ENCLOSURE (B) 11

STUDIES ON THE COMPOSITION OF PARAFFIN WAX IN CRUDE OIL

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Studies were carried on to investigate the composition of paraffin wax contained in Sanga Sanga (Borneo) and Pendopo (Sumatra) crude oils. Both of these crude oils were fractionated by vacuum distillation at 0.2-0.3mm Hg, and each fraction was dewaxed with the acetone-benzene solution. The crude waxes obtained were segregated by fractional crystallization with acetone, and the composition and distribution of various pure paraffin waxes in both crude oils were determined. The results were as follows:

1. The content of wax was 9.57% by weight in Sanga Sanga crude oil and 13.19% in Pendopo crude oil.

2. Waxes in Sanga Sanga crude oil were composed of 89.5% of normal paraffins, carbon atom numbers of which were 19-32, and 10.5% of the other waxy compounds.

3. Waxes in Pendopo crude oil were composed of 71.4% normal paraffins having 19-35 carbon atoms, and 28.6% of other waxy compounds.

4. The distributions of normal paraffins in Sanga Sanga and Pendopo crude oil were almost the same, in that the content of paraffin consisting of 24 atoms was greatest, that of 21 carbon atoms was second and that of 28 carbon atoms was third.

These studies were begun in June 1943 and finished in December 1943.

I. INTRODUCTION

A. At the Naval Fuel Depot in BALIKPAPAN synthetic lubricating oils were prepared from sweated paraffin wax of Sanga Sanga crude oil and have been used in aero engines. In the future this method should be applied industrially at various places. To obtain some reference data for this work the author carried out studies on the composition and the distribution of paraffin wax in crude oils during 1943.

B. Key Personnel

Chemical Engineer Lieutenant H. NAKAO

II. DETAILED DESCRIPTION

A. Samples

The samples of crude oil were obtained in the barrel from oil wells and uniform samples were taken from the barrels. The general properties of the crude oils are shown in Table I(B)11. The component analysis of the fractions of crude oil are given in Table II(B)11.

B. Experimental Methods

1. Fractionation of Crude Oils. The crude oils were topped to 200°C (in the case of Pendopo crude to 250°C) at atmospheric pressure, and the residue was fractionated in a high vacuum of 0.2-0.3mm

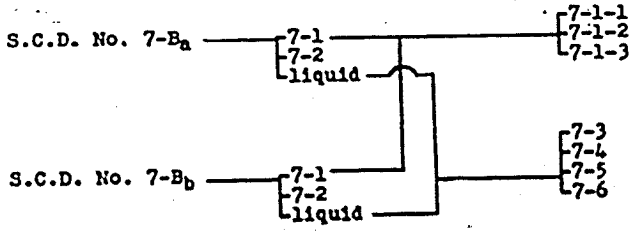
Hg, passing nitrogen into the distillation flask through a capillary tube, and measuring the pressure with a McLeod's manometer between the receiver and vacuum pump.

2. Dewaxing. The fractions of vacuum distillation were treated with a mixed solvent of acetone and benzene, and cooled to a temperature 1°C lower than the dewaxing temperature. After filtering in a cylindrical filter (previously cooled to dewaxing temperature) at the reduced pressure, the wax was washed with a small amount of acetone of the same temperature. The conditions of dewaxing were as follows:

Solvent: A mixture of 35% acetone and 65% benzene by volume.
Dewaxing temperature: -20°C
Volume ratio of oil to solvent: 1:4
(volume of oil is measured at 50°C and that of solvent at 25°C.)

Washing the wax with acetone, light yellow or white waxes were obtained, and the loss of waxes by washing was less than 0.5 grams for 17 grams of wax. This wax was dried at ordinary temperature and the content of wax determined.

3. Fractional Crystallization of Wax. The above mentioned wax was dissolved with an adequate amount of acetone and fractionally crystallized by the difference of solubility. The most soluble part was recovered by cooling to -20°C. If the fractional crystallization of wax was recognized as unsatisfactory, the desired part was fractionally crystallized again. The outline of the fractional crystallizations is shown as follows: The systematic diagram of the fractional crystallization of waxes of No. 7 fraction of "Sanga Sanga crude" (S.C.D. No. 7-B) is as follows:



Namely, S.C.D. No. 7-B was divided into two parts, and from each of them, two crystal fractions (7-1 and 7-2) were separated out at ordinary temperature. The remaining solutions were mixed and fractionally crystallized once more at a lower temperature. The 7-1 fraction was again subjected to a fractional crystallization, since it was observed to be a mixture of various waxes. The properties of the 7-2 fractions of both B_a and B_b perfectly coincided and these were recognized as the same compound.

The other fractions were also fractionally crystallized by the same procedure. Thus the parts consisting of n-paraffins, were obtained almost in the pure state.

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4. Analysis of Fractionated Waxes. The chemical composition of the fractionated waxes were determined by their refractive indexes at 90°C, melting points and molecular weights.

The refractive index was measured by "Abbe's refractometer" keeping the inlet temperature exactly at 90°C. After placing the samples in the refractometer, the refractive index decreased slowly, but soon kept a constant value. This was caused by the time lag for raising the wax temperature. The last constant value was taken as the constant for the wax.

The melting point was measured by the capillary method in a liquid paraffin bath. Care was taken in regard to the relative position of thermometer and sample, its heating, etc. The error caused by the thermometer was not greater than ±0.1°C.

The molecular weight was measured by (1) Rast's method. The measuring apparatus was the same as the melting point measuring apparatus, but a high melting point wax was used in the oil bath in place of liquid paraffin. Pure camphor (by Japanese Medicine Specifications) was used as the solvent. The ratio of solvent to solute was 9:1. The melting points determined varied within a range of ±0.3°C, and the error of the calculated molecular weights, therefore, will be 10-20, and it was difficult to determine the substances by this method only.

As a consequence, the purity of the paraffin wax was determined chiefly by melting point and refractive index. But molecular weight is important for systematic consideration of such substances.

C. Results of the Experiments

1. Fractional Distillation. The results of fractional distillation of crude oils are shown in Tables III(B)11 and IV(B)11.

2. Dewaxing. The results of dewaxing are given in Tables V(B)11 and VI(B)11.

When the residue was dewaxed, a black viscous substance was obtained. Then, after washing with a great volume of acetone, a brown powder was obtained. The characteristics of it were not determined.

3. Fractional Crystallization of Wax and Its Properties. Waxes were fractionally crystallized by the above mentioned method and the properties of the fractionated waxes are given in Tables VII(B)11 and VIII(B)11.

The relationship between refractive index and melting point are graphically summarized in Figures 1(B)11 and 2(B)11.

D. Discussion of Results.

It was observed that the normal paraffins could be almost completely separated by fractional distillation and fractional crystallization. These determinations were carried out on the basis of the relationship between melting point and refractive index, reported in the literature (3)- (16), and the molecular weights were calculable for checking these determinations.

The range of the carbon numbers of waxes contained in Sanga Sanga crude oil was from 19 to 32, and in Pendopo crude oil from 19 to 35.

The graphically plotted relationship in Figure 3(B)11 between the carbon number of normal paraffin and its percentage content showed that the distribution of paraffin waxes in both crude oils, is similar. That is, the maximum percentage of paraffin wax is at C_{24}, the second largest at C_{21} and the third largest at C_{28}.

The substances other than normal paraffins were analyzed by D.S. McKittrick's method, (17) which distinguishes iso-paraffins, naphthenic and aromatic compounds by the relationship between melting point and refractive index. When the points relating the melting point and refractive index are plotted, Sanga Sanga crude oil compounds are included in the area of iso-paraffinic compounds. On the other hand, those of Pendopo crude oil exist in the area of aromatic compounds (See Figures 1(B)11 and 2(B)11).

The calculated content of normal paraffins and other compounds in waxes are given in Table IX(B)11.

From the Table IX(B)11 it is observed, that the content of the substances other than the normal paraffin in Pendopo crude oil is greater than that in Sanga Sanga crude oil, and not only iso-paraffins, but also compounds of naphthenic or aromatic nature are contained.

As these compounds play an important role in dewaxing processes, dewaxing Pendopo crude oil is more difficult than dewaxing Sanga Sanga crude oil.

The existence of these compounds, in addition to the normal paraffins in the crude wax should have an important effect on its thermal cracking.

III. CONCLUSIONS

The wax of Sanga Sanga crude oil consisted of normal paraffin having 19-32 carbon atoms and about 10% of hydrocarbons of other series, mainly iso-paraffins.

The wax of Pendopo crude oil consisted of 71% of normal paraffins having 19-32 carbon atoms and about 29% of other hydrocarbons.

The percentage distribution of normal paraffins tended to be similar in Sanga Sanga crude oil and Pendopo crude oil, that is, the maximum percentage being at C_{24}, the second largest at C_{21} and the third largest at C_{28}.

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Table I(B)11
GENERAL PROPERTIES OF THE CRUDE OILS

	Sanga Sanga crude oil	Pendopo crude oil
Appearance	greenish black	greenish black
Reaction	neutral	neutral
Density	0.758 (25/4°C)	0.723 (30/4°C)
Water content (%)	0.02	0.3
Sediment (%)	none	0.05
Pour point (°C)	23	+24
Conradson's carbon (%)	0.34	1.52

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Table II(B)11
COMPONENT ANALYSIS AND PROPERTIES OF FRACTIONS

Fractions	Components etc.	Sanga Sanga's	Pendopo's
From initial point to 150°C	Density (15/4°C)	0.7733	0.7594
	Aniline pt. (°C)	58.0	60.0
	Unsaturates (%)	0.32	1.52
	Aromatics (%)	37.89	20.19
	Naphthenics (%)	24.72	26.10
	Paraffinics (%)	37.07	52.19
From 150°C to 200°C	Density (15/4°C)	0.8100	0.8929
	Aniline pt. (°C)	67.5	69.3
	Unsaturates (%)	0.48	1.20
	Aromatics (%)	44.78	27.27
	Naphthenics (%)	4.38	1.67
	Paraffinics (%)	50.36	69.86
Over 200°C	Density (35/4°C)	0.7092	0.7492
	Pour pt. (°C)	+29	+28

Table III(B)11
FRACTIONAL DISTILLATION OF SANGA SANGA CRUDE OIL

Name of fraction	Temp. range converted to ordinary pressure(°C)*	Abs. press. (mm Hg)	Temp. range (°C)	Yield (wt %)	Sum of the yield (wt %)
S.C.D. No. 1	1st drop-200	ord. press.	-200	26.14	26.14
2	200 - 250	0.2	-58	1.58	27.72
3	250 - 300	0.12	-85	7.61	35.33
4	300 - 350	0.09	-113	14.42	49.75
5	350 - 400	0.2	-162	22.27	72.02
6	400 - 450	0.3	-200	11.41	83.43
7	450 - 480	0.3	-225	6.02	89.45
8	480 - 500	0.3	-233	1.35	90.80
9	500 - 530	0.21	-250	1.69	92.49
10	530 -	residue		6.94	99.43

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Table IV(B)11
FRACTIONAL DISTILLATION OF PENDOPO CRUDE OIL

Name of fraction	Temp. range converted to ordinary pressure(°C)*	Abs. press. (mm Hg)	Temp. range (°C)	Yield (wt %)	Sum of the yield (wt %)
P.C.D. No. 1-2	1st drop-250	ord. press.	-250	37.40	
3	250 - 300	0.65	-106	6.61	44.01
4	300 - 350	0.31	-133	9.86	53.87
5	350 - 400	0.30	-168	5.33	59.80
6	400 - 450	0.26	-200	7.00	66.20
7	450 - 500	0.25	-234	9.86	76.06
8	500 - 535	0.21	-253	5.36	81.42
9	535 - 565	0.30	-283	3.26	84.68
10	565 -	residue		14.14	98.82

Table V(B)11
DEWAXING OF SANGA SANGA'S FRACTIONS

Name of fraction	Amount of dewaxing oil (gm)	Yield of wax	
		in gm	in wt %
S.C.D. No. 4	41.0	0	0
5	87.5	4.0	4.6
6	43.5	17.2	39.5
7	45.5	20.0	43.9
8	15.0	7.0	46.6
9	10.0	4.0	40.0

*The temperatures were converted by the (2) E.S.L. Beale's conversion table.

Table VI(B)11
DEWAXING OF PENDOPO'S FRACTION

Name of fraction	Amount of dewaxing oil (gm)	Yield of wax	
		in gm	in wt %
P.C.D. No. 3	50.0	0	0
4	48.0	1.0	2.08
5	49.0	9.5	19.1
6	50.0	22.0	44.0
7	50.0	24.1	48.2
8	42.0	21.0	50.0
9	21.0	9.0	42.8

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Table VII(B)11
CHARACTERISTICS OF S.C.D-B SERIES

Name of wax	Melting point(°C)	Refractive index ($n_D^{90°C}$)	Molecular weight
5 - 1	47.5	1.4198	322
5 - 2	38.7	1.4162	286
5 - 3	37.0	1.4149	276
5 - 4	32.5	1.4132	270
6 - 1	52.0	1.4211	342
6 - 2	47.5	1.4198	328
6 - 3	44.7	1.4187	302
6 - 4	42.3	1.4176	304
6 - 5	40.7	1.4170	291
7-1-1	63.7	1.4268	406
7-1-2	61.5	1.4257	397
7-1-3	58.3	1.4248	375
7 - 1	60.7	1.4258	-
7 - 2	59.5	1.4248	386
7 - 3	55.5	1.4235	358
7 - 4	50.5	1.4239	384
7 - 5	49.2	1.4246	377
7 - 6	44.8	1.4269	388
8-1-1	67.5	1.4278	431
8-1-2	66.5	1.4274	426
8-1-3	64.3	1.4269	396
8-1-4	59.7	1.4267	405
8 - 1	64.0	1.4273	-
8 - 2	60.0	1.4264	412
8 - 3	57.8	1.4277	453
8 - 4	51.7	1.4310	482
8 - 5	45.5	1.4341	479
9-1-1	69.0	1.4290	443
9-1-2	66.2	1.4281	425
9-1-3	62.7	1.4274	430
9 - 1	66.3	1.4280	-
9 - 2	60.5	1.4271	417
9 - 3	57.3	1.4279	454
9 - 4	54.5	1.4291	487
9 - 5	48.7	1.4324	476
9 - 6	43.8	1.4362	480

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Table VIII(B)11
CHARACTERISTICS OF P.C.D.-B SERIES

Name of wax	Melting point(°C)	Refractive index ($n_D^{90°C}$)	Molecular weight
4 - 1	44.8	1.4188	305
4 - 2	40.5	1.4185	294
4 - 3	32.8	1.4135	272
5 - 1	42.2	1.4171	298
5 - 2	38.2	1.4154	292
5 - 3	36.0	1.4174	282
6 - 1	51.8	1.4209	353
6 - 2	49.3	1.4203	337
6 - 3	47.0	1.4192	331
6 - 4	42.2	1.4178	305
6 - 5	39.7	1.4182	312
6 - 6	36.0	1.4198	317
7 - 1	61.9	1.4255	401
7 - 2	57.8	1.4243	362
7 - 3	52.8	1.4229	358
7 - 4	44.0	1.4261	385
7-Spc.-1	62.5	1.4264	409
7-Spc.-2	58.3	1.4246	367
7-Spc.-3	53.3	1.4230	361
7-Spc.-4	43.3	1.4281	371
8-1-1	68.0	1.4284	425
8-1-2	63.2	1.4267	391
8-1-3	58.2	1.4246	371
8 - 1	66.0	1.4286	-
8 - 2	56.0	1.4318	407
8 - 3	50.8	1.4327	398
8 - 4	42.8	1.4368	381
8 - 5	24.5	1.4591	-
8 - Spc.	48.2	1.4374	402
9-1-1	74.7	1.4315	503
9-1-2	72.2	1.4304	481
9-1-3	70.5	1.4295	448
9 - 1	72.8	1.4320	-
9 - 2	67.2	1.4328	506
9 - 3	49.5	1.4521	-
9-Spc.-1	59.3	1.4387	503
9-Spc.-2	48.8	1.4417	442
9-Spc.-3	45.7	1.4447	433

Table IX(B)11
THE CALCULATED COMPONENTS OF CRUDE OILS

	Sanga Sanga	Pendopo
Content of whole wax (wt % to crude oil)	9.57	13.19
Content of normal paraffins (wt % to whole wax)	89.5	71.4
Content of other substance (wt % to whole wax)	10.5	28.6

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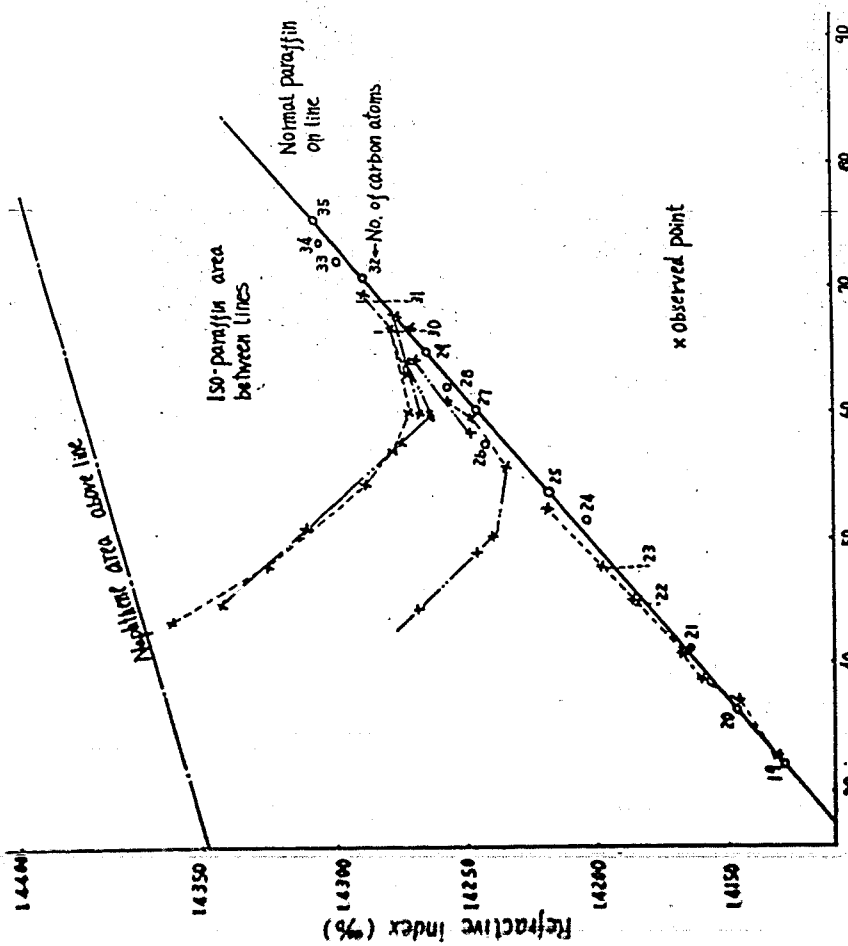

Figure 1(B)11
CHARACTERISTICS OF SANGA SANGA WAX

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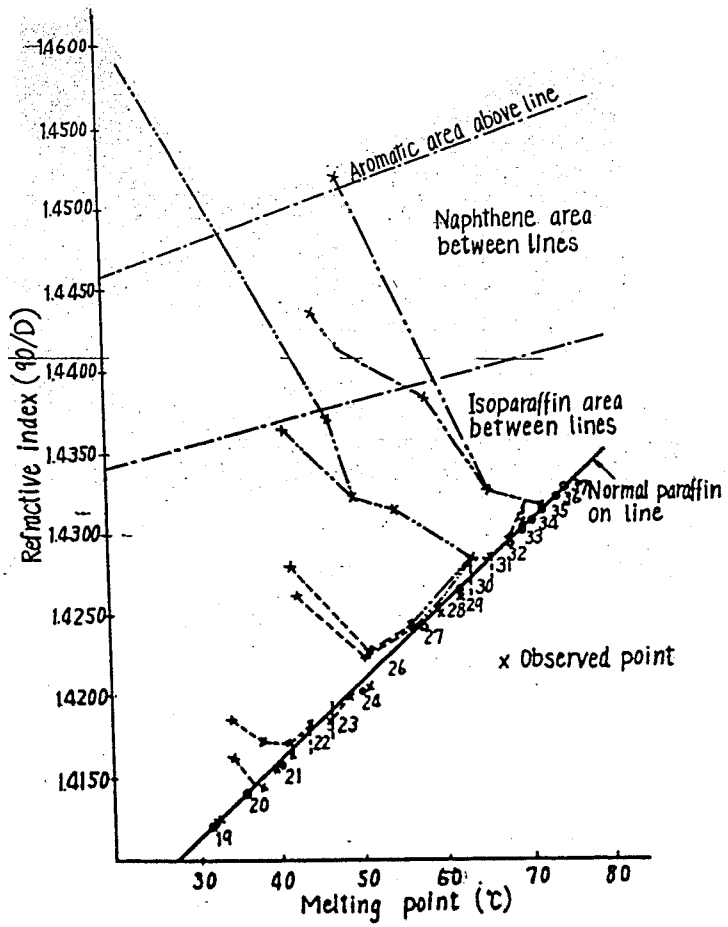

Figure 7(B)11
CHARACTERISTICS OF PENDOO WAX

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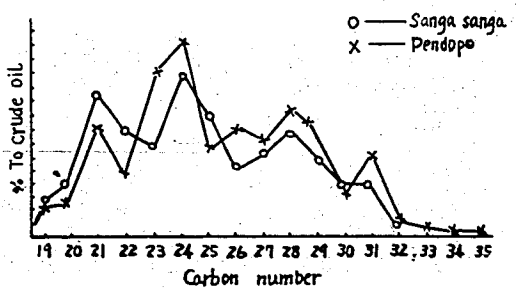

Figure 3(B)11
DISTRIBUTION OF NORMAL PARAFFIN