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A STUDY OF THE CORRELATION OF ANILINE POINTS WITH
OTHER PROPERTIES OF PETROLEUM FRACTIONS

BY

CHARLES F. MOORE

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A thesis submitted to the faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

Signed

Charles F. Moore

Charles F. Moore

Golden, Colorado

Date May 12, 1952

Approved:

James O. Ball
J.O. Ball, Professor and Head,
Petroleum Refining Department

Expt. The Author. J.B. Co. v. 3. 27

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SUMMARY

This investigation indicates that more use could be made of aniline points for correlation work with other variables. The correlations developed in this report are only tentative; more work should be done to define their limits. The two major uses developed in the investigation are listed below.

The correlation of A.P.I. gravity and aniline point with boiling range appears to have good possibility of being a rapid and easy method of accurately determining the base and entire nature of a crude oil.

The blending values for the hydrocarbon classes - aromatics, naphthenes, and paraffins - indicates a new method of analysis for these groups. This method would be less likely to be affected by such contaminants as sulfur compounds that affect methods involving tests such as refractive index.

INTRODUCTION

In the last few years the determination of aniline points for various petroleum fractions has become a common test. As an example, in 1945 the U.S. Bureau of Mines began to determine aniline points for certain fractions -- 8,9,10, 11, and 12. However at present the Bureau of Mines engineers include them for all fractions⁷.

Up to now the use of aniline points has been very limited. The two main uses are:

- (1) Determination of diesel index for diesel fuels
- (2) Calculation of percentage of aromatics in a petroleum fraction.

Much of the limited use of aniline points has been due to the lack of good correlation data with other properties.

The author believes that an investigation should be conducted to determine possible correlations of aniline points with such basic properties as A.P.I. gravity, boiling range, and hydrocarbon classes -- paraffins, naphthenes, and aromatics. Once correlations are developed for these properties, a wider and more useful application may be made of aniline points.

METHOD OF APPROACH

This investigation is divided into two main sections. In the first section, which is experimental, petroleum fractions are analyzed for:

- (1) Boiling range
- (2) A.P.I. gravity
- (3) Aromatic and saturates content
- (4) Aniline points before and after the removal of aromatics.

In the second section, which is correlative, the experimental data and data obtained from literature are correlated with aniline points.

In the experimental section the aromatics and saturates content are obtained by the new chromatographic adsorption method using silica gel as the adsorbent. In this investigation the chromatographic method of analysis was for the quantitative analysis for the aromatic fraction.

The chromatographic adsorption by the use of silica gel for the determination of aromatics is superior to the old analysis by sulfonation. Sulfonation may remove some of the light saturates from the raffinate in the volatile fractions and may not completely remove the aromatics in the high boiling fractions. The chromatographic analysis is highly selective to aromatics and is accurate over a very wide boiling range.

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Chromatographic analysis is based upon the selective adsorption of silica gel for the various hydrocarbon classes. The degree of adsorption of the silica gel for hydrocarbons ranges from the smallest degree for saturates — paraffins and naphthenes — to a medium degree for olefins, and to a highest degree for aromatics. By use of a desorbing fluid, such as isopropyl alcohol, the hydrocarbons are desorbed according to their degree of adsorption on the silica gel and move down the column. As the fraction moves down the column and is alternately adsorbed and desorbed, the hydrocarbons are separated from each other into bands.

By use of a fluorescent indicator which fluoresces in the presence of a fluorescent light, the amount of each class may be determined (see Procedure, page 8). When viewed in a fluorescent light with an indicator, the aromatics appear as a deep purple, the olefins as a yellow, and the saturates as a blue color⁵.

EXPERIMENTAL

Equipment and Apparatus

Aniline Point

For the determination of the aniline points of the fractions, which range from almost water-white to extremely dark in color, the new Aniline Point Thin-Film apparatus was used. In this work the apparatus manufactured by the Precision Scientific Company was used.

Chromatographic Analysis

The equipment for the chromatographic analysis is primarily a silica gel column. The column is fitted with a small plug of glass wool in the bottom to retain the gel and with a reservoir at the top to hold the displacing fluid. The diameter of the column is one of the controlling factors in securing accurate results. A smaller diameter column will give a more distinct break between the bands and also a band in which the plane is more nearly normal to the axis of the column.

A.P.I. Gravity

The determination of the API gravity of the samples was conducted using a set of standard gravity hydrometers.

Materials and Reagents

Properties

Pure aniline, $C_6H_5NH_2$, an amino derivative of benzol, has a boiling point of $361^{\circ}F.$ and a melting

point of 18°F . It dissolves in 31 parts of water, is poisonous, and is a good solvent for many compounds. The aniline to be used should be distilled just before being used and, for accurate work, should be standardized against a pure hydrocarbon such as n-heptane⁸.

Silica gel is an adsorbent prepared from coagulation of a colloidal solution of silicic acid. The gel is a hard, glossy substance, similar to quartz sand in appearance, and has the formula $\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

Materials used

The materials and reagents used in this investigation are listed below:

- (1) Silica gel No. 923-02-09-226, 100-200 mesh, Davidson Chemical Corporation.
- (2) Fluorescent indicator, Patent Chemical Company
- (3) Isopropyl alcohol, commercial grade, Phillips Petroleum Company
- (4) Cyclohexane, commercial grade, Phillips Petroleum Company.
- (5) Aniline, Aniline Corporation.

Procedure

Aniline Points

The aniline points were determined by the standard A.S.T.M.: D 611 - 47T method. For some of the very dark oils it was not possible to obtain accurate results by this method; therefore a modification of the A.S.T.M. procedure was employed.

In this modification the sample to be tested is diluted with a definite ratio of cyclohexane. The ratio of cyclohexane to oil to be used is dependent upon the darkness of the sample but should be held to a minimum. Since the change of aniline point with a change in the ratio of cyclohexane to oil is linear, the volume percentage of oil is plotted against the aniline point and extrapolated to 100 percent oil (see Fig. 1). This will give the equivalent aniline point of an undiluted sample.

Chromatographic Analysis

In the preparation of the adsorption column, the lower end of the column is plugged with a small piece of glass wool, filled with activated silica gel, and tapped until no further settling of the gel is noticeable. It is extremely important that the gel in the column be evenly packed to ensure a smooth and even progression of the sample as it moves down the column.

From the sample to be analyzed, 5 ml. of oil is measured into the graduate and mixed with 1 drop of fluorescent indicator. Out of this mixture 1 ml. is introduced into the prepared silica gel column. Air pressure of 3-5 psi. is applied until all of the fluid has entered the gel. The air pressure is removed and about 0.5 ml. of gel is added to the column to prevent mixing between the sample and the desorbing fluid. The reservoir is filled with desorbing fluid, isopropyl alcohol, and air pressure of 8-10 psi. is applied to the column.

As the sample moves down the column, the silica gel selectively separates the saturates and aromatics (see Method of Approach, page 4). After the sample has 20-25 cm. down the column, the total length as well as the individual length of each band is measured. Successive measurements are taken until the ratio of length is constant for the individual band.

The volume percentage for each of the hydrocarbon classes is found by the following calculation:

$$\% \text{ Aromatics} = \frac{(\text{length of aromatics})(100)}{(\text{total length of sample})}$$

$$\% \text{ Saturates} = \frac{(\text{length of saturates})(100)}{(\text{total length of sample})}$$

$$\% \text{ Olefins} = \frac{(\text{length of olefins})(100)}{(\text{total length of sample})}$$

If the sample being investigated has high boiling component present, it may be necessary to provide heat

to the column to keep the sample fluid enough to flow through the gel. When heat is used, care must be taken to use a desorbing agent that has a boiling point above the temperature of the heated column.

A.P.I. Gravity

The A.P.I. gravity of all the samples was determined by the standard A.S.T.M.: D 287-39 procedure.

Boiling Range

The boiling range of the samples were obtained from the true boiling point distillation data.

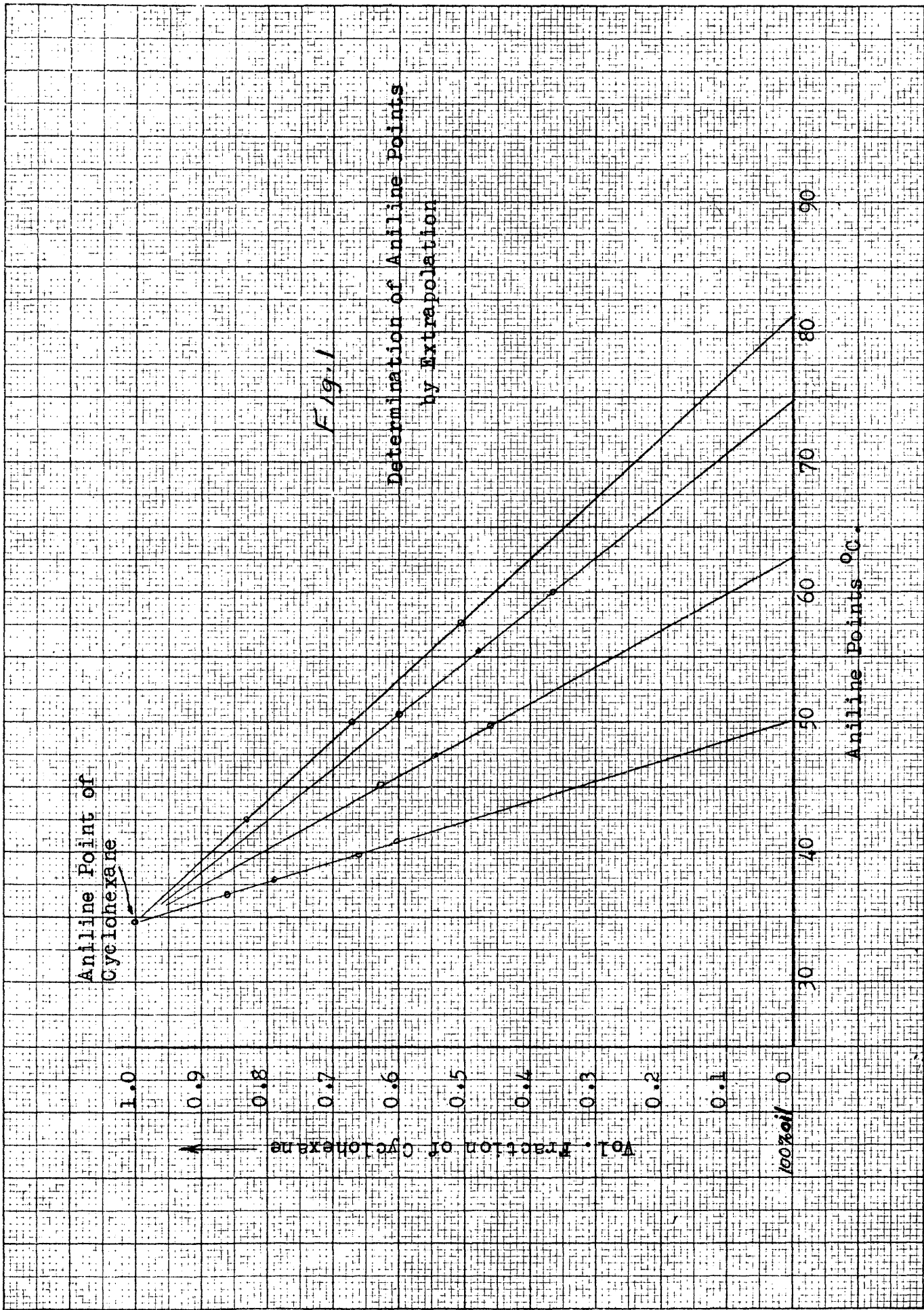


Fig. 1

Determination of Aniline Points by Extrapolation

Aniline Point of Cyclohexane

Aniline Points °C.

Vol. Fraction of Cyclohexane

100% oil 0

Data

The samples analyzed in the laboratory were obtained from a true-boiling-point distillation. The samples were taken in 3 percent cuts from a charge stock of 3,500 ml. Two crudes were used in this investigation. One, an intermediate base, was from Rangely, Colorado, and the second one, a paraffinic base, was from Lance creek, Wyoming.

For the determination of the aromatic hydrocarbon class content, cuts were chosen whose boiling ranges were approximately equal. The maximum difference for each set of cuts at either end of their boiling ranges was 5^oF. The author does not believe that this difference is sufficient to cause an appreciable error in the results.

The fractions from the two crudes were analyzed for API gravity, aniline points, and aromatic content. These results are tabulated in Table 1.

After the original properties of the samples were determined the aromatics were removed by adsorption with the silica gel. The aniline points and API gravity of the aromatic free fraction were determined. These values are tabulated in Table 2.

TABLE 1
Properties of Original Fractions

** Boiling Range	Rangely Crude			Lance Creek Crude		
	API Gravity	Aniline Point°C	% Aromatics	API Gravity	Aniline Point°C	% Aromatics
	69.1	55				
150 - 190	64	53.9	4.2	70.5	57.7	3.9
275 - 290	59.2	53.0	10.7	65.3	56.5	12.6
	51.3	52.3		60.8	55.2	
				53.2	56.8	
340 - 380	46.2	54.6	16.2	48.2	61.8	14.2
	45	57.1		46.2	66.1	
440 - 460	40.6	64.7	18.1	43.7	71.3	13.7
	38.2	68.8				
525 - 545	36.7	72.6	18.9	39.7	77.2	13.5
575 - 610	34.2	78.1	21.8	36.7	83.5	16.2

* Boiling Range °F.

TABLE 2
Properties of Aromatic Free Fractions

*Boiling Range	Rangely Crude		Lance Creek Crude	
	Sp. Gravity	Aniline Point	Sp. Gravity	Aniline Point
150 - 190	.718	57.4°C	.705	60.9 °C
275 - 290	.732	65.6°C	.731	72.2 °C
340 - 380	.780	69.1°C	.768	81.2 °C
440 - 460	.795	84.6°C	.792	84.7 °C
525 - 545	.805	89.1°C	.801	90.7 °C
575 - 610	.813	95 °C	.808	95.9 °C

* Boiling Range of original sample ° F.

CORRELATIVE

This correlation section is divided into three parts, which are explained in the following paragraphs.

Aniline Point and A.P.I. Gravity

A plot is made of aniline point and the A.P.I. gravity from the laboratory data (see Table 1). A study of this graph (see Fig. 2) shows the changes in the composition of the fraction as the boiling range increases.

The aniline-point decrease with a decrease in gravity to the minimum point shows the effect of the decreasing amount of the low-molecular-weight straight-chain paraffins. The increase in the aniline point with a continued decrease in A.P.I. gravity, after the minimum point is reached, is caused by the increase in the naphthenes and paraffin side chains.

The graph of the two crudes are very similar and suggest a possible new method of determining the base of a crude. Further investigation of this possibility was carried out by using data from the literature of the U.S. Bureau of Mines.

The literature data was selected for crude oils from the following fields: Smith Mills Consolidated Field, Kentucky², Lagunillas, Venezuela⁶, Loudon, Illinois, and LaGrange, Mississippi³. Since these oils range from highly paraffinic for the LaGrange crude to highly naphthenic for

the Lagunillas crude a wide range for the base of crudes is available.

A graph of the aniline points and API gravity of the oils (Fig.3) shows very clearly some of the difficulties in determining the base of a crude. A crude such as Loudon may be highly paraffinic in its light fractions, and may be intermediate or naphthenic in its heavier fractions.

This correlation of aniline point and API gravity indicates a simple and accurate method may be made for the determination of the base of a crude. The relative position of the points of the fractions of the crude being investigated, will give a good indication of the paraffinicity or naphthenicity of the sample and the crude.

Aniline Point, A.P.I. Gravity, and Boiling Range

A correlation of aniline points and API gravity with boiling range is shown in Fig.4. This graph shows good correlation for crude fractions for the boiling ranges from 368°F. to 590°F.

It is believed that the aromatics are the controlling factor in this correlation since they have the greatest effect in depressing both the aniline point and the API gravity.

Aniline Point, Boiling Range, and Hydrocarbon Classes

Ordinary straight-run petroleum fractions are composed of three main hydrocarbon classes: paraffins, naphthenes, and aromatics. The relative percentage of each class has a definite effect upon the aniline point of the fraction.

Since each individual class has its own effect upon aniline point of the fraction, an average, or blending value must exist for each class. This average, or blending, value is assumed to be constant for fractions having the same boiling range.

In order to have a constant blending value for fractions of the same boiling range, the assumption is made that each individual class has the same components; i.e. in samples of the same boiling range a class such as aromatics all have the constituents. This assumption is not entirely accurate but the variation in the compounds composing a class is not large enough to affect the blending of the class appreciably.

The blending values for the hydrocarbon classes were calculated by using a combination of laboratory data and data from literature. Laboratory data was used to determine the blending values of aromatics, and literature data was used to determine the naphthene and paraffin blending values.

For the calculation of the blending values of paraffins and naphthenes the data used were for the Turner Valley, Canada⁴, crude and the Abqaiq, Saudia Arabia⁴, crude. These two crudes were selected because they have been analyzed very thoroughly and the data is believed to be extremely accurate.

The tabulated data for the two crudes are given in Table 3.

Table 3

Analysis of a Turner Valley and an Abqaiq Crude Oil

Boiling Range °F.	Turner Valley				Abqaiq Field				Aniline Point °C
	Arom. %	Naph. %	Pffe. %	Aniling Point °C.	Arom. %	Naph. %	pffe. %	Aniline Point °C	
167 - 212	2.2	53.1	44.7	55.8	1.5	37.2	61.3	59.1	
257 - 302	16.0	33.4	50.6	51.8	7.1	50.9	42.0	57.6	
347 - 392	19.5	39.8	40.7	58.0	13.0	52.8	34.2	61.0	
437 - 482	23.5	47.1	29.4	61.1	15.6	55.3	29.1	67.9	
527 - 572	26.4	49.2	24.4	65.5	16.5	56.3	27.2	74.3	
572 - 617	30.8	44.2	25.0	69.2	18.3	65.9	15.8	77.7	

The blending aniline values for the hydrocarbon classes are calculated by the method in the following procedure.

Calculation of blending aniline values

It is necessary to calculate the blending aniline value of aromatics from the laboratory data because the aromatic free fraction aniline point is not available from the literature. The blending values of aromatics are determined as follows:

$$A(X) + K(AP') = AP \quad (a)$$

Where A is the percentage of aromatics in the sample

X is the blending value of aromatics

K is the percentage paraffins and naphthenes

AP' is the aniline point of the aromatic free fraction

AP is the aniline point of the original sample

The blending aniline value for paraffins and naphthenes are calculated by solving the following two equations.

$$A_1X + B_1Y + C_1Z = AP_1 \quad (b)$$

$$A_2X + B_2Y + C_2Z = AP_2 \quad (c)$$

The aromatics, A, are determined by chromatographic analysis and aromatic aniline blending value, X, determined by Eq.(a). Substituting these values into Eq. (b) and (c) reduce the three unknowns to two unknowns.

In Eq. (b) and (c) as follows:

A, B, and C are the percentages of aromatics, naphthenes, and paraffins in the samples.

X, Y, and Z are the blending values of aromatics, naphthenes, and paraffins
 AP_1 and AP_2 are the aniline points of the samples.

Sample calculation

Aromatic blending value

The following data are from Table 1 and Table 2 for fractions having a boiling range 275-290^oF
 Boiling Range 275-290^oF.

Properties	Rangely Crude	Lance creek Crude
Aromatics, %	10.7	12.6
Naph.+ Paraffins	89.3	87.4
Original aniline point	53.0 ^o C	56.5 ^o C
Aromatic free aniline point	65.5 ^o C	71.9 ^o C

Substituting in Eq(a) for:

Rangely Crude

$$A(X) + K(AP') = AP$$

$$0.107(X) + 0.893(65.5) = 53.0$$

$$\underline{X = -52.0}$$

Lance Creek Crude

$$0.126(X) + 0.874(71.9) = 56.5$$

$$\underline{X = -52.4}$$

Average value of X = -52.2

The rest of the aromatic blending values were calculated in the same manner and plotted on the graph (Fig.5). Values may be obtained from it for any boiling range.

The naphthene and paraffin blending values were calculated from Table 3 for the boiling range 347-390°F.

Boiling Range 347-390°F.

Properties	Turner Valley Crude	Abqaiq Field Crude
Aromatics %	19.5	13.0
Naphthenes %	39.8	32.8
Paraffins %	40.7	34.2
Aniline point °C.	58.0	61.0

Substituting in Eq. b & c and using the aromatic blending value from Fig. 5 the following two equations result:

$$A_1 X + B_1 Y + C_1 Z = AP_1 \quad (b)$$

$$A_2 X + B_2 Y + C_2 Z = AP_2 \quad (c)$$

$$0.195 (-12) + 0.398(Y) + 0.407(Z) = 58$$

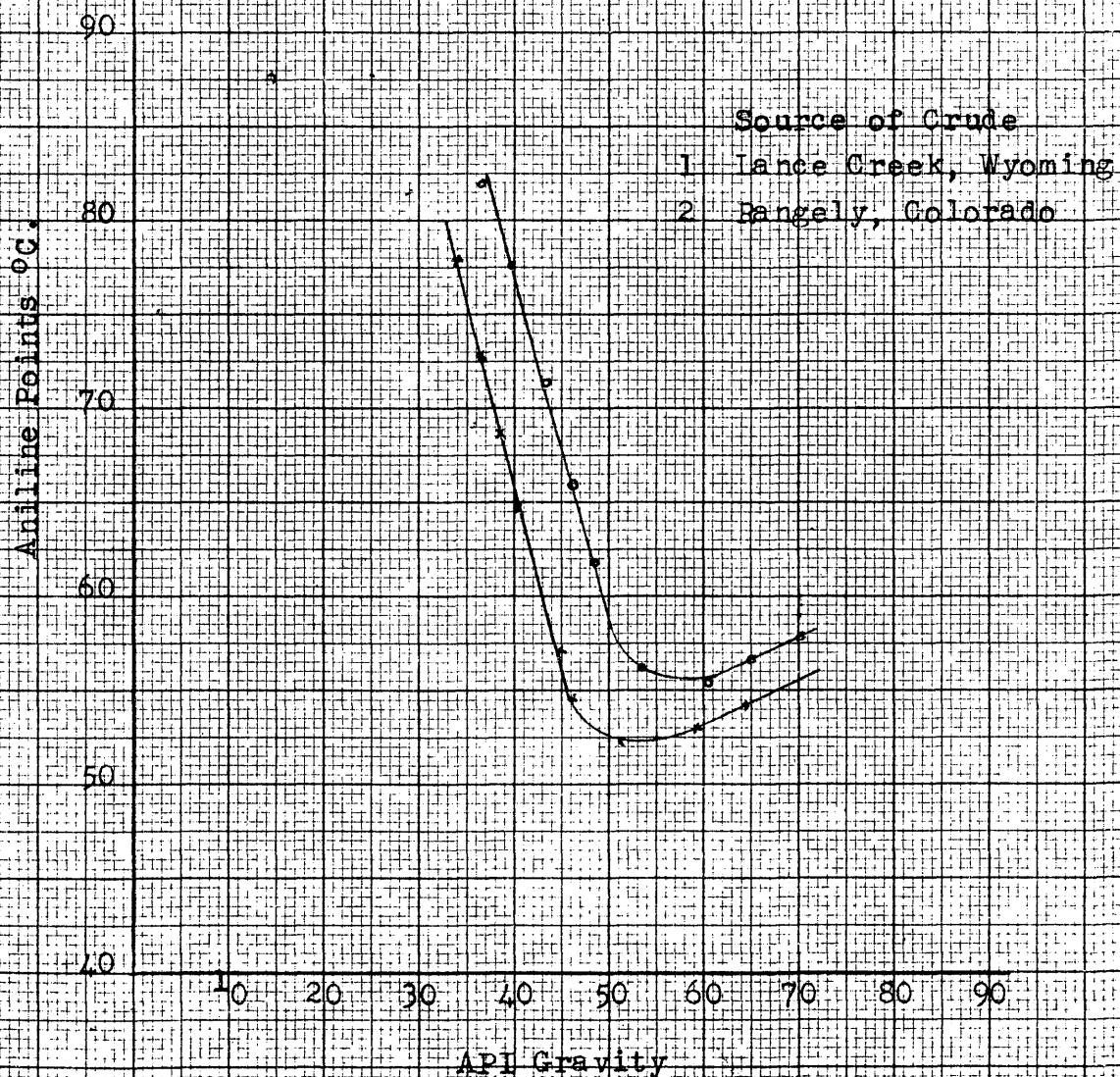
$$0.130 (-12) + 0.328(Y) + 0.342(z) = 61$$

$$\underline{Y = 61.8}$$

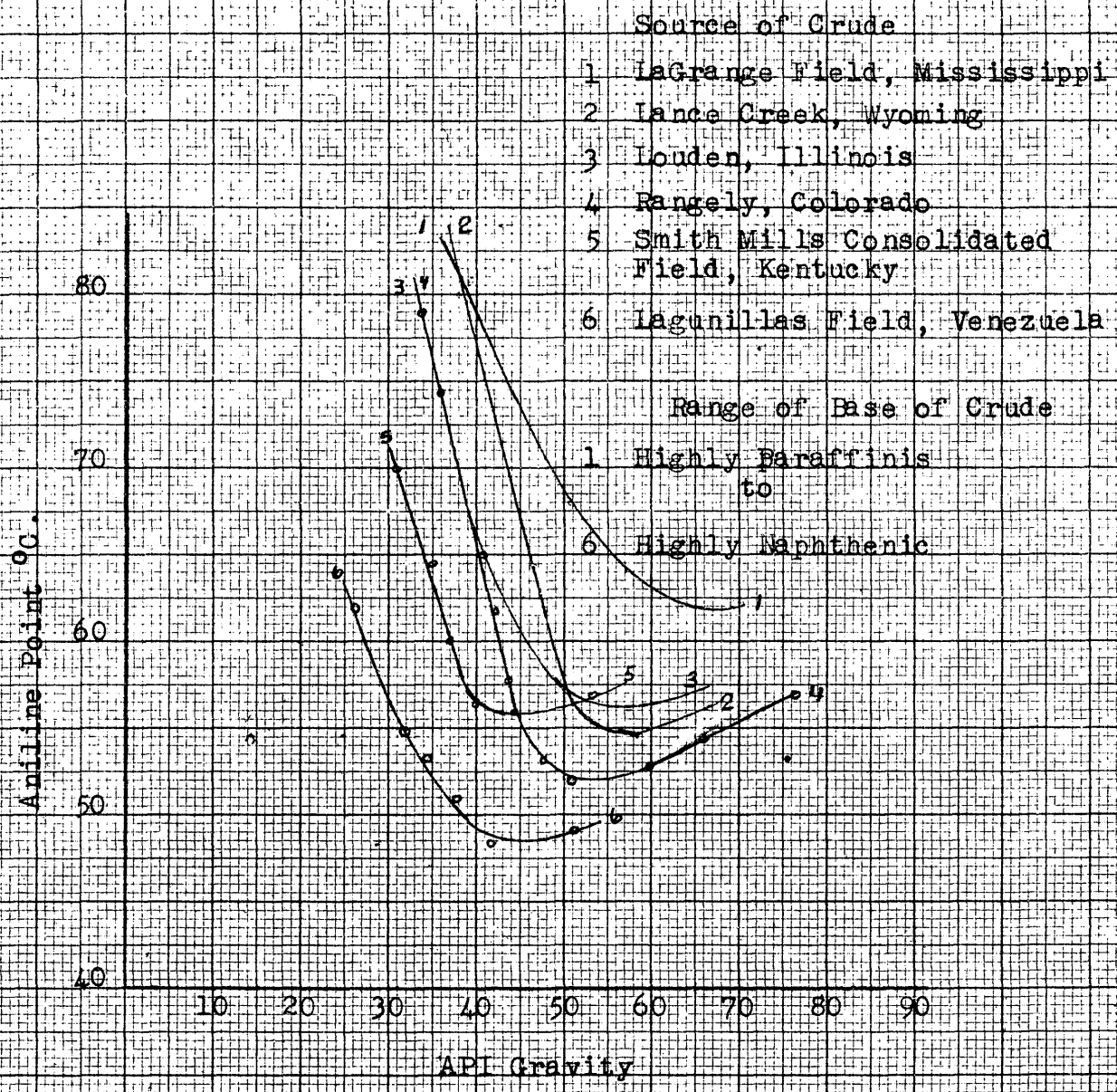
$$\underline{Z = 87.0}$$

The rest of the naphthene and paraffin blending values are calculated in the same manner. The values for all the boiling ranges are shown on the graph(Fig.5).

Fig. 2

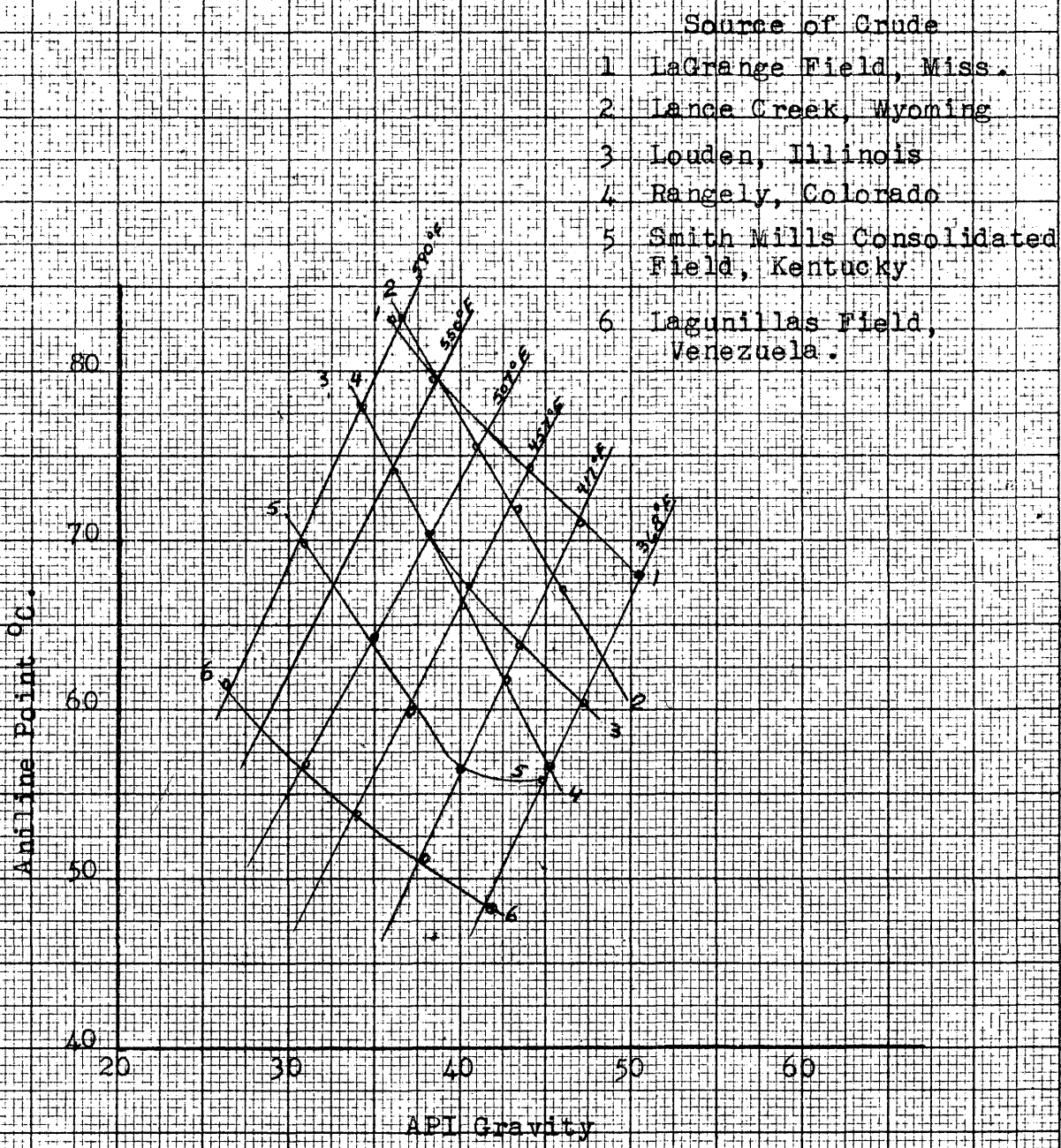


Correlation of API Gravity & Aniline Points



Correlation of API Gravity and Aniline Points for Oils Having a wide range of base

Fig. 3

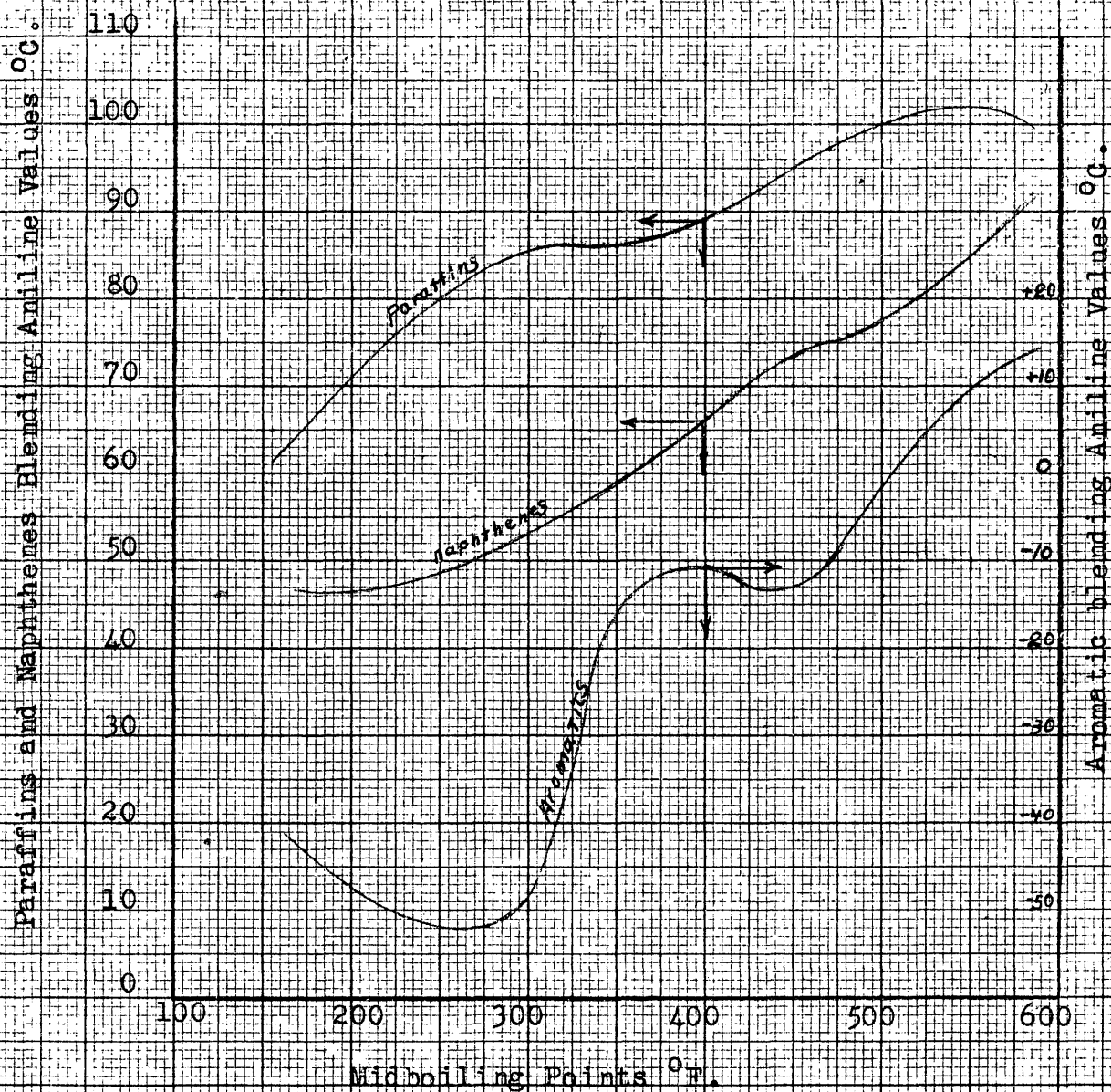


Correlation of Aniline Point, API Gravity,
and Boiling Range.

Fig. 4

MADE IN U.S.A.

Fig. 5



Correlation of Midboiling Points and Blending Values for Aromatics, Naphthenes, and Paraffins

SUGGESTED NEW METHOD OF ANALYSIS

The availability of the blending values for the hydrocarbon classes and the method behind their derivation lead the author to believe that rapid and fairly accurate determination may be made of a fraction to ascertain the percentage of each class.

The method of approach for the determination of hydrocarbon classes would be the reverse of the procedure followed in the derivation of the blending values. The paraffins and naphthenes would be obtained by solving the following two equations simultaneously:

$$A(X) + B(Y) + C(Z) = AP \quad (1)$$

$$A + B + C = 1 \quad (2)$$

where A, B, and C are the percentage of aromatics, naphthenes, and paraffins

X, Y, and Z are the blending values for aromatics, naphthenes, and paraffins

A, the percentage of aromatics is determined by the chromatographic analysis. With A known the equations reduce to two equations that can be solved for the values of paraffins and naphthenes.

CONCLUSIONS

This study indicates a very good correlation with aniline point and such properties as boiling range, A. P. I. gravity, and hydrocarbon class content.

Since aniline point, as used here, is defined as the temperature of mutual solubility of equal volumes of aniline and oil, the correlation would be expected because the factors of boiling range, A. P. I. gravity, and hydrocarbon class are all related to the temperature of mutual solubility.

The correlation of aniline point and A. P. I. gravity could be applied to the evaluation of a crude oil in all of its boiling ranges. The correlation gives an indication of the paraffinic or naphthenicity of an oil and thus shows the best types of products that may be produced from the oil.

The aniline blending values for the different hydrocarbon classes leads the author to believe that a simple and accurate method may be available to determine the paraffin and naphthene content in a petroleum fraction.

All of these correlations are very incomplete and more work should be done to definitely establish the range and usefulness of the correlations.

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