An Investigation of the Properties of Wax Obtained from Shale Oil

By

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Signed Joseph Shoaf
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Approved James O. Ball

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TABLE OF CONTENTS

ILLUSTRATIONS

TABLES AND CURVES

SUMMARY

This is a report of the investigations made on the various properties of waxes from the fractions of a shale oil. The shale oil cuts were obtained by charging the crude shale oil to a true boiling point unit and taking off 2 percent cuts, which were dewaxed by diluting with methyl-ethyl-ketone and chilling. The entire fractionation was conducted under vacuum and the temperatures corrected to 760 mm Hg. pressure.

The fractions boiling below 890°F were easily separated into a white, odorless, and tasteless wax, by using one crystallization and washing of the solid precipitate with cold methyl-ethyl-ketone.

The melting points of the solid materials separated from the shale oil fractions varies with the boiling range of the shale oil. The higher the boiling range of the crude shale oil, the higher the melting point of the wax in general.

Correlations of refractive index, specific gravity, refractivity intercept, molecular weight, and the melting points of the waxes show that they appear to fall into the paraffin class of hydrocarbons.

INTRODUCTION

The investigation in this report was undertaken to determine the properties of wax from shale oil. This crude shale oil was produced in a continuous-process pilot-plant retort by passing superheated steam through a downward-moving bed of shale. The crude oil vapors and steam were then condensed and separated. The crude shale oil obtained from the retorting of Colorado Green River shale was fractionated under vacuum in a true boiling point distillation unit. The hydrocarbons that make up the wax probably do not exist as such in the oil shale but are most likely a product of decomposition of the kerogen, or organic matter, that is contained in the oil shale.

The wax was separated from the shale oil fractions by the use of methyl-ethyl-ketone in a solvent extraction process. This solid substance crystallized out in plates which had a pearly lustre. The extracted material from the fractions was then air dried and weighed. After weighing the individual solid fractions, molecular weight determinations were made on seven of the fractions; refractive indices and melting points were determined and the refractivity intercepts calculated which are all tabulated in this report of investigation.

Review of Previous Work

A literature search of the various books and articles pertaining to this investigation was made. Articles dealing with procedure, method, analysis, solvents, and the like were investigated. Not much research has been done on the products derived from the shale oil in recent years, except by the United States Bureau of Mines. It was therefore necessary to use individual judgment in many of the procedures in this investigation. The various published books and articles on oil shale have been read, and these books and articles are listed in the bibliography.

EXPERIMENTAL WORK

Apparatus and Equipment

The apparatus and equipment as well as the chemical compounds used in this report of investigation are to be found in any well furnished chemical engineering or petroleum refining laboratory. The materials used are amply described in the procedure as well as the photographs of the apparatus.

Procedure

Five liters of crude shale oil obtained from a continuous-process pilot-plant retort, using oil shale from the Colorado Green River formation, by passing superheated steam through a downward-moving bed of shale, was charged to the true boiling point distillation apparatus (Figure 1). Twenty-nine fractions were distilled overhead, each fraction consisting of 100 cubic centimeters, or 2 percent, of the oil charged to the unit per cut. The entire distillation was carried out under vacuum and was discontinued at the end of the twenty-ninth fraction as the liquid temperature in the oil reservoir approached 600°F. The operations as performed in this report are listed in the operational flow diagram (Table 1).

A sample of crude shale oil was taken to determine the procedure necessary to obtain a white wax. The selection of a dewaxing solvent involved the selection of a material that

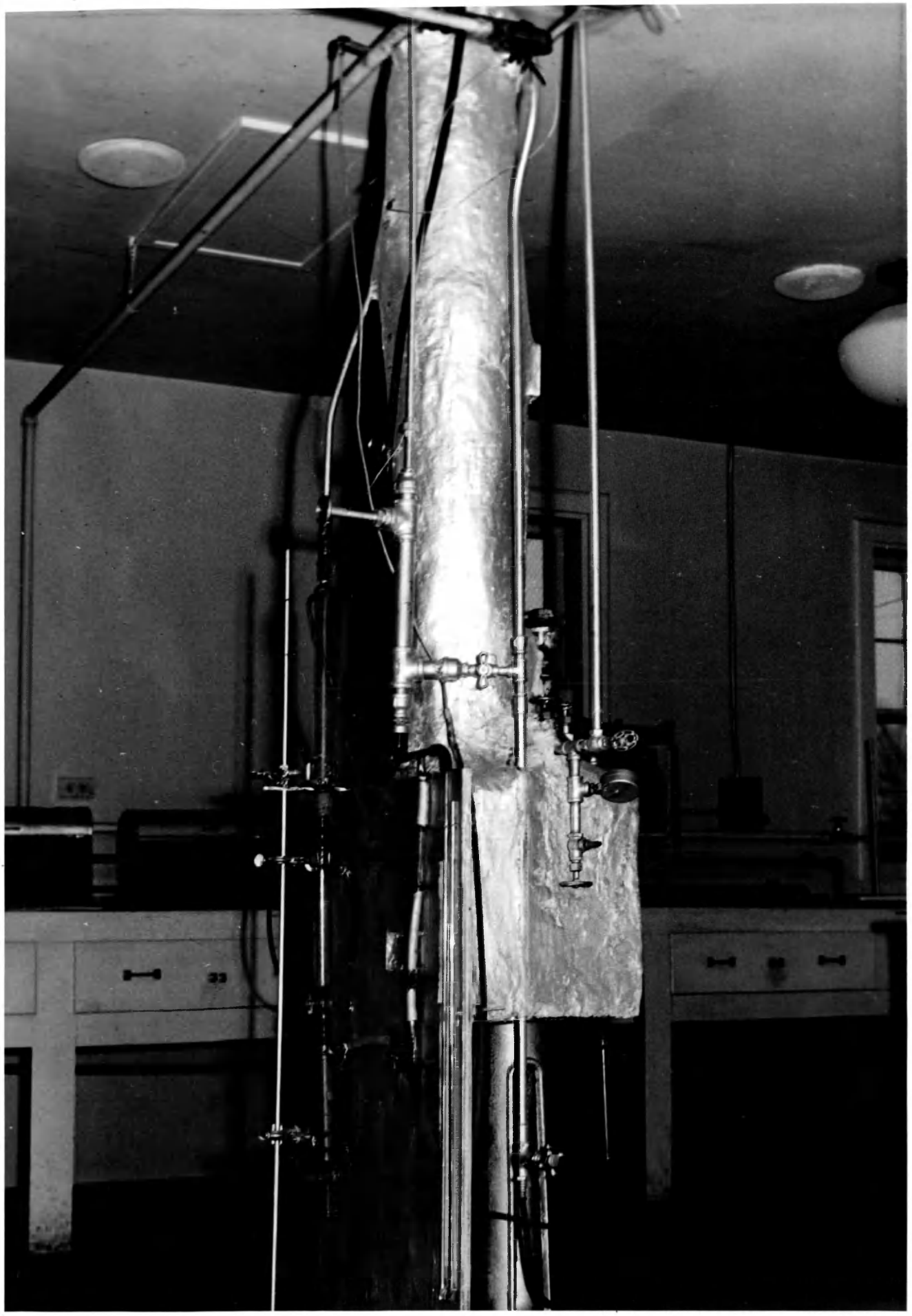


Figure 1, True Boiling Point Distillation Apparatus.

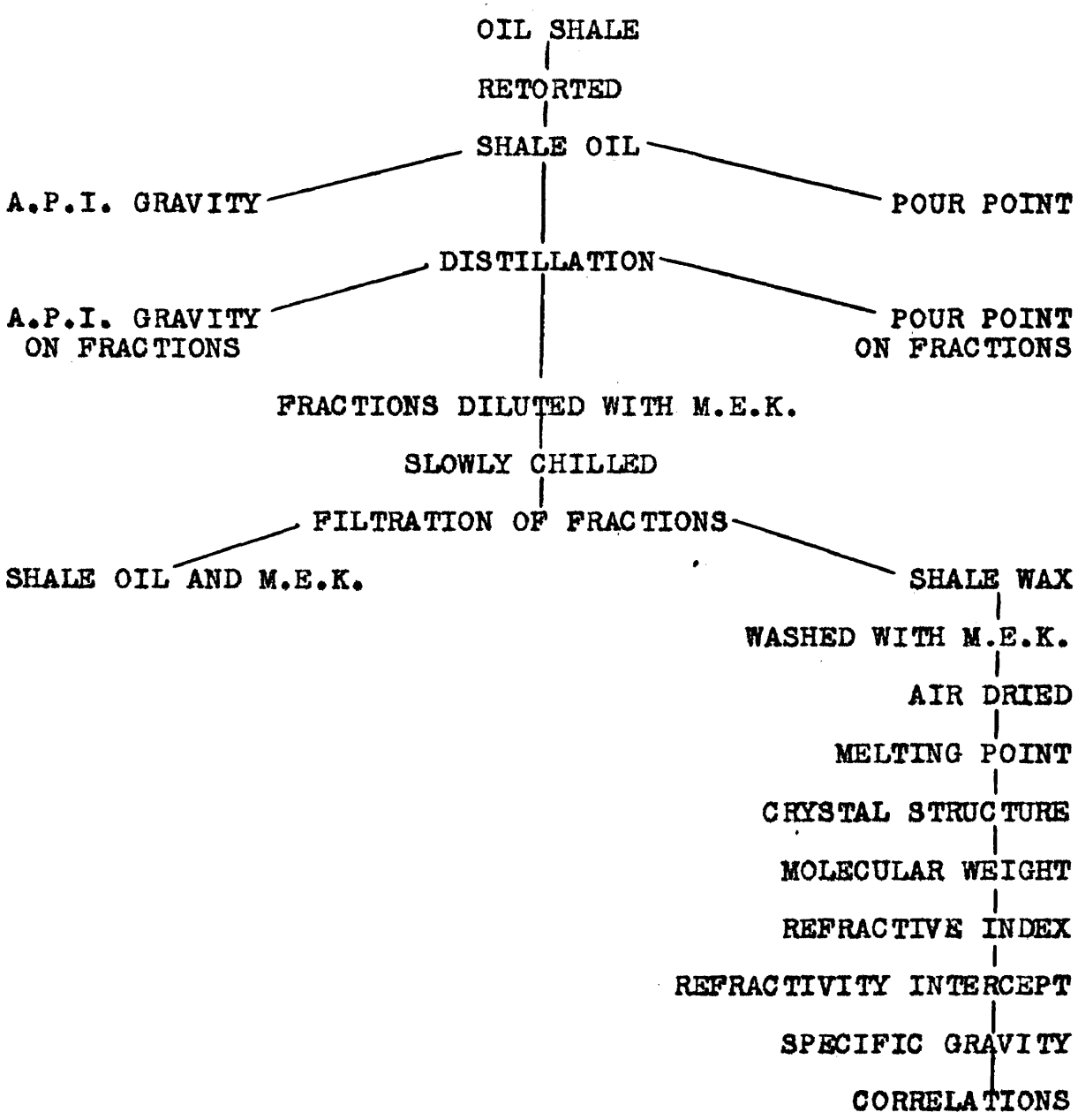


Table 1

Operational Flow Diagram

has a strong solvent action for the oil while permitting the wax to form insoluble crystals suitable for an easy separation from the oil-solvent solution. Amyl alcohol, acetone, and methyl-ethyl-ketone were tried as individual solvents; then mixtures of the above with cresol, pyridine, and benzene were tried as dewaxing solvents for the crude shale oil. When the crude oil was used with the above solvents, the solid materials precipitated in all of the tests were black. It was necessary to treat this black material further to obtain a white wax. To obtain a white wax from the crude shale oil it was precipitated using methyl-ethyl-ketone, which appeared to be the best solvent of those tried, the black solid was then dissolved in a light naphtha and treated with concentrated sulphuric acid. The acid sludge was separated, and kerosene was added to the wax-naphtha solution. This solution was contacted with silica-gel for twenty-four hours at 230°F. The wax-kerosene solution was separated from the silica-gel and diluted with methyl-ethyl-ketone. This mixture was slowly chilled to -20°F and filtered. The precipitate retained on the filter paper was a fine-grained, white wax. In the dewaxing of the actual fractions it was not necessary to use the above outlined procedure on any of the fractions other than the residuum.

The shale oil fractions from the distillation were all dewaxed by the use of methyl-ethyl-ketone as the solvent.

The oil solvent mixture was slowly chilled to the desired temperature in a refrigerator unit, the precipitate was then filtered through jacketed funnels using a small pump to circulate a cold ethylene glycol solution through the funnels. A vacuum pump was used to increase the rate of filtration (Figure 2). The crystals obtained by this method on the shale oil fractions were all white except the last three, which were a light bronze in color. The various physical properties of the waxes were then taken and correlations made as are listed.

Distillation of Shale Oil

Five liters of the crude shale oil were charged to the distillation unit (Figure 1), and 2 percent fractions were withdrawn. The distillation was carried out under vacuum and continued until the liquid temperature in the pot reached 600°F. The gravities of the oil fractions from the distillation were determined by use of a Westphal balance. The pour points of the oil fractions were determined by the A.S.T.M. Procedure D97-47.

Dewaxing

The wax was removed from the shale oil by solvent extraction using methyl-ethyl-ketone as the solvent. Twenty-five cubic centimeters of the shale oil was slightly warmed and mixed with 200 cubic centimeters of warm methyl-ethyl-

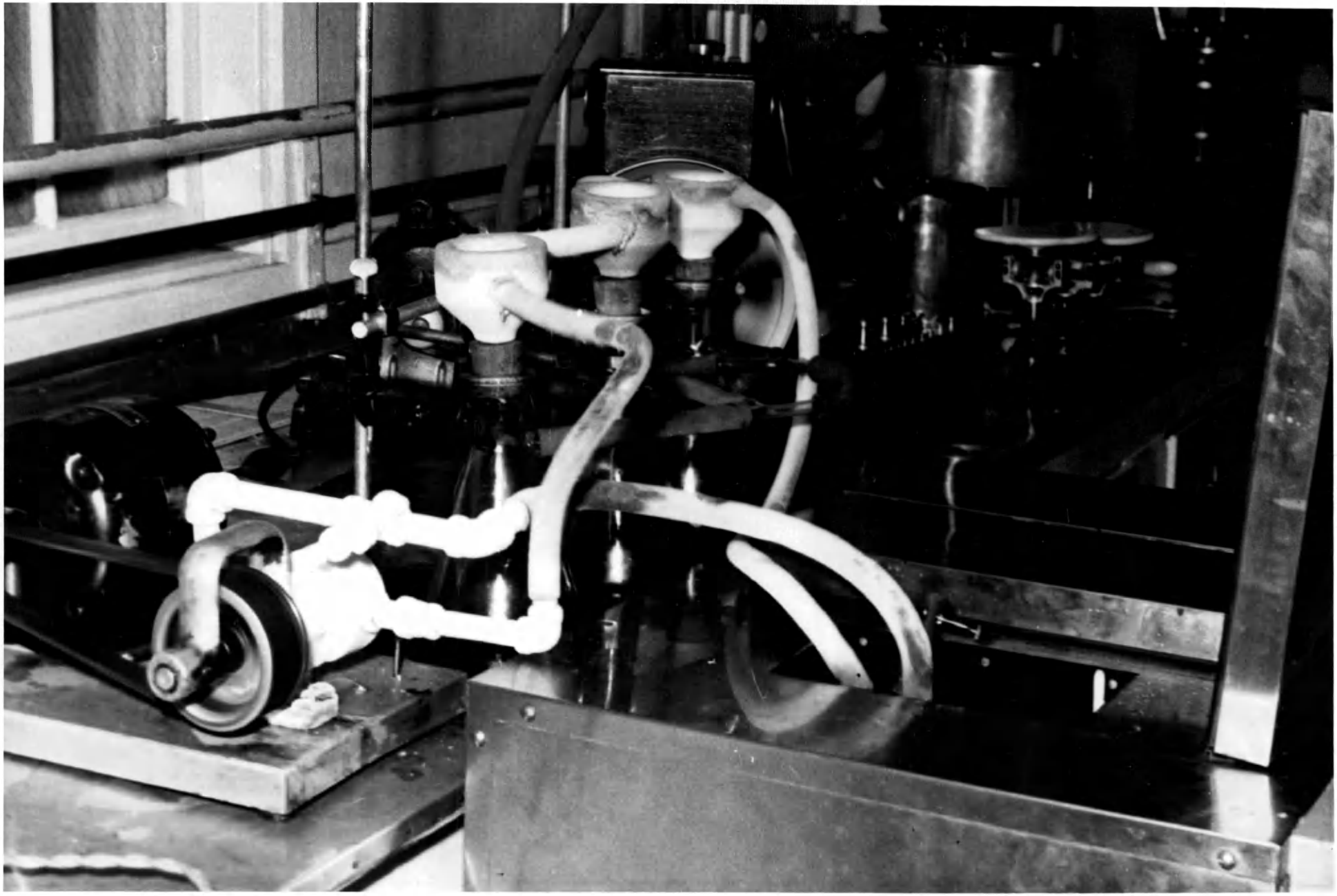


Figure 2, Filtration and Chilling Apparatus Used in the Dewaxing of Shale Oil.

ketone. This solution was cooled very slowly at a rate of from 2 to 5 degrees per hour to the required temperature. The wax was filtered out of the oil-solvent solution. Circulation of cold ethylene-glycol through jacketed filter funnels enabled the maintenance of the proper temperature within 5°F during the filtration process. The crystals were washed with cold methyl-ethyl-ketone until it became white and was air dried. A vacuum pump was used to increase the rate of filtration (Figure 2).

Properties Determined

Melting Points of Wax: Melting points were determined by use of the capillary melting point tube 12/.

Crystal Structure: The crystal structures of the waxes were observed with the aid of a microscope (Figures 9, 10, 11).

Molecular Weight: The molecular weights were determined on seven fractions of wax using the Rast Camphor Method 13/.

Refractive Index: Refractive indices were determined using the Abbe refractometer. Refractive indices were taken at 70°C and recalculated to the required temperature. The temperature correction for oils and waxes was -0.0004 for each °C rise in temperature 11/.

Refractivity Intercepts: The refractivity intercepts of the various wax fractions were calculated from the equation

$$\text{refractivity intercept} = n - d/2$$

where n is the refractive index and d is the density of the wax.

Gravities: The gravities of the wax fractions were obtained by preparing water-alcohol solutions of know densities, dropping small globules of wax in the solutions, and observing whether the wax floated, sank, or remained suspended. The gravities of the liquid oil fractions were obtained by use of the Westphal Balance.

DATA

True Boiling Point Distillation

The shale oil was distilled under vacuum and broken up into 29 fractions. The temperature of the cuts and the gravities are tabulated in Table 2.

Properties of the Wax Fractions

The refractive indices and the refractive intercepts of the various wax fractions are tabulated in Table 3. The melting points of the wax fractions and the molecular weight determinations are listed in Table 4.

Fraction	Volume, Percent Distilled	Pour Point, °F	T, °F at 760 mm	Gravity °A.P.I.
1	2		330	
2	4		440	43.1
3	6		452	40.2
4	8		485	37.8
5	10		490	35.8
6	12		515	33.1
7	14		528	33.0
8	16	5	550	29.7
9	18	0	570	29.5
10	20	5	590	28.9
11	22	5	605	28.6
12	24	10	620	27.9
13	26	40	630	27.1
14	28	40	650	26.6
15	30	40	662	25.5
16	32	40	675	24.6
17	34	55	680	24.6
18	36	60	695	24.1
19	38	65	722	23.8
20	40	70	748	23.7
21	42	70	772	23.5
22	44	95	780	23.5
23	46	95	810	23.2
24	48	95	840	23.2
25	50	95	875	23.1
26	52	100	890	21.7
27	54	110	900	21.3
28	56	110	904	21.3
29	58	110	908	20.7
Residuum				10.4
Crude Shale Oil		90		19.2

Table 2

True Boiling Point Distillation Data

Fraction	Refractive Index at 84°C	Refractivity Intercept at 20°C
5	1.3800	
6	1.3959	
7	1.3672	
8	1.3706	
9	1.3628	
10	1.4147	1.0115
11	1.4146	1.0114
12	1.4157	1.0125
13	1.4116	1.0084
14	1.4182	1.0250
15	1.4182	1.0250
16	1.4153	1.0121
17	1.4223	1.0181
18	1.4166	1.0134
19	1.4202	1.0170
20	1.4269	1.0237
21	1.4241	1.0209
22	1.4264	1.0232
23	1.4261	1.0229
24	1.4272	1.0240
25	1.4286	1.0254
26	1.4306	1.0274
27	1.4312	1.0280
28	1.4299	1.0257
29	1.4299	1.0257

Sample calculation of the Refractivity Index, Fraction 18

N = refractive index at 20°C
D = density at 20°C

R.I. = N-D/2 = 1.4422 - 0.8576/2 = 1.0134

Table 3

Refractive Indices and Refractivity Intercepts of Wax Fractions

Fraction	Melting Point, °F	Molecular Weight
5	18	
6	24	
7	33	
8	43	233
9	51	
10	56	239
11	59	
12	66	
13	79	292
14	98	
15	100	
16	102	
17	106	
18	109	321
19	115	
20	118	
21	120	
22	122	339
23	126	
24	130	
25	134	
26	137	
27	141	
28	141	
29	141	363
Residuum	162	520

Sample calculation of the Molecular Weight, Fraction 18

M = molecular weight
C = constant for the solvent used
P = grams of the wax/100 grams of solvent
Delta = temperature depression °C

M = (C x P)/Delta = (400 x 21.3)/26.6 = 321

Table 4

Melting Points and Molecular Weights of Wax Fractions

DISCUSSION

Meaning of the Data

The true boiling point distillation was used to obtain good fractionation of the shale oil as well as to determine the boiling temperatures of the fractions. The various properties of the shale oil fractions obtained with the aid of the distillation are illustrated in Figure 3. It was assumed that the boiling temperatures of the various wax fractions were approximately the same as those of the corresponding shale oil fractions from which the waxes were extracted.

The melting points of the waxes plotted versus the percentage distilled are illustrated in Figure 4. The dotted line represents fractions 5 to 10 which were chilled to -60°F and dewaxed at -20°F. The solid line represents fractions 11 to 29 which were cooled to -20°F and from which the wax was filtered out at 0°F. Figure 4 illustrates how the melting points is increased with the percentage of oil fractionated. The curve indicates that a high-melting-point wax could be obtained from the 30 to 60 percent portion of the shale oil.

The change in melting point with the different boiling ranges of the fractions is shown in Figure 5. The dotted line represents the same procedure of dewaxing the fractions

A.P.I. Gravity, Pour Point, and True Boiling Point Curves

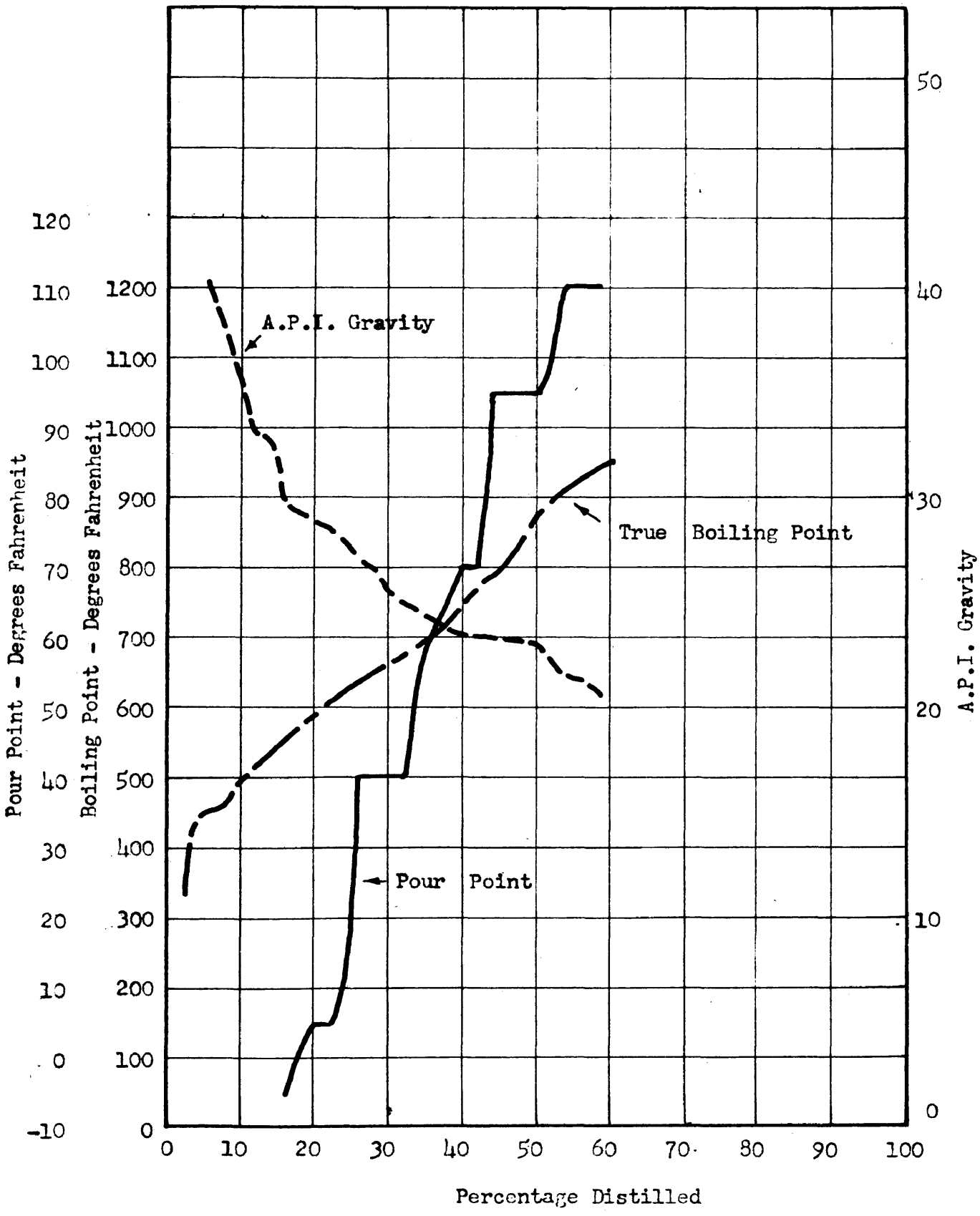


Figure 3.

Melting Point Curve

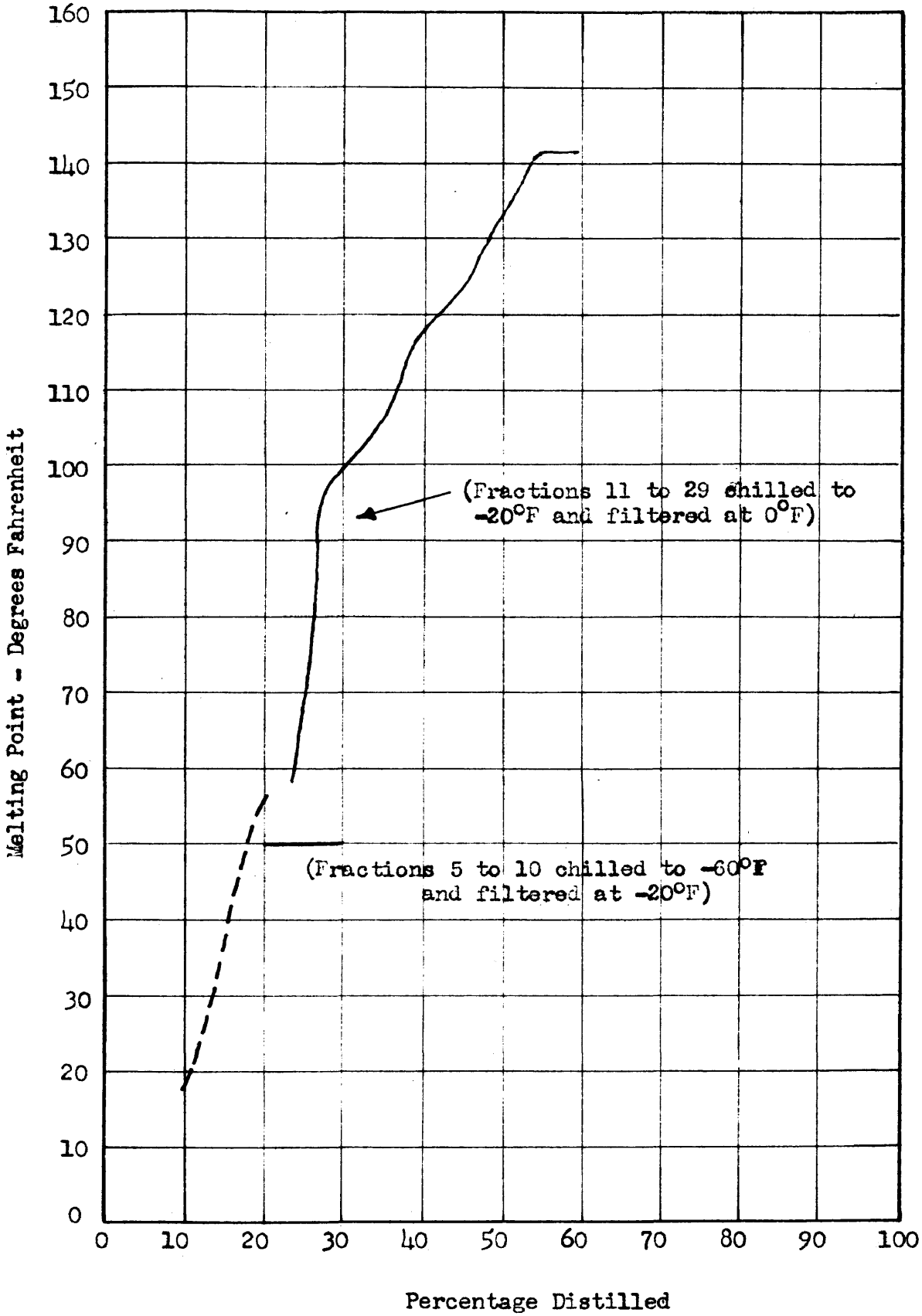


Figure 4.

Melting Point Curve

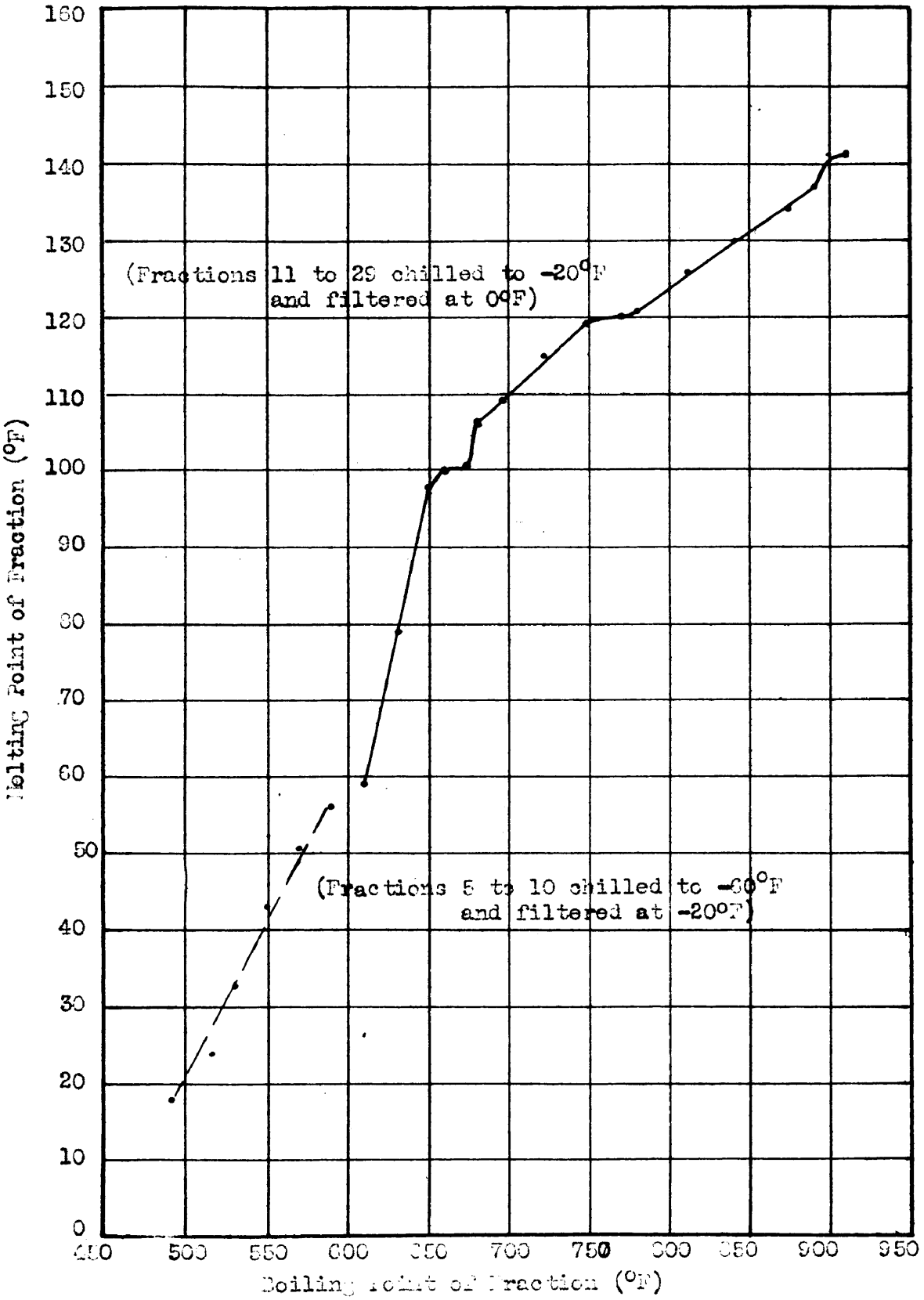


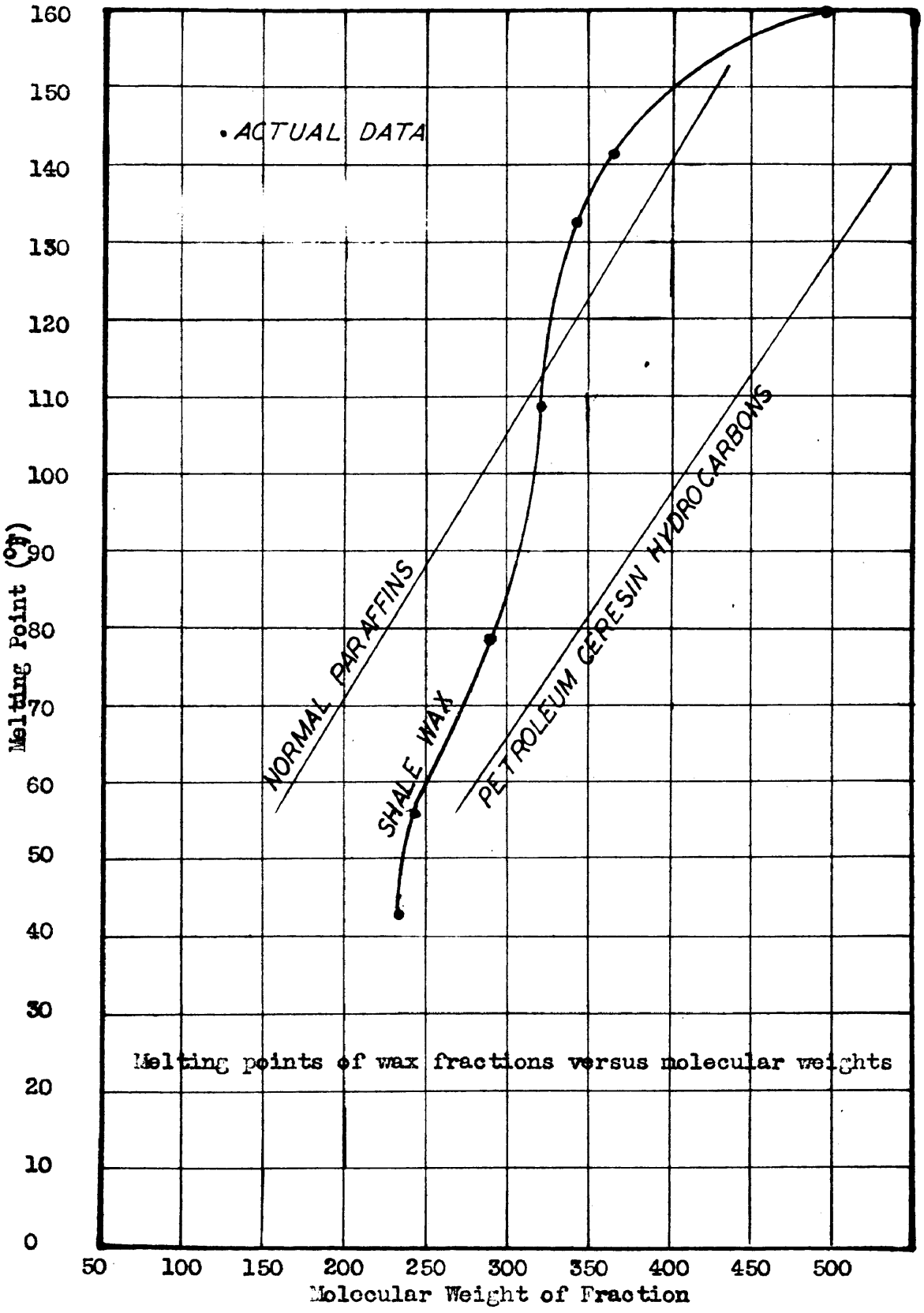
Figure 5.

as above. This figure indicates the shale oil fraction which boils between 650 and 900°F will produce a material that has a melting point range of 100 to 140°F.

Normal paraffins predominate in petroleum waxes from Mid-Continent crudes according to Sachanen, Wassilieff, and Sherdeva 20/. These authors studied the narrow fractions of petroleum fractions from two Russian crude oils obtained from the Grozny and Surachany oil fields. The fractions were obtained by crystallization in ethene dichloride and distillation under high vacuum. The molecular weight, specific gravity, melting point, and viscosity, as well as the ultimate analysis, were determined. The elemental composition and formulas correspond closely to hydrocarbons of the series C_nH_{2n+2}. Figure 6 represents the melting points of the fractions versus the molecular weight of the data from Sachanen with the data obtained from this investigation added. The shale wax corresponds closely to the properties of the normal paraffins and petroleum ceresin hydrocarbons.

The refractive index of each wax fraction was plotted versus the melting point of the fraction. A correlation was taken from Sachanen 19/ which graphically illustrates that it is very likely that the wax obtained from the shale oil to consist mainly of paraffins (Figure 7).

The refractivity intercept is a very useful constant for differentiating naphthenes from paraffins and aromatics,



Melting points of wax fractions versus molecular weights

Figure 6.

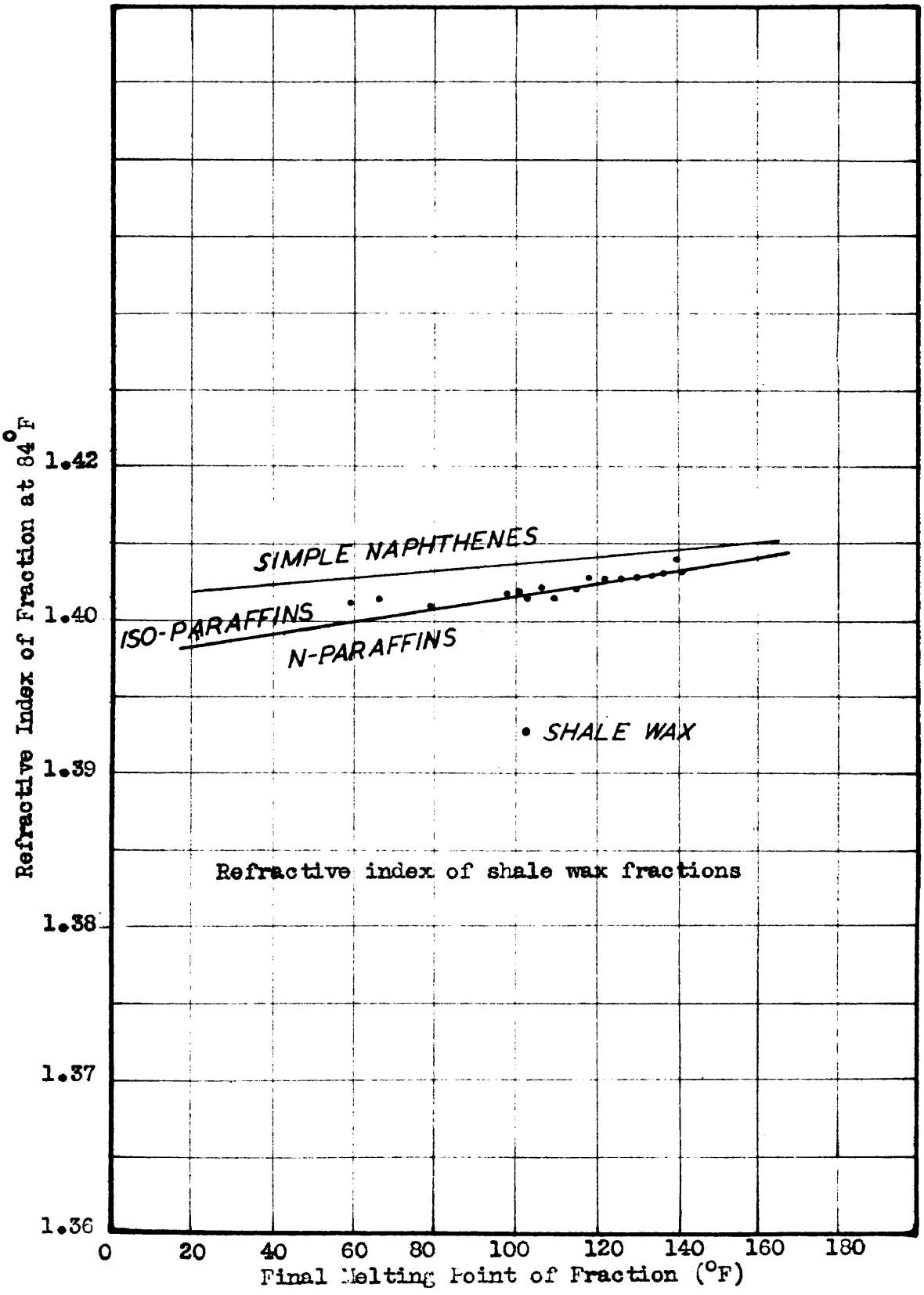

Refractive Index of Fraction at 84°F
1.42
1.40
1.39
1.38
1.37
1.36
SIMPLE NAPHTHENES
ISO-PARAFFINS
N-PARAFFINS
SHALE WAX
Refractive index of shale wax fractions
0
20
40
60
80
100
120
140
160
180
Final Melting Point of Fraction (°F)

Figure 7.

for identifying homologous series, and for analyzing certain binary and tertiary mixtures of pure or approximately pure compounds 14 and 15/. In case of hydrocarbon mixtures, the refractivity intercept may be used to distinguish between saturated cyclic and aromatic compounds, both of which have relatively high density and refractive indices. The refractivity intercepts of the lower alcohols, mercaptans, ethers, sulfides, ketones, organic halides, etc., are in general less than 1.00, whereas hydrocarbons, with the possible exception of some high molecular weight polynuclear naphthenes, are above 1.010. Therefore, the refractivity intercept provides a ready means for distinguishing between hydrocarbons and compounds containing appreciable proportions of oxygen, sulfur, or halogen. The refractivity intercepts for the shale oil waxes as calculated in Table 5 are all greater than 1.011 and correspond very closely with refractivity intercepts calculated from the data of Sachanen 21/, for paraffin waxes.

In viewing the formation of the wax crystals and their appearance, through a microscope, it appeared that all of the fractions that have a melting point above 58°F crystallise in a sort of film or in layers of films. The structure of the residuum appeared to be granular. Sachanen 22/ says that, "petroleum wax consists of at least two groups of hydrocarbons, which are classified as normal paraffins and

isoparaffins. The latter may belong to different homologous series, depending upon the structure and position of the side chains. The side chains of isoparaffins are short and are located in the middle or in the central parts of the molecules. Normal paraffins (and possibly the terminal slightly branched paraffins) crystallize in plates at lower temperatures and in neddles at higher temperatures, i.e., from 5 to 10° below the melting point. Isoparaffins crystallize in needles at any temperature." The manner in which the shale waxes crystallize would tend to be another indication that they are of the paraffin type. The plate like structure of the shale waxes are illustrated in Figures 9, 10 and 11.

The weight percentage of wax present in each fraction was determined by obtaining the weight of the shale oil fraction before dewaxing and the weight of the wax removed from the fraction. The weight percentage plotted against the cut number is shown in Figure 8. The crosses represent the chilling of the fractions to -60°F and the filtering at -20°F, whereas the circles represent the chilling of the fractions to -20°F and the separating of the wax at 0°F.

Errors Known and Possible

Possibility of error in this investigation may exist in the determination of the specific gravity and weight percentages of the waxes. It has been possible to recheck the various properties by recrystallization for the refractive index,

Weight Percent Curves

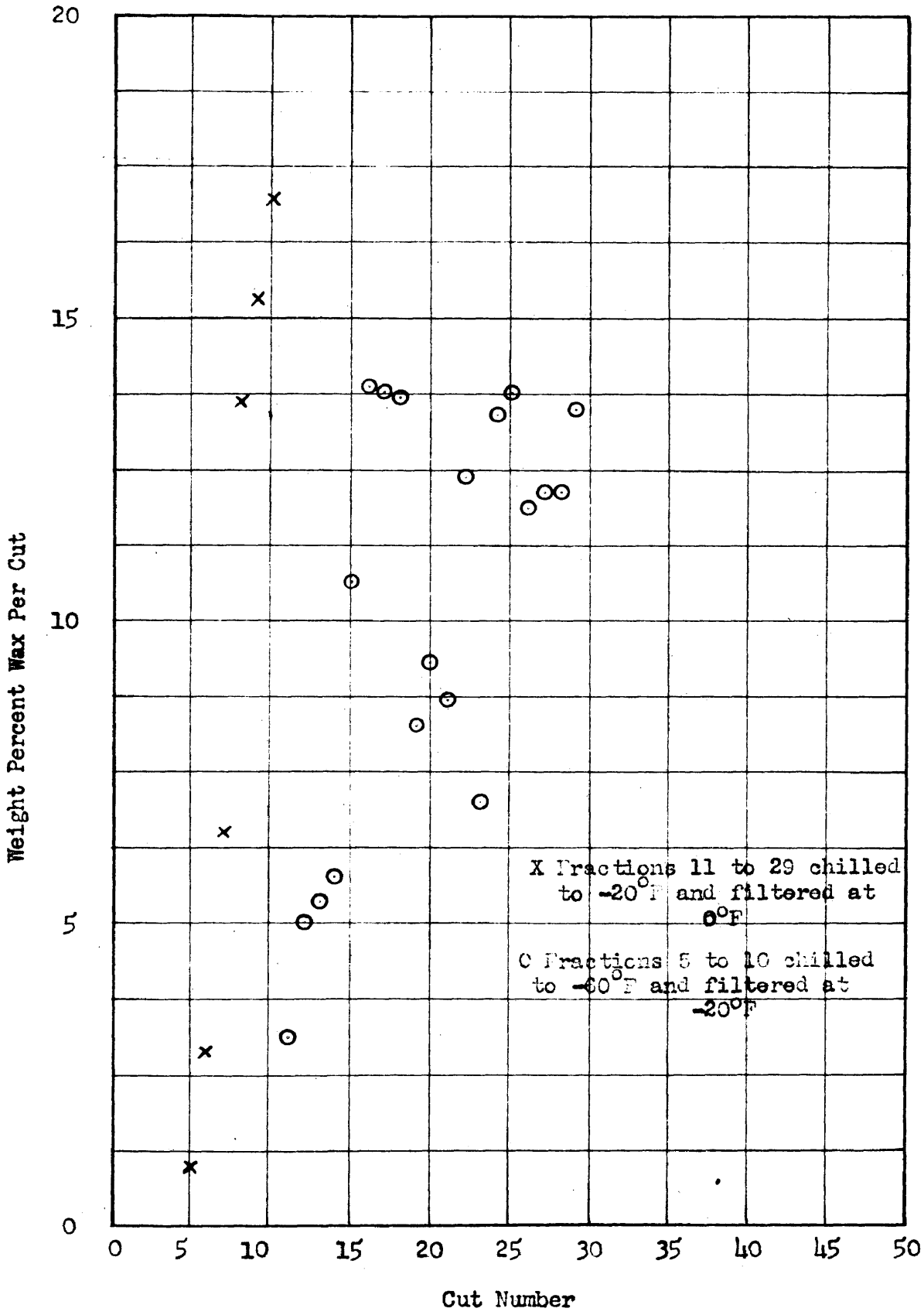


Figure 8.

Figure 9, Photograph of Shale Wax Enlarged 75 X.

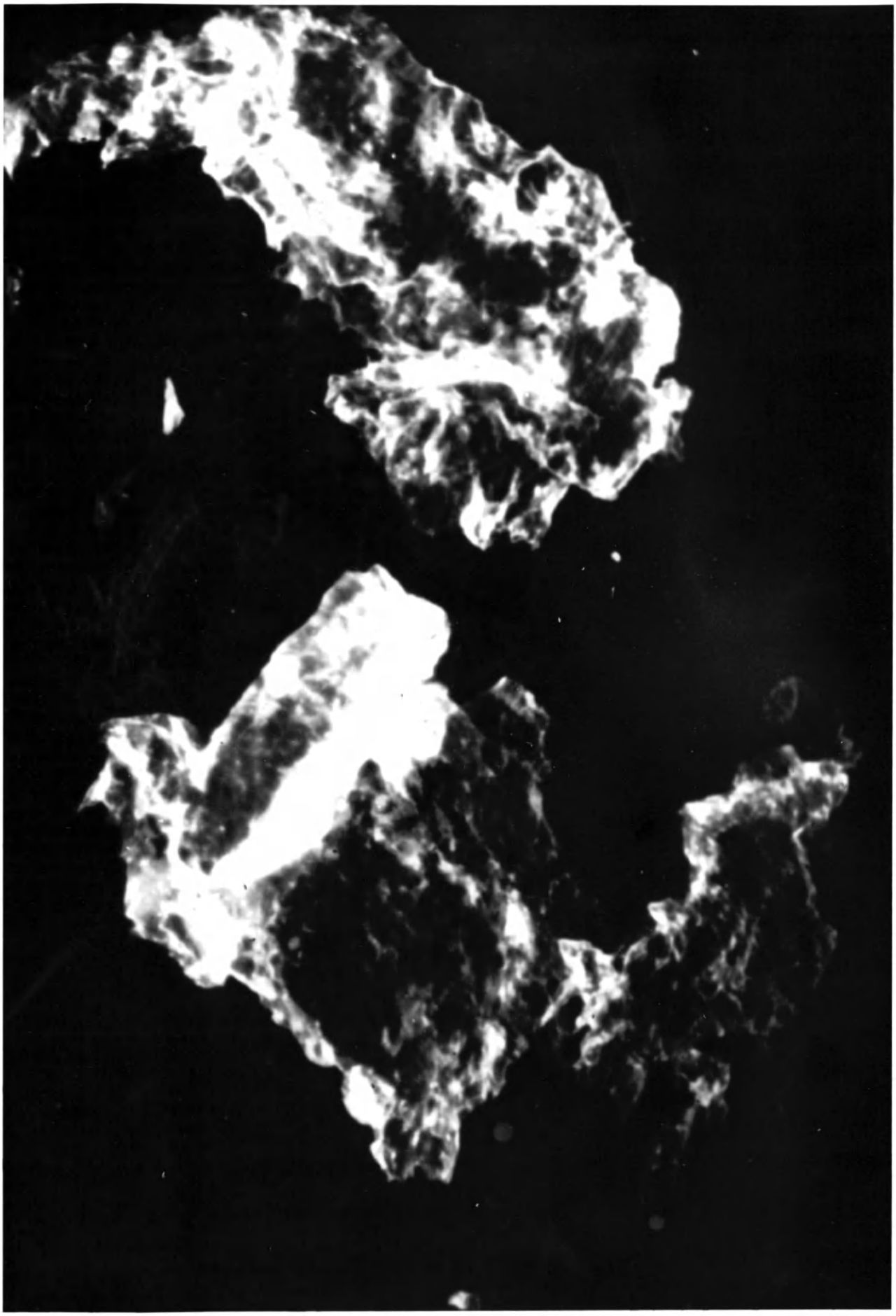


Figure 10, Photograph of Shale Wax Enlarged 75 X.

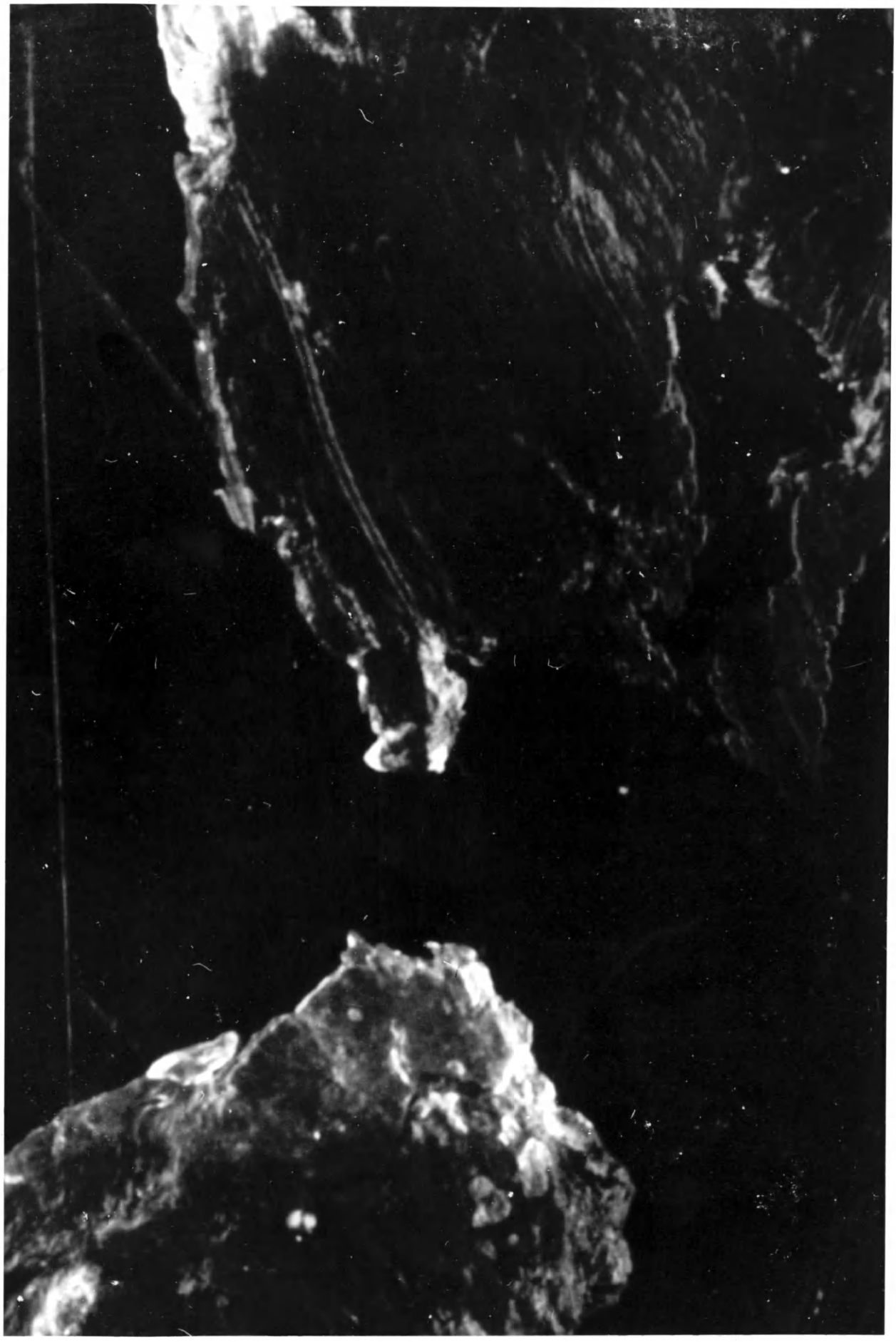


Figure 11, Photograph of Shale Wax Enlarged 75 X.

performing duplicate determinations for the melting points and molecular weight calculations.

The specific gravity of the wax fractions appeared to be 0.8607 at 60°F. This value was corrected to 20°C and used in the calculation of the refractivity intercepts. Since the molecular weights varied from 239 in fraction 10 to 363 in fraction 29, there is little doubt that the density should vary slightly also. It was not possible in the limited time and with the small samples available to determine the densities to a greater accuracy.

It was not possible at the time to run duplicate samples of shale oil fractions to check the weight percentages. Larger samples of materials would perhaps give a greater accuracy as a loss in recovery of 1/10 gram of wax would give an error ranging from 2 to 15 percent of the recorded value. Another factor may be the temperature of the cooling solution and the filter funnels which were maintained at ±5°F of the desired dewaxing temperature.

The purity of the samples and the accuracy of the refractive indices were checked by recrystallising a portion of wax in ethyl alcohol and reading the refractive index of the sample at two different temperatures before and after the recrystallization. The possible error in using 0.0004 as a temperature correction factor was 0.00002 for each °C change in temperature. The refractive index varied only

0.0002 upon recrystallization of the sample. This would indicate that the one extraction with methyl-ethyl-ketone produced a nearly pure wax.

CONCLUSIONS

Methyl-ethyl-ketone has been shown to be an excellent dewaxing solvent for dewaxing shale oils. The wax after extraction from the shale oil required only washing with the cold solvent to produce a white product which was odorless, tasteless, and white in all but the last three fractions. The last three fractions were odorless but had a slight bronze color to them instead of white like the rest of the fractions.

The data indicates that it is possible to obtain waxes from almost all the fractions of the shale oil. The melting points of these varied with the boiling temperatures of the shale oil fractions. As the temperature of the fractions increased, the melting points increased, except for the last three fractions, where the melting point remained constant at 141°F. The molecular weights also increased with the increase in temperature of the various fractions.

Correlations with the data in Sachanen 23/ illustrate that the waxes obtained from the shale oil are all hydrocarbons with a paraffinic structure.

Observation of the plate-like structure of the fractions through a microscope disclosed that all of the waxes crystallized in a similar manner when the same method of crystalliza-

tion is used for each fraction.

The molecular weights of the waxes from shale oil approximate those of the paraffin hydrocarbons.

The data obtained from this investigation would indicate that it is possible to produce a commercial grade of wax from shale oil. The type and quality of wax desired could readily be obtained by the blending of the various melting point waxes.

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