvent free oil

subscript e = denotes solvent rich, or extract phase

" r = denotes oil rich, or raffinate phase

" f = denotes oil feed

" 1, 2, n = denotes equilibrium stage number

X = some property of the oil which is additive on a volume basis. In this thesis X is limited to refractive index.

Now, writing material balances around the entire column (refer to Fig. 1):

Oil Balance

$$F = R + E \tag{1}$$

Solvent Balance

$$QR + WE + FS_f = S_rR + S_eE \tag{2}$$

Since X is an additive property (as shown by Fig. 15):

$$X_fF = X_rR + X_eE \tag{3}$$

Rearranging (1) and Substituting in (2)

(4) $QR + W(F-R) + FS_f = S_rR + S_e\,(F-R)$

or (5) $QR + WF - WR + FS_f = S_rR + S_eF - S_eR$

or (6) $F(W + S_f - S_e) = R(W + S_r - S_e - Q)$

or (7) $\frac{R}{F} = \frac{(W+S_f-S_e)}{(W+S_r-S_e-Q)}$

Now substituting Equation (1) in Equation (3)

(8) $X_fF = X_rR + X_e\,(F-R)$

or (9) $X_fF = X_rR + X_eF - X_eR$

or (10) $F(X_f-X_e) = R(X_r-X_e)$

or (11) $\frac{R}{F} = \frac{X_f-X_e}{X_r-X_e}$

Equating Equations (7) and (11)

(12) $\frac{(W+S_f-S_e)}{(W+S_r-S_e-Q)} = \frac{X_f-X_e}{X_r-X_e}$

or (13) $\frac{(S_e-W)-S_f}{X_e-X_f} = \frac{(S_e-W)-(S_r-Q)}{X_e-X_r}$

Equation (13) is the equation for a straight line connecting three points, of the coordinates: X_e, (S_e-W); X_f, S_f; X_r, (S_r-Q), on a plot of X versus S, as in Figure 2. Equation (13) will be used later in the discussion to aid in the graphical solution of extraction problems.

Writing material balances around the first stage in the bottom of the column (refer to Fig. 3):

Oil Balance

(14) $E_2 = R_1 + E$

Solvent Balance

(15) $S_{e2}E_2 + WE = S_{e1}R_1 + S_eE$

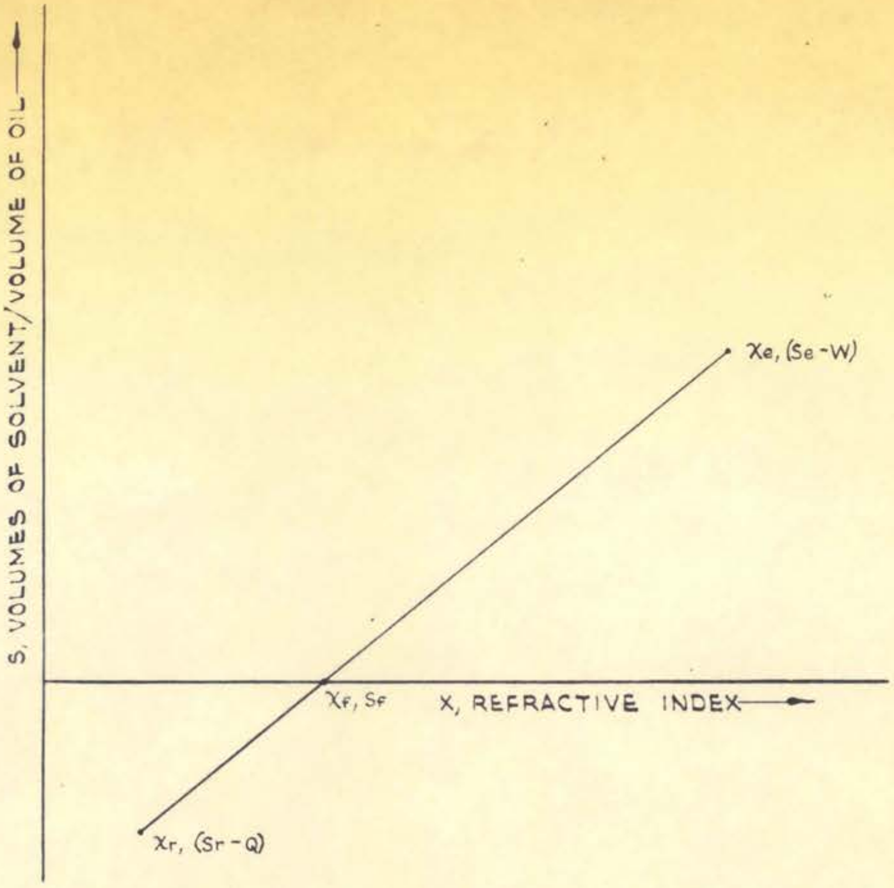

FIG. 2
GRAPHICAL REPRESENTATION OF EQUATION 13

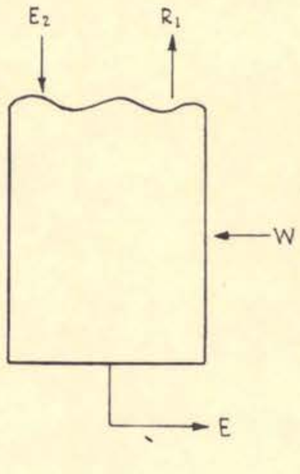

FIG. 3
FIRST STAGE IN COLUMN

X Balance

(16) $X_{e2}E_2 = X_{r1}R_1 + X_eE$

Substituting Equation (14) in Equations (15) and (16):

(17) $$\frac{(S_e-W) - S_e2}{X_e - X_{e2}} = \frac{(S_e-W) - S_{r1}}{X_e - X_{r1}}$$

Equation (17) is shown plotted in Figure 4.

Now writing material balances around the upper portion of the column (refer to Fig. 5).

Oil Balance

(18) $R_n = R + E_{n+1}$

Solvent Balance

(19) $QR + S_rR_n = S_rR + S_{e(n+1)}E_{n+1}$

X Balance

(20) $X_{rn}R_n = X_rR + X_{e(n+1)}E_{n+1}$

Substituting Equation (18) in Equations (19) and (20)

(21) $$\frac{S_{e(n+1)} - S_{rn}}{X_{e(n+1)} - X_{rn}} = \frac{S_{e(n+1)} - (S_r-Q)}{X_{e(n+1)} - X_r}$$

A plot of Equation (21) is shown in Figure 6.

Now to plot Equation 13, 17 and 21 on the same graph (refer to Fig. 7).

Line BC is a plot of Equation 13, joining the extract and raffinate leaving the column. The distance CD represents the amount of water injection used, volumes of water per volume of extract oil. Point D then represents the solvent content and quality of extract phase leaving the column, and therefore must lie on an equilibrium curve. This curve, of which line LD is a portion, represents equilibrium between water, phenol and extracted oil. The raffinate in equilibrium with the extract leaving the column is given by point G. Points on line KG represent the solvent content and

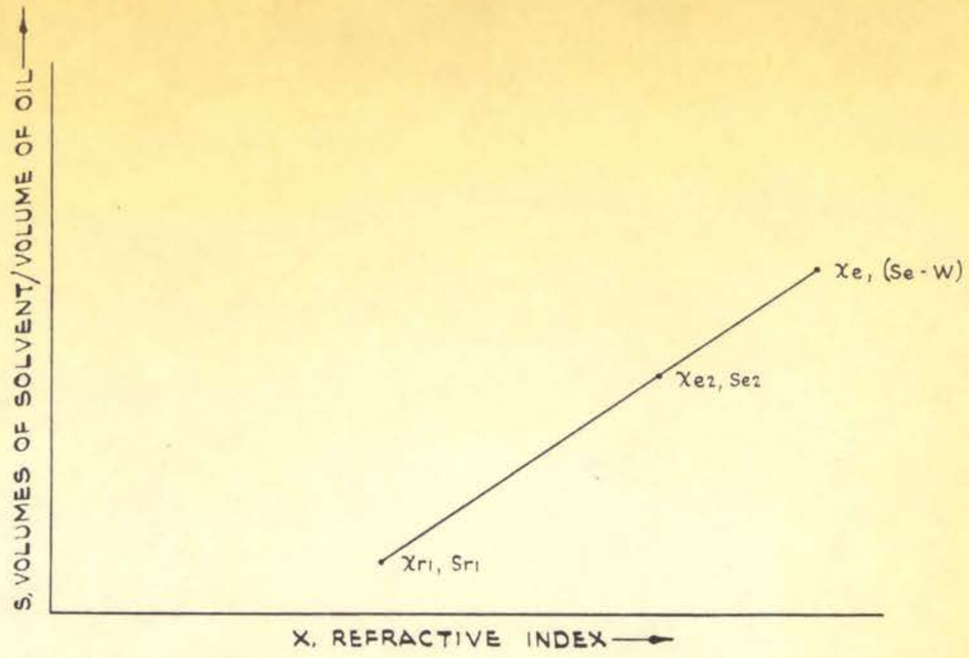

FIG. 4
GRAPHICAL REPRESENTATION OF EQUATION 17

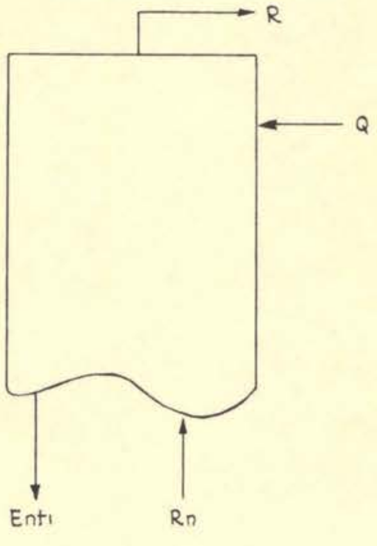

FIG. 5
UPPER PORTION OF COLUMN

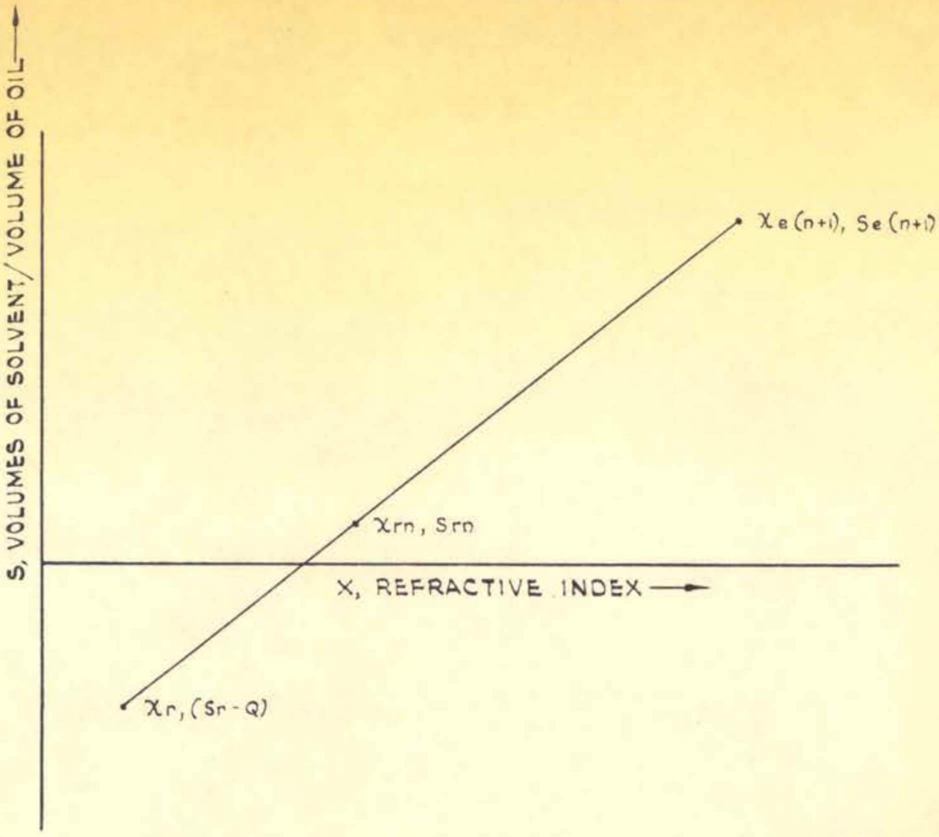

FIG. 6

GRAPHICAL REPRESENTATION OF EQUATION 21

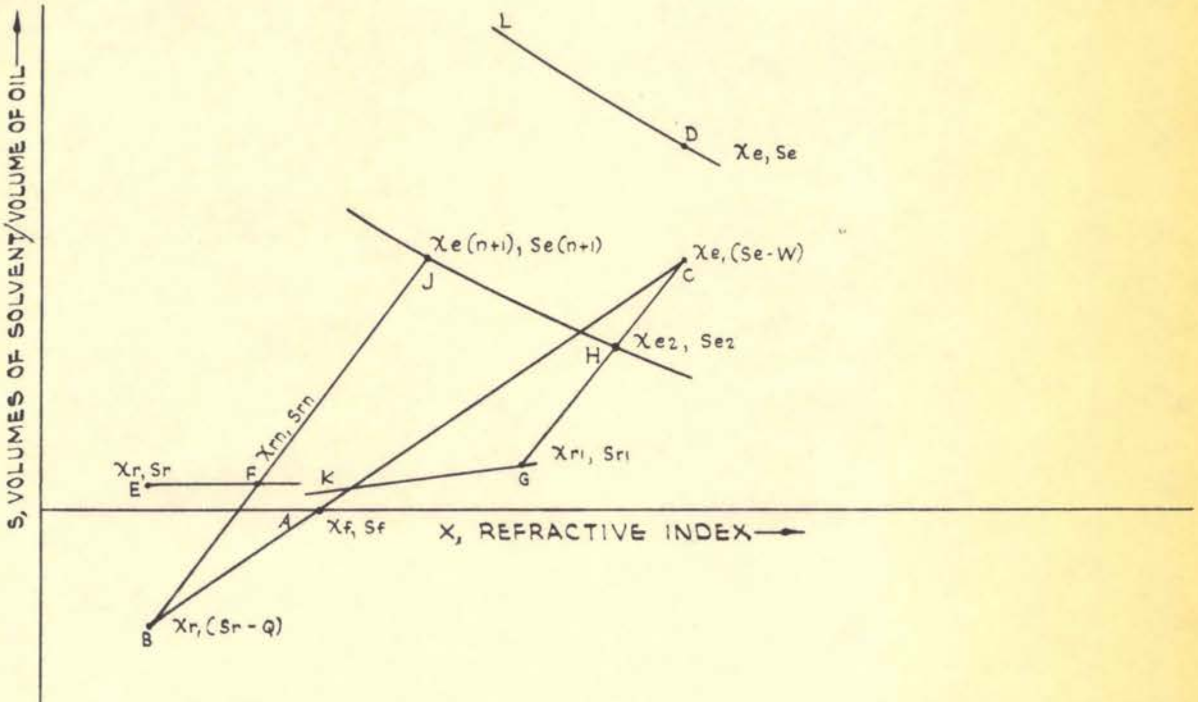

FIG. 7

GRAPHICAL REPRESENTATION OF EQUATIONS 13.17 & 21 quality of raffinate phase in equilibrium with extract phase as represented by points on line LD.

Line LD and KG represent equilibrium conditions in which water injection is used. However, water injection is used only in the bottom portion of the column. The phenol in the upper section of the column is essentially anhydrous, therefore another equilibrium curve must be used in conjunction with the upper portion of the column. Lines EF and JH are portions of such a curve. Points on line EF represent solvent content and quality of raffinate phase in equilibrium with extract phase as represented by points on line JH. This curve represents equilibrium of oil and phenol.

Thus it is seen that two sets of equilibrium data are necessary for representing phenol extraction process wherein water injection is used. These sets of data are (1) equilibrium data for the system: phenol-water-extracted oil (2) equilibrium data for the system: phenol-oil.

IV. ILLUSTRATION OF TYPICAL CALCULATIONS

The utilization of Equations (13), (17) and (21) will now be demonstrated (refer to Fig. 8):

$$(13)\quad \frac{(S_e-W)-S_f}{X_e-X_f} = \frac{(S_e-W)-(S_r-Q)}{X_e-X_r}$$

$$(17)\quad \frac{(S_e-W)-S_{e2}}{X_e-X_{e2}} = \frac{(S_e-W)-S_{r1}}{X_e-X_{r1}}$$

$$(21)\quad \frac{S_{e(n+1)}-S_{rn}}{X_{e(n+1)}-X_{rn}} = \frac{S_{e(n+1)}-(S_r-Q)}{X_{e(n+1)}-X_r}$$

To illustrate a typical problem: given the following information:

1. Desired quality of raffinate oil
2. Desired yield of raffinate oil
3. Solvent to oil ratio
4. Equilibrium data

Calculate graphically the number of stages required.

In order to use the diagram the given information must be in units that can be added and subtracted on the diagram:

1. Quality of raffinate oil. - Since the quality of product is usually expressed in viscosity index, this must be converted to refractive indices. This is accomplished by means of a curve relating viscosity index and refractive index of this particular oil.

2. Yield of raffinate oil. - Calculate the R.I. of extract oil from the relation:

$$Y = \frac{X_e-X_f}{X_e-X_r}$$

3. Solvent to oil ratio. - This information is usually given in terms of solvent and oil charged, but for use on the diagram it must be expressed in terms of solvent charged and raffinate oil produced:

$$Q = \frac{(P)\,(F)}{(R)} = \frac{P}{Y} \text{ volumes solvent/volumes raffinate oil.}$$

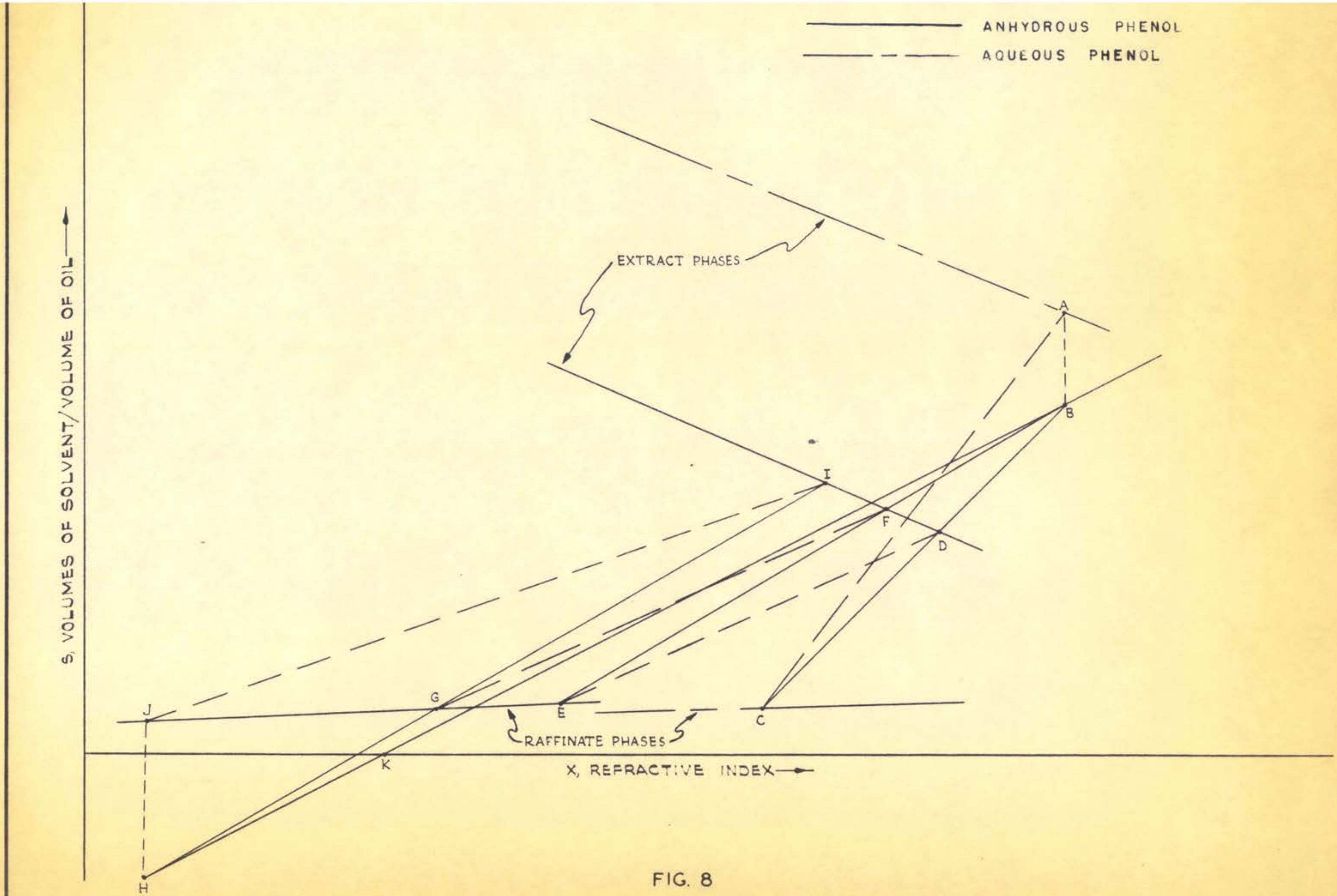

FIG. 8

TYPICAL DIAGRAM FOR PHENOL - OIL SYSTEM

4. Reflux Water. - Reflux is provided by water injection. The rate of water injection is based on the solvent charge rate, usually 10 per cent of the solvent rate:

$$W = (0.1)\ (Q)\ \frac{(Y)}{(1-Y)} \text{ volumes water/volume of extract oil.}$$

Now all the pertinent data are expressed in the proper units and can be applied directly to the Ponchon diagram.

The following steps are given for the solution of the problem (refer to Fig. 8):

1. Locate the quality of the oil charge stock on the diagram. Point K.
2. Locate quality of raffinate oil. Point J.
3. Locate quality of extract oil. Point A.
4. Draw the line JH, whose length is Q. Q is calculated as previously described.
5. Draw line HK, extending it past point A.
6. Draw vertical line from A to intersection of extension of HK, at point B. Length of line AB should equal the value of W, calculated as previously described. The line HKB is a plot of Equation 13.
7. To find the composition of the raffinate leaving the bottom stage, proceed from point A along a tie line to point C. Point C represents the quality and solvent content of the raffinate oil leaving the first stage.
8. Connect points C and B. Note intersection of line CB with anhydrous phenol equilibrium line, extract phase, point D. Line CDB is a plot of Equation 17 and locates the quality and composition of the extract stream leaving the second stage (point D). It will be noted that point D lies on the anhydrous equilibrium line while point A is on the 10 per cent water line. Since water is injected at only one point in the column,

there can be only one equilibrium stage involving 10 per cent water. This stage is the bottom stage and the water leaves this stage with the phenol going out the bottom of the column. The raffinate oil released by the water injection contains very little phenol and practically no water. The extract stream coming down the column contains anhydrous phenol and as a result, all stages above the first stage involve equilibria of oil and essentially anhydrous phenol.

9. To find the raffinate in equilibrium with the extract from the second stage, proceed along a tie line from point D to point E.
10. Connect points E and B locating point F, extract from the third stage.
11. Proceed along a tie line from point F to point G. Point G represents raffinate in equilibrium with extract represented by point F.
12. Since point G is near point K, the oil charge, this portion of the diagram represents the upper or stripping section of the column, and hence we can now use Equation 21. Connect points G and H, extending the line to point I. Point I represents the extract leaving the fourth stage.
13. Proceed along a tie line from point I to point J which is the raffinate in equilibrium with the extract at point I, and as will be noted, is also the raffinate from the column since this was the quality of raffinate desired.
14. Count the number of equilibrium stages. In this example there were four stages.

Another problem will be presented, the solution of which involves trial and error procedure.

Given the following data:

1. Equilibrium data
2. Number of equilibrium stages available
3. Quality of raffinate oil
4. Quality of bottoms

Calculate phenol to oil ratio necessary (see Fig. 9)

1. Locate quality of charge oil on diagram. Point A
2. Locate quality of raffinate oil on diagram. Point B
3. Locate quality of extract oil on diagram. Point C
4. Assume a value for Q. Locate on diagram. Point D
5. Calculate W, as previously shown. Locate on diagram. Point E
6. Connect points D, A, E to give line DAE.
7. Graphically step off the known number of stages.
8. If the last stage coincides with point B, raffinate composition, then assumed value of Q was correct. If not then a new value for Q must be assumed and the procedure repeated.
9. When the correct value of Q is obtained, calculate the value of phenol to oil ratio from the equation: $P = QY$.

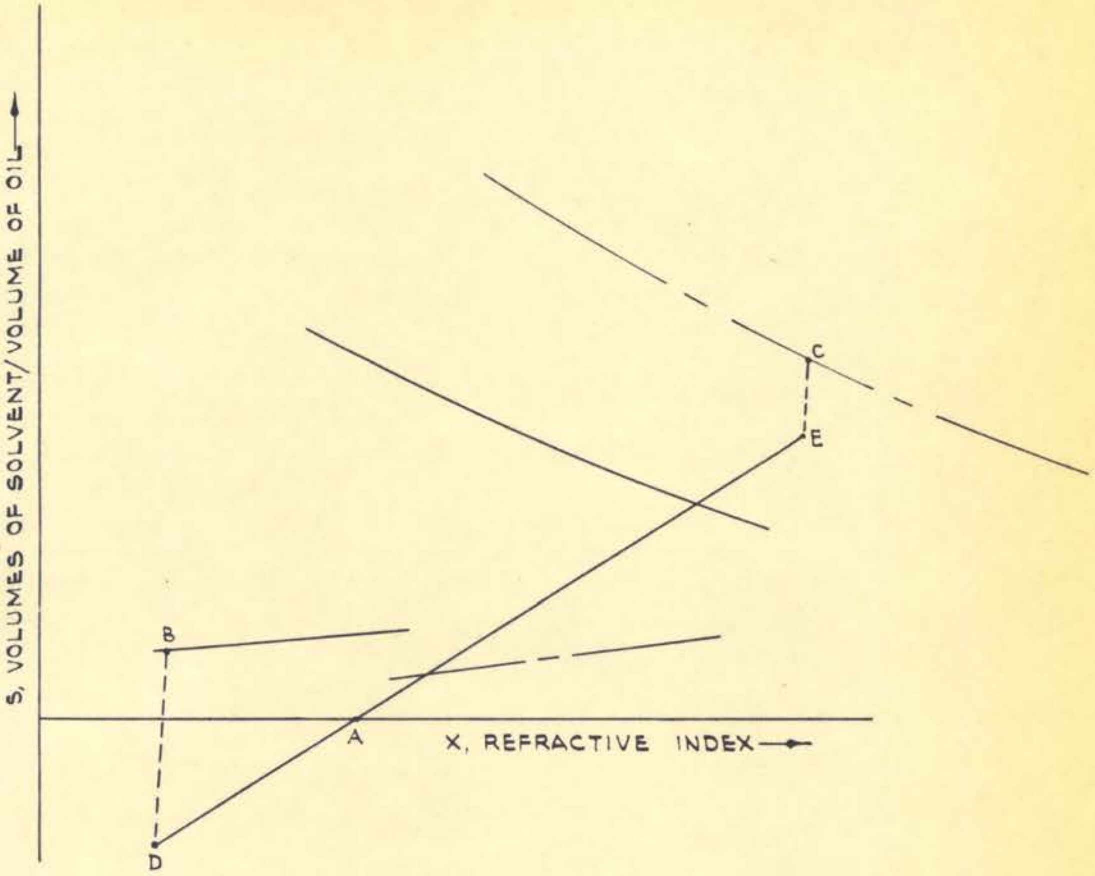

FIG. 9

DIAGRAM FOR SOLUTION OF SECOND PROBLEM

V. EXPERIMENTAL WORK

A. Equilibrium Data

In the phenol extraction process, the use of equilibrium data is complicated by the use of one solvent in the upper section of the column and a different solvent in the bottom section. Anhydrous phenol, or phenol containing 2.5 per cent water, is the solvent in the upper section of the column while aqueous phenol containing approximately 15 per cent water is the solvent in the bottom section. This difference in solvents is accomplished by injecting water into the extract phase at the bottom of the column. The water causes oil to be rejected from the extract, and the water being more soluble in the extract phase is carried out the bottom of the column in solution in the extract phase.

In order to be of use in the process then, an equilibrium diagram must show the equilibrium of anhydrous phenol and oil as well as aqueous phenol and oil. In Figures 10 and 14, it will be noted that equilibrium data involving both anhydrous and aqueous phenol were obtained on one SAE 10 oil and one SAE 20 oil. The aqueous phenol experiments were limited to these two oils because only small samples of the other oils were available. However, the two sets of complete data should illustrate the method of presentation of data. The data for the SAE 10 oil was done at two temperatures, 155°F for the aqueous phenol and 170°F for the anhydrous phenol, since the subsequent continuous extraction was done using that temperature gradient over the column.

In addition to the data on the SAE 10 and 20 oils, equilibrium data involving only phenol with no water injection were obtained on oils ranging in viscosity from SAE 10 grade to SAE 250 grade.

The data obtained show that the raffinate oils all seem to have approximately the same solvent power for phenol. This is true in the case of raffinates produced by anhydrous phenol or aqueous phenol and regardless of refractive index and viscosity of the charge oil. Phenol is soluble in raffinate oils to the extent of 0.15-0.30 volumes of solvent per volume of oil. The extract oils behave quite differently. The solvent content of the extract phase is greatly affected by the viscosity and refractive index of the oil and the use of anhydrous or aqueous phenol. Reference to Figures 10 and 14 will illustrate this point very well.

B. Continuous Extraction

The theory of design of liquid-liquid extraction columns is not at a very advanced stage at this time and the actual design of columns relies heavily on past experiences, rule of thumb measures and pilot plant data. Therefore, prior to any large scale operations, the proposed process must be investigated on a pilot plant scale. Bench scale data can play a very important part in the correct interpretation of pilot plant data. It is well to secure bench scale data, such as equilibrium data, even prior to pilot plant data. Equilibrium data indicate the results to be expected and the directions in which pilot plant work should be conducted.

The SAE 10 and 20 oils, on which both anhydrous and aqueous phenol equilibrium data were obtained, were subjected to continuous phenol extraction on a pilot plant scale. Data from these extractions are presented in Tables VI and VII. The SAE 10 oil used in the continuous extraction was taken from a different drum of the same batch as that used in obtaining equilibrium data. Refractive index of the sample used in equilibrium studies was 1.4688 as compared to 1.4691 for the sample subjected to continuous extraction. Thus, the oils are essentially identical.

A phenol to oil ratio of 3.2 was used in the case of the SAE 10 oil and 2.3 in the case of the SAE 20 oil. Under the conditions employed in the continuous there were 2 equilibrium stages in the extraction of the SAE 10 oil and 3 in the extraction of the SAE 20 oil.

If the solvent content and refractive indices of the extract and raffinate oils from Table VI are plotted in Figure 12, the point representing the extract phase does not fall on the equilibrium curve. The solvent content is lower than is indicated by the equilibrium curve. For purposes of stage calculations, this point was placed on the curve by extrapolating along a tie line from the actual point to the intersection of the tie line with the equilibrium curve. There are several things which could cause this discrepancy, the three most important ones being: (1) Very slow and unequal diffusion rates of the components, (2) insufficient mixing of the injected water with the extract phase and (3) incomplete separation of the rejected oil from the extract phase. Both of the last two phenomena have been observed during operation of the extraction apparatus.

C. Refractive Index, Viscosity Index, Density Correlation

In order to effectively utilize the Ponchon type equilibrium diagram, an easily determined additive property of the oil must be employed. Some of the more well known additive properties such as specific gravity and viscosity-gravity constant are accurate but are undesirable from the standpoint of time consumed in analytical determinations. Refractive index is a property that is very easily and rapidly determined. The data in Figure 15 show that refractive index is a linear function of density and hence is an additive property.

The raffinates produced in phenol extraction are waxy and solid at room temperature. The temperature at which the refractive index determinations were made was set sufficiently high, 70°C, to insure fluidity of all products.

The data in Figure 16 show an interesting correlation of refractive index and viscosity index. The straight line relationship is very convenient in that it reduces the amount of data required to define the curve. By use of this relationship the quality of the oil, as indicated by viscosity index, can be used on the equilibrium diagram in the form of refractive index. The possibilities for the use of this correlation as a refinery control tool are obvious.

VI. CONCLUSIONS

A method of utilizing equilibrium data in solvent extraction calculations has been presented. This method should be of aid in the following types of problems:

1. Calculation of the number of stages necessary for a given separation, as in the design of new equipment.
2. Evaluation of columns already in existence.
3. Evaluation of new lube stocks.

Equilibrium data can be an aid in the analysis of certain types of column mechanical difficulties. Analysis of the streams leaving the column will produce data which can be plotted on the equilibrium diagram. In case the stream data do not fall on the equilibrium curve, entrainment or poor water mixing is indicated.

VII. EXPERIMENTAL PROCEDURES

A. Equilibrium Experiments

1. Anhydrous and Aqueous Phenol (2.5% Water)

Oil and phenol were mixed in desired proportions in a separatory funnel. The funnel and contents were placed in a constant temperature bath for one hour. The funnel was withdrawn occasionally for shaking. At the end of an hour, the funnel was withdrawn from the bath. The bottom layer, extract phase, was withdrawn into a weighed flask for solvent removal. The raffinate was withdrawn into another flask for solvent removal. The transfer of each phase to the flask was not quantitative. A portion of each phase right at the interface was discarded to avoid contamination of one phase with the other.

Each flask was weighed before and after solvent removal in order to obtain solvent content of the respective phases. The refractive indices of the oils were determined.

This procedure was repeated, varying the phenol to oil ratio from as low as 0.5 to as high as 10 in some cases. A Ponchon type equilibrium diagram was prepared from the data obtained.

2. Water Injection

The extract oils from the continuous extraction column are very dark in color and have very high refractive indices. In order to get equilibrium data in this range of these refractive indices, the extract oils obtained from the equilibrium experiments with anhydrous phenol were used to obtain data with aqueous phenol containing 12-20 per cent water. Oil and phenol were mixed in the separatory funnel as before. Water was added to this mixture and the funnel placed in the constant temperature bath.

The procedure was the same as that used for anhydrous phenol and aqueous phenol containing 2.5 per cent water.

Since the water injection rate to the column was 10 per cent of the phenol charge rate, the amount of water mixed with the oil and phenol was 10 per cent of the phenol originally mixed with the oil. For instance: 400 ml phenol and 200 ml oil were mixed together, heated, shaken and phases separated. The extract was to be used with aqueous phenol containing 12-20 per cent water. Therefore 40 ml of water would be added to the extract oil-phenol mixture, and since some of the original phenol was withdrawn in the first separation, the water content of the remaining phenol was considerably greater than 10 per cent, which is what happens in the continuous column also.

B. Continuous Extractions

The continuous extractions were carried out in a spinning band type, one inch diameter by eight feet length glass column. The charge rates of oil, phenol and water were controlled by Hills-McCanna plunger type pumps. Temperatures over the column and of the streams were controlled by electrical heating coils and thermocouple-actuated controllers. When steady state operation appeared to have been reached in the column, small samples of raffinate were taken at 30 minute intervals, stripped free of phenol and the refractive index of the phenol free oil determined. When two successive refractive indices differed by no more than 0.0003, samples of raffinate and extract were collected. These samples were collected in amounts sufficient for determination of the physical properties of the oil.

C. Analytical Procedure

1. Viscosity Index

The viscosity index of an oil is a number calculated from the viscosities of the oil at 100°F and 210°F and indicates the rate of change of viscosity with increasing or decreasing temperature.

The viscosities at 100°F and 210°F were determined in a modified Ostwald viscosimeter. The viscosimeter was immersed in an oil bath maintained at the desired temperature by an electric immersion heater. After determining the viscosities, the viscosity index was obtained from the tabulated data in Circular No. 30.52 of the Standard Oil Development Company[4]. These data are merely calculated values of viscosity indices for various determined viscosities at 100°F and 210°F, and are calculated from the basic equation:

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

where:

V.I. = viscosity index of the oil in question.

L = viscosity at 100°F of a zero viscosity index standard oil whose viscosity at 210°F is the same as the viscosity of the oil in question.

H = viscosity at 100°F of a 100 viscosity index standard oil whose viscosity at 210°F is the same as the viscosity of the oil in question.

V = viscosity at 100°F of the oil in question.

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[4] "Standard Oil Development Company Circular No. 30.52", Bayonee, N.J., Standard Oil Development Company, 1939.

2. Density

Density determinations were made by placing a sample of oil in a container (pycnometer) of a known volume. The pycnometer and contents were placed in a constant temperature bath and let remain there for one hour. At the end of one hour the pycnometer was removed and let cool to room temperature. The weight of pycnometer full and empty was obtained. The density of the oil was then calculated using the volume of container, weight of oil and temperature correction obtained from the National Standard Petroleum Oil Tables[6].

3. Refractive Index

The refractive indices of the oils were determined with an Abbe refractometer. The sample was held at 70°C by means of circulating hot water through a jacket around the sample.

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[6] U. S. Department of Commerce, National Standard Petroleum Oil Tables, Washington, D. C., U. S. Government Printing Office, 1936.

SUMMARY

A graphical method for the solution of solvent extraction problems for the systems: phenol-lube oils is presented. The solutions of typical extraction problems are demonstrated. Equilibrium data for several phenol-lube oil systems are presented. Data obtained in the continuous countercurrent extraction of an SAE 10 and SAE 20 oil are presented. Using the equilibrium data and the continuous extraction data, the number of equilibrium stages necessary for a given separation is calculated by the method outlined.

Correlations of the physical properties of the raffinate and extract oils are made. These correlations permit rapid determination of equilibrium data for the system phenol-lube oil.

BIBLIOGRAPHY

1. Hunter, T. G., The Science of Petroleum, Vol. III, pp. 1818, London, England, Oxford University Press, 1938.
2. Maloney, J. O. and Schubert, A. E., "Transactions of the American Institute of Chemical Engineers", 36, 741 (1940).
3. Ponchon, "Tech. Moderne", 13,20 (1921).
4. "Standard Oil Development Company Circular No. 30.52", Bayonne, N. J., Standard Oil Development Company, 1939.
5. Treybal, R. E., Liquid Extraction, pp. 34, First Edition, New York, N. Y., McGraw-Hill Book Company, 1951.
6. U. S. Department of Commerce, National Standard Petroleum Oil Tables, Washington, D. C., U. S. Government Printing Office, 1936.

APPENDIX

TABLE I.

EQUILIBRIUM DATA FOR PHENOL-WATER-SAE 10 OIL (X105)

	Charge Conditions			Raffinate Phase		Extract Phase	
Run Number	Charge Oil	Approximate Phenol to Oil Ratio, Volume	Ratio of Water to Initial Phenol, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume
1	X105	2.5	0	1.4667	0.3	1.4948	2.5
2	X105	1	0	1.4604	0.3	1.4932	3.6
3	X105	2	0	1.4560	0.2	1.4806	5.2
4	X105	4	0	1.4517	0.2	1.4770	6.2
5	X105	10	0	1.4477	0.2	1.4700	11.8
6	X105	6	0	1.4493	0.2	1.4760	7.8
7	Extract Phase from Run 5	--	0.1	1.4503	0.1	1.4963	34.1
8	Extract Phase from Run 3	--	0.1	1.4630	0.1	1.5300	14.3
9	X105	2	--	---	---	---	--
10	Extract Phase from Run 9	--	0.1	1.4620	0.1	1.5285	14.9
11	X105	1	--	---	---	---	--
12	Extract Phase from Run 11	--	0.1	1.4712	0.1	1.5400	11.1
13	X105	0.8	--	---	---	---	--
14	Extract Phase from Run 13	--	0.1	1.4743	0.1	1.5498	10.5

Temperature of Extractions = 170°F for the Extractions with no water and 155°F for extractions using water.

PHYSICAL PROPERTIES OF CHARGE OIL

Gravity, °API	29.6
Specific Gravity, 60/60°F	0.8786
Viscosity at 210°F, SUS	40.66
Viscosity-Gravity Constant at 210°F	0.825
Refractive Index at 70°C	1.4687

TABLE II.

EQUILIBRIUM DATA FOR PHENOL - MID-CONTINENT, WEST TEXAS SAE 20 OIL

Charge Conditions			Raffinate Phase		Extract Phase	
Run Number	Charge Oil	Approximate Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume
1	Mid-Continent, West Texas SAE 20	2	1.4660	0.2	1.5068	6.3
2	Mid-Continent, West Texas SAE 20	3	1.4632	0.2	1.5028	8.0
3	Mid-Continent, West Texas SAE 20	6	1.4600	0.1	1.4943	11.3
4	Mid-Continent, West Texas SAE 20	9	1.4576	0.1	1.4882	14.8

Temperature of Extractions = 170°F

PHYSICAL PROPERTIES OF CHARGE OIL

Gravity, °API	26.3
Specific Gravity, 60/60 °F	0.8970
Viscosity at 210°F, SUS	56.36
Viscosity-Gravity Constant at 210°F	0.832
Refractive Index at 70°C	1.4800

TABLE III.

EQUILIBRIUM DATA FOR PHENOL-WATER-SAE 20 OIL (X115)

	Charge Conditions			Raffinate Phase		Extract Phase	
Run Number	Charge Oil	Approximate Phenol to Oil Ratio, Volume	Ratio of Water to Initial Phenol, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume
1	X115	2	0	1.4650	0.1	1.5045	6.2
2	X115	3	0	1.4625	0.2	1.4983	7.8
3	X115	6	0	1.4585	0.2	1.4905	10.8
4	X115	9	0	1.4565	0.1	1.4846	13.4
5	Extract Phase from Run 1	--	0.1	1.4770	0.2	1.5471	17.4
6	Extract Phases from Runs 2 & 3	--	0.1	1.4702	0.3	1.5325	26.2
7	Extract Phases from Runs 3 & 4	--	0.1	1.4660	0.2	1.5216	34.7
8	X115	0.6	0	---	---	---	--
9	Extract Phase from Run 8	--	0.1	1.4920	0.3	1.5670	13.8

Temperature of Extractions = 170°F

PHYSICAL PROPERTIES OF CHARGE OIL

Gravity, °API	26.7
Specific Gravity, 60/60°F	0.8944
Viscosity at 210°F, SUS	55.00
Viscosity-Gravity Constant at 210°F	0.829
Refractive Index at 70°C	1.4783

EQUILIBRIUM DATA FOR PHENOL-SAE 250 OIL (X110)

Charge Conditions			Raffinate Phase		Extract Phase	
Run Number	Charge Oil	Approximate Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume
1	X110	2	1.4810	0.2	1.5270	8.8
2	X110	1	1.4850	0.6	1.5350	6.8
3	X110	0.5	1.4888	0.3	1.5382	4.8
4	X110	6	1.4752	0.2	1.5110	14.4
5	X110	10	1.4737	0.2	1.5081	19.2
6	X110	1	1.4848	0.4	1.5340	6.3

Temperature of Extractions = 195°F

PHYSICAL PROPERTIES OF CHARGE OIL

Gravity, °API	22.2
Specific Gravity, 60/60°F	0.9205
Viscosity at 210°F, SUS	223.4
Viscosity-Gravity Constant at 210°F	0.835
Refractive Index at 70°C	1.4920

TABLE V.

EQUILIBRIUM DATA FOR AQUEOUS PHENOL - SAE 10 OIL (X111)

Charge Conditions			Raffinate Phase		Extract Phase	
Run Number	Charge Oil	Approximate Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume	Refractive Index at 70°C of Phenol Free Oil	Phenol to Oil Ratio, Volume
1	X111	2	1.4564	0.2	1.4956	6.6
2	X111	8	1.4496	0.2	1.4778	14.2
3	X111	4	1.4533	0.2	1.4873	9.1
4	X111	1	1.4614	0.2	1.5042	4.3
5	X111	0.5	1.4661	0.2	1.5102	3.3
6	X111	6	1.4510	0.1	1.4810	10.0
7	X111	3	1.4549	0.1	1.4914	7.4
8	X111	6	1.4516	0.4	1.4820	9.7

Temperature of Extractions = 150°F

PHYSICAL PROPERTIES OF CHARGE OIL

Gravity, °API	29.1
Specific Gravity, 60/60°F	0.8813
Viscosity at 210°F, SUS	40.99
Viscosity-Gravity Constant at 210°F	0.828
Refractive Index at 70°C	1.4703

TABLE VI.

CONTINUOUS PHENOL EXTRACTION OF AN SAE 20 OIL (X115)

Run Number	X115 Charge Stock	A236
Solvent		Anhydrous Phenol
Temperatures, °F		
Top Column		170
Solvent Inlet		171
Oil Inlet		170
Water Inlet		130
Bottom		170
Feed Rates, Gallons per hour		
Solvent at 140°F		0.583
Oil at 60°F		0.252
Water at 60°F		0.058
Solvent to Oil Ratio, Volume		2.31
Water to Solvent Ratio, Volume		0.10
Extraction Yield, Volume Per Cent		76.0
Inspection Data		
Raffinate Oil		
Gravity, °API	26.7	31.6
Specific Gravity, 60/60°F	0.8944	0.8677
Viscosity at 210°F, SUS	55.00	50.93
Viscosity-Gravity Constant at 210°F	0.829	0.7968
Refractive Index at 70°C	1.4783	1.4594
Solvent Content, Volumes Per Volume of oil		0.15
Dewaxed Raffinate Oil		
Gravity, °API		30.3
Specific Gravity, 60/60°F		0.8746
Viscosity at 100°F, SUS		315.8
Viscosity at 210°F, SUS		53.39
Viscosity Index		98.5
Refractive Index at 70°C		1.4623
Pour Point, °F		0
Extract Oil		
Gravity, °API		13.1
Specific Gravity, 60/60°F		0.9789
Viscosity at 210°F, SUS		98.2
Viscosity-Gravity Constant at 210°F		0.926
Refractive Index at 70°C		1.5380
Solvent Content, Volumes per Volume of oil		9.2
Calculated Number of Equilibrium Stages		3

TABLE VII.

CONTINUOUS PHENOL EXTRACTION OF AN SAE 10 OIL (X107)

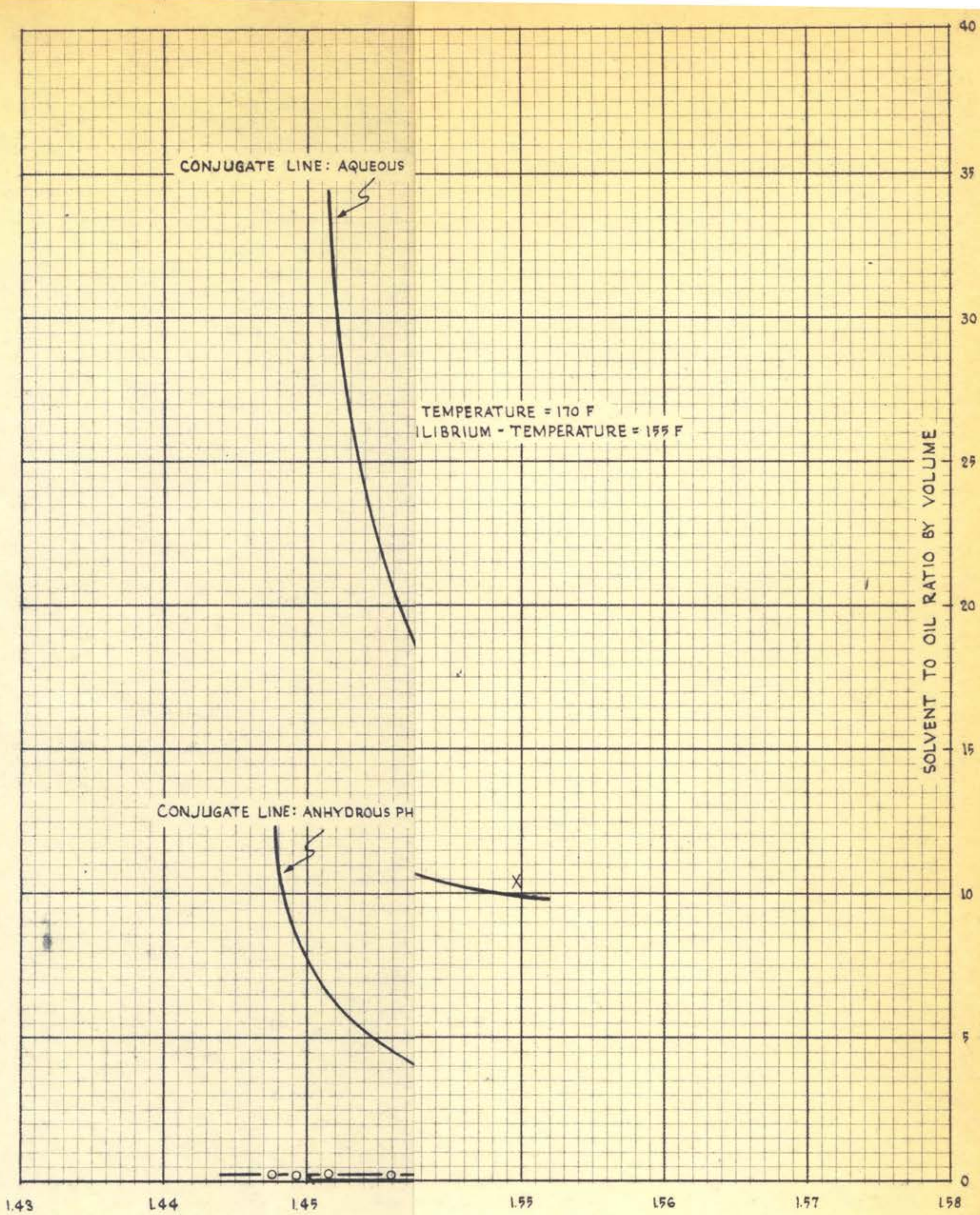
Run Number	X107 Charge Stock	A151
Solvent		Anhydrous Phenol
Temperatures, °F		
Top Column		170-175
Solvent Inlet		175
Oil Inlet		155
Water Inlet		155
Bottom		155
Feed Rates, Gallons per hour		
Solvent at 140°F		0.408
Oil at 60°F		0.128
Water at 60°F		0.0392
Solvent to Oil Ratio, Volume		3.19
Water to Solvent Ratio, Volume		0.0961
Extraction Yield, Volume Per Cent		76.0
Inspection Data		
Raffinate Oil		
Gravity, °API	29.3	34.3
Specific Gravity, 60/60°F	0.8789	0.8535
Viscosity at 210°F, SUS	41.30	40.09
Viscosity-Gravity Constant at 210°F	0.8252	0.7932
Refractive Index at 70°C	1.4691	1.4503
Solvent Content, Volumes per Volume of oil		0.18
Dewaxed Raffinate Oil		
Gravity, °API	27.7	33.0
Specific Gravity, 60/60°F	0.8889	0.8602
Viscosity at 100°F, SUS	153.5	126.1
Viscosity at 210°F, SUS	42.34	41.43
Viscosity Index	69	98
Refractive Index at 70°C	1.4742	1.4546
Pour Point, °F	0	5
Extract Oil		
Gravity, °API		15.4
Specific Gravity, 60/60°F		0.9633
Viscosity at 210°F, SUS		49.40
Viscosity-Gravity Constant at 210°F		0.9248
Refractive Index at 70°C		1.5253
Solvent Content, Volumes per Volume of oil		15.9
Calculated Number of Equilibrium Stages		2

Note: This oil, designated X107, is the same as oil X105 but was sampled from a different drum.

TABLE VIII.

CORRELATION OF PHYSICAL PROPERTIES OF RAFFINATES AND EXTRACTS FROM PHENOL REFINING A MID-CONTINENT SAE 10 OIL

Refractive Index at 70°C	Density, Grams per milliliter @ 60°F	Viscosity Index of Dewaxed Raffinate
1.4685	0.8771	69
1.4511	0.8520	94
1.4505	0.8511	94
1.4490	0.8484	96
1.4486	0.8478	97
1.4532	0.8554	90
1.4492	0.8498	97
1.4482	0.8473	98
1.4510	0.8493	94
1.4738	0.8874	
1.4542	0.8604	
1.4537	0.8599	
1.4520	0.8571	
1.4517	0.8558	
1.4538	0.8618	
1.5250	0.9604	
1.5291	0.9669	
1.5201	0.9546	
1.5484	0.9925	
1.5203	0.9558	
1.5323	0.9707	


CONJUGATE LINE: AQUEOUS
TEMPERATURE = 170 F
ILIBRIUM - TEMPERATURE = 155 F
CONJUGATE LINE: ANHYDROUS PH
SOLVENT TO OIL RATIO BY VOLUME
40
35
30
25
20
15
10
5
0
1.43
1.44
1.45
1.55
1.56
1.57
1.58

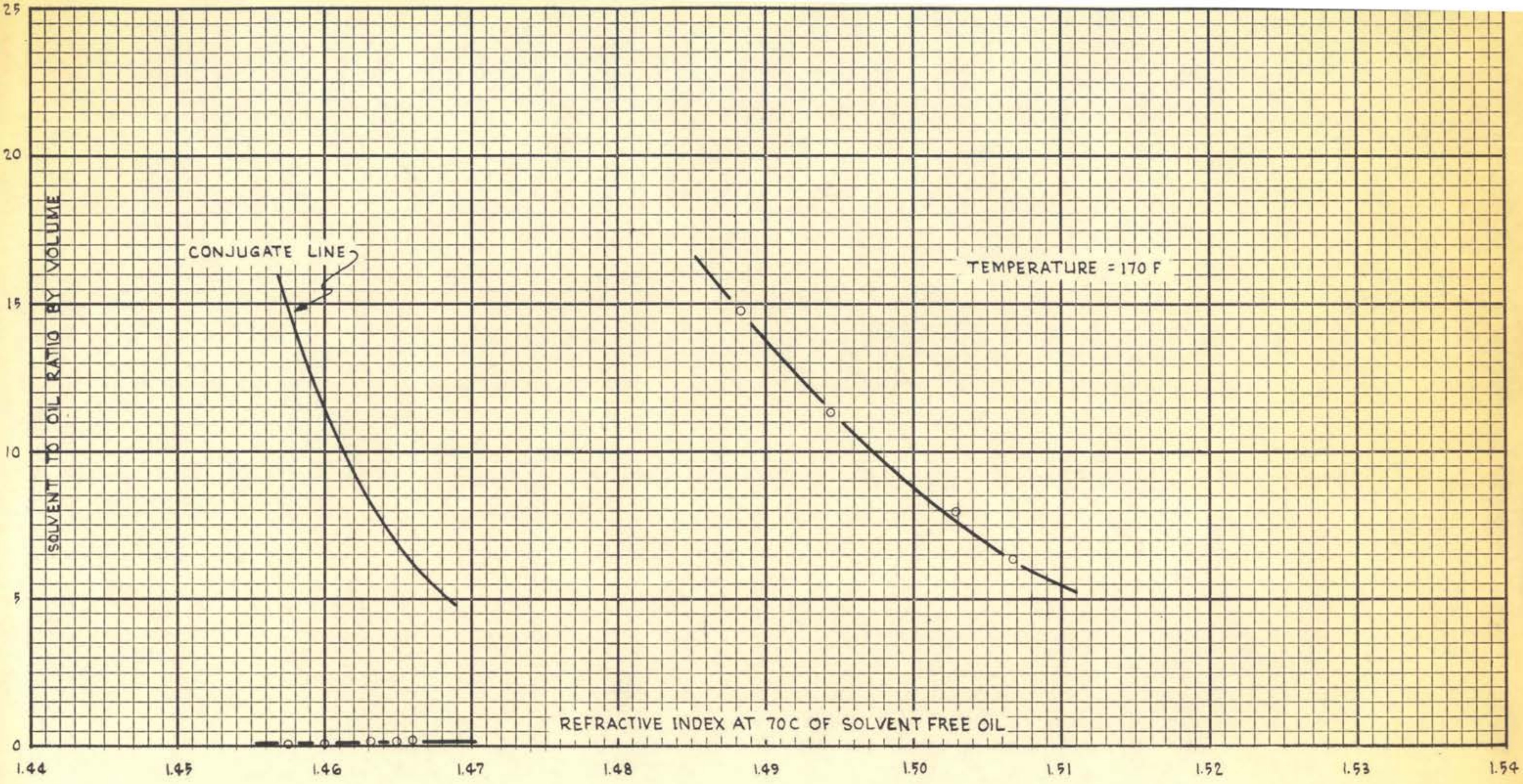
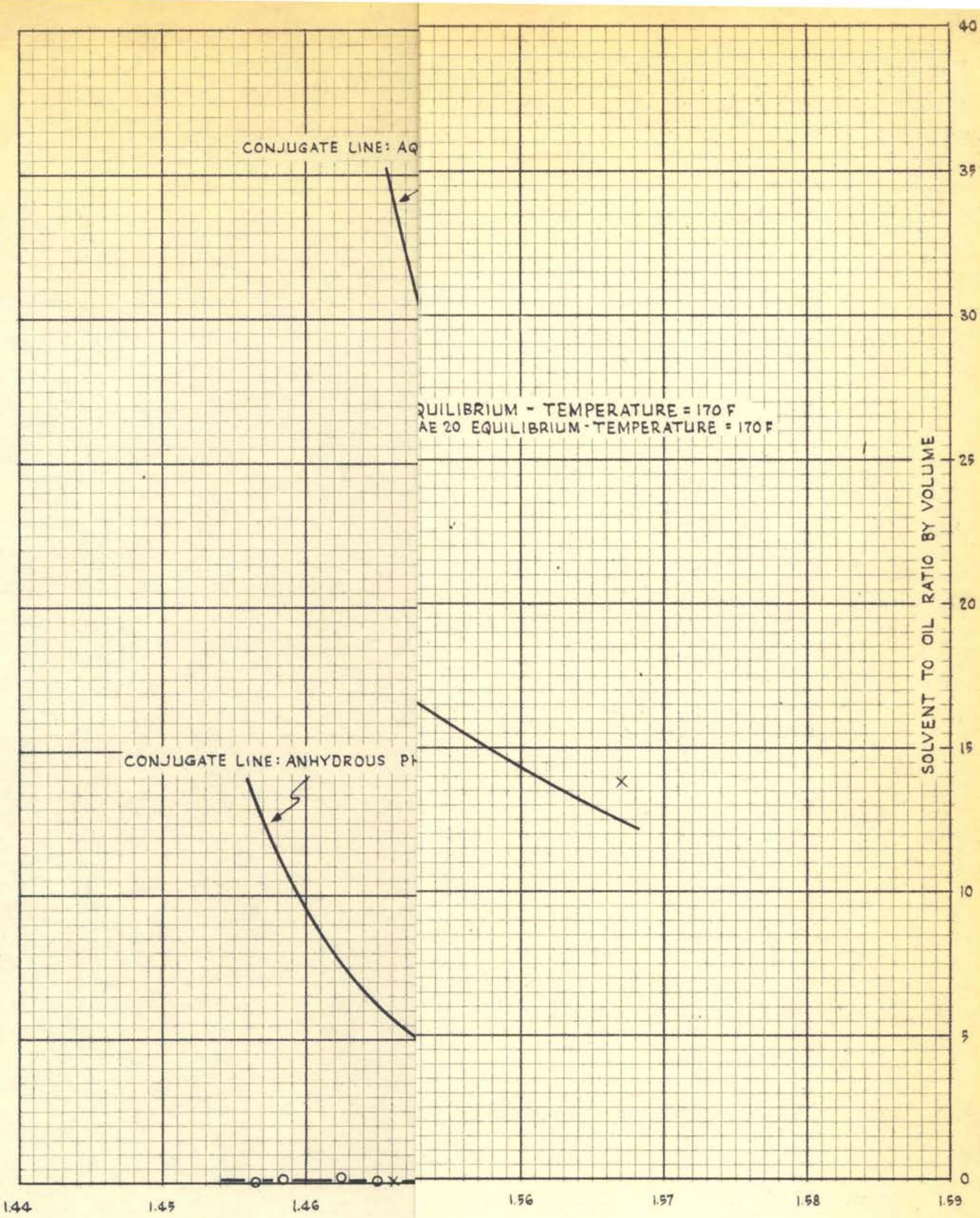


FIG. 11

EQUILIBRIUM DATA FOR
PHENOL-MID-CONTINENT, WEST
TEXAS SAE 20 OIL


CONJUGATE LINE: AQ
QUILIBRIUM - TEMPERATURE = 170 F
AE 20 EQUILIBRIUM - TEMPERATURE = 170 F
CONJUGATE LINE: ANHYDROUS PH
SOLVENT TO OIL RATIO BY VOLUME
40
35
30
25
20
15
10
5
0
1.44
1.45
1.46
1.56
1.57
1.58
1.59

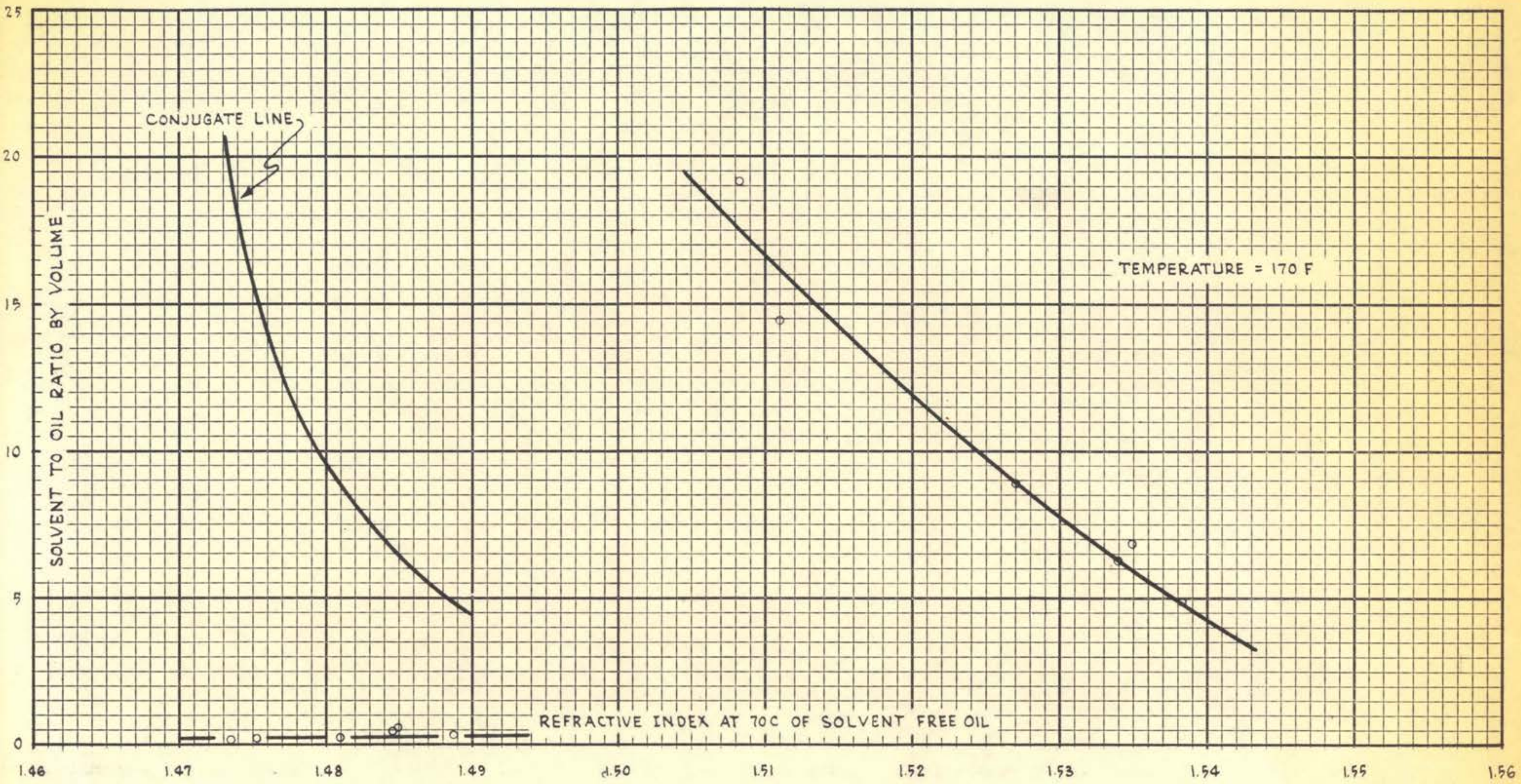


FIG. 13

EQUILIBRIUM DATA FOR PHENOL - RAW SAE 250 OIL (X110)

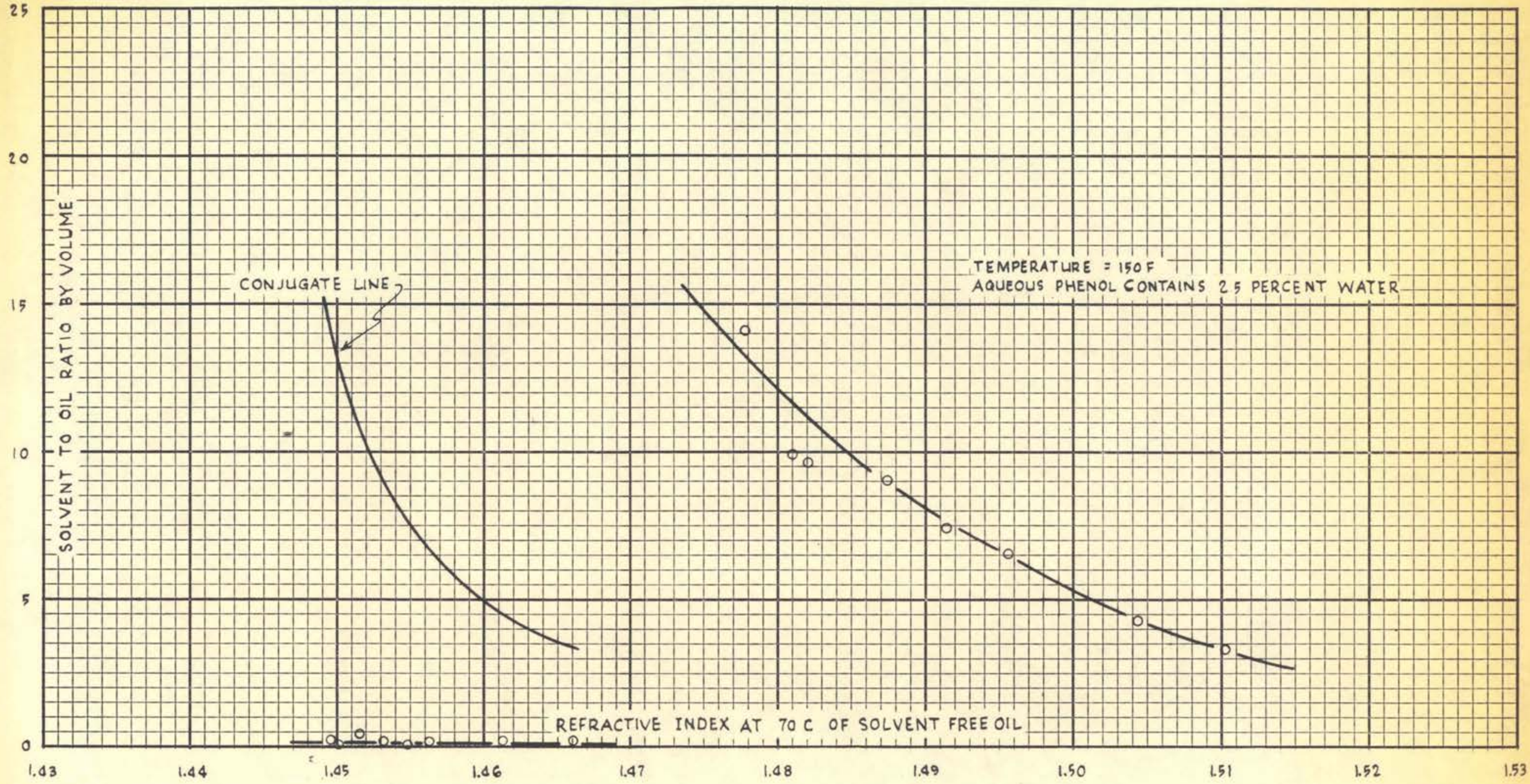


FIG. 14

EQUILIBRIUM DATA FOR AQUEOUS PHENOL - SAE 10 OIL (XIII)

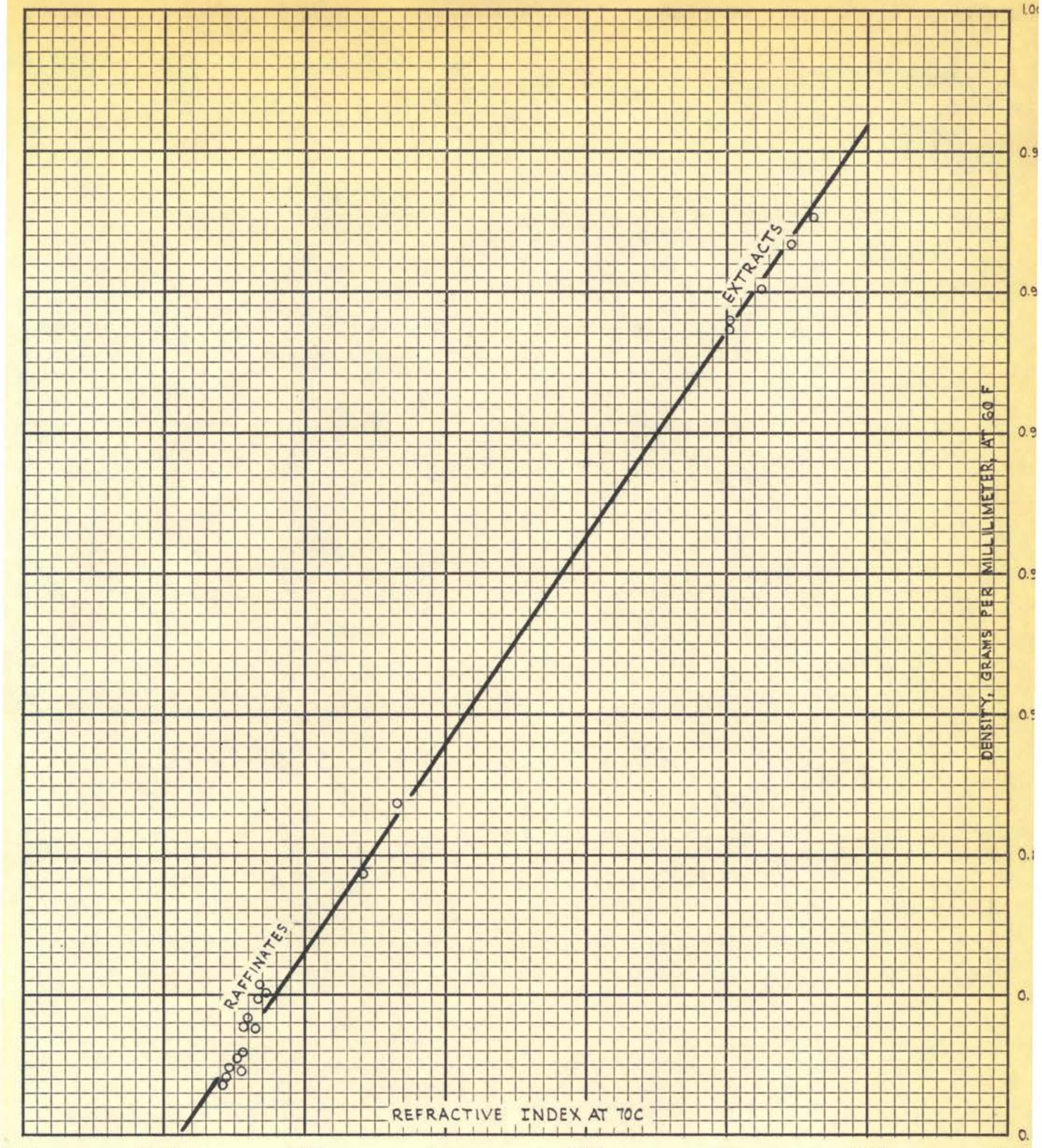


FIG. 15

CORRELATION OF REFRACTIVE INDEX
AND DENSITY FOR PHENOL
REFINING A MID-CONTINENT SAE 10 OIL

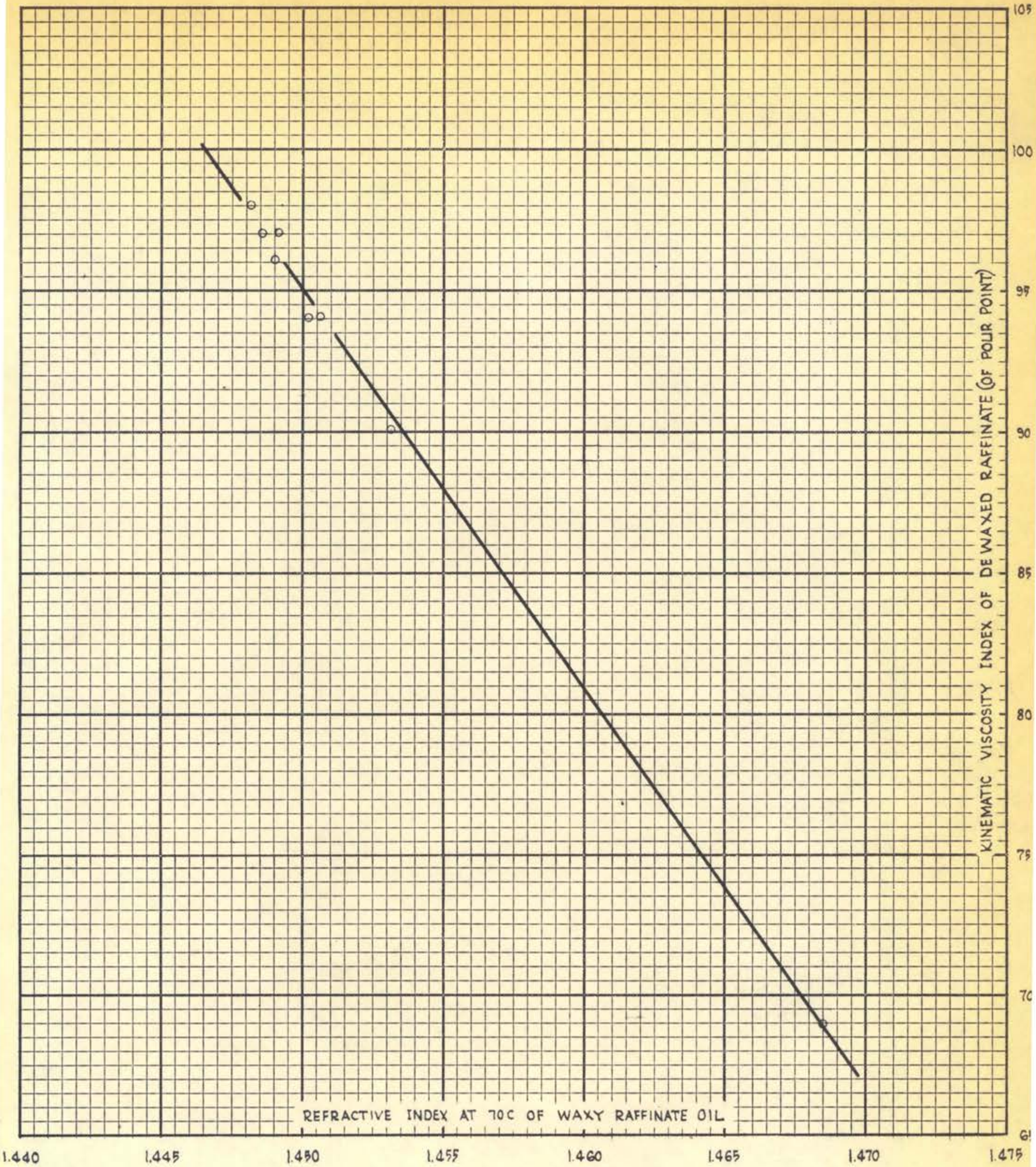


FIG. 16

CORRELATION OF RAFFINATE
QUALITY AND REFRACTIVE INDEX FOR
PHENOL REFINING A MID-CONTINENT SAE 10 OIL

VITA

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