ENCLOSURE (B) 22

EXPERIMENTAL MANUFACTURING METHOD FOR PRECISE OILS

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LIST OF TABLES AND ILLUSTRATIONS

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I. DESCRIPTION OF CRUDE OIL

Niizu's crude oil from NIIGATA district which has a very low pour point was used as raw material. The properties of the crude oil are shown below.

Properties of Niizu Crude Oil

Density (d_4^{15})	0.945
Flash Point (°C)	112
Viscosity (R.I.) at 30°C	486
at 50°C	160
Pour Point (°C)	below-20
Sulphur (%)	0.477
Paraffin wax (%)	0.687
Conradson's C. R. (%)	5.25
Tar (%)	40.0
Water and Mud (%)	39.0
Reflected Color	blackish brown
Appearance	Opaque

II. FRACTIONATION OF THE CRUDE OIL

The crude oil mentioned above was fractionated in a vacuum of 5mm Hg using a 3kl Heckmann's vacuum still. The fractions had the average properties shown in Table 1(B)22.

III. TREATMENT OF THE FRACTIONS OF CRUDE OIL

A. Sulphuric Acid Treatment

Each fraction of crude oil was separately treated with 50% by wt. of conc. sulphuric acid. In detail, 400 liters of oil was mixed with 25% by wt. of conc. sulphuric acid, and, after sufficient mechanical stirring for 30-60 min., it was settled for 30-60 min. The settled sludge was removed, and above process was repeated once more. No additional heat was applied, but, in summer, cooling was sometimes needed to maintain the temperature below 40°C.

B. Alkali Treatment

The acid-treated oil was washed with 5% alkali solution, until perfect neutralization was attained (Phenolphthalein was used as an indicator). Neither additional heating nor cooling was needed, and the temperature of the mixture was usually 30-70°C because of the initial heat of the acid-treated oil and alkali solution and the heat of neutralization.

C. Washing With Water

The alkali treated oil was sufficiently (5-10 times) washed with hot water. The temperature was variable, (50-70°C) depending on the viscosity of the oil.

D. Clay Treatment

The oil was then treated with 5% by wt. of dry clay at 80-120°C for 1-1.5 hrs and filtered with continuous stirring while hot. Acid clay was usually used, but active clay was sometimes desirable in order to improve the color of the product.

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IV. BLENDING OF THE TREATED FRACTIONS OF THE OIL

Viscosities of the refined oil fractions at 10°C and 30°C was measured and the required precise oils were obtained by blending as shown in Table II(B)22.

V. PRECISE OIL NO.5

A. Raw Material - Dodecene

The raw material of precise oil No. 5 was dodecene, which was manufactured from coconut oil at Tokyo Factory of Daiichikogyo-Seiyaku Co. Ltd.

Raw cocoonut oil was first purified by means of alkali treatment, and hydrogenated at 300°C and 300 atm., using 10% of Cu - catalyst. The hydrogenated product contained about 40% by wt. of lauryl alcohol and was fractionated in vacuum. Lauryl alcohol was dehydrated at 300°C using active clay catalyst. Dodecene was obtained by fractionation of the final product and had the following properties:

Density, (d_4^{25})	0.7681
Acid value	0.12
Sap. value	0.12
B. P. (°C)	210 - 212

B. Polymerization of Dodecene

Dodecene was first washed with 1 N hydrochloric acid in order to remove ketones, then washed with 5% alkali solution and water, and dried with clay. The purified dodecene was polymerized at 90°C, for 10 hrs, using 10% by wt. of anhydrous aluminium chloride as catalyst. In detail, the catalyst was added in small increments within 1 hr at 50°C, and, after complete addition, the temperature was gradually raised to 90°C. The same temperature was maintained for 10 hrs by means of steam heating. The polymerization product was then dechlorinated by heating to about 120°C with 2% by wt. of calcium oxide and 4% of active clay. The resulting product was fractionated in vacuum of 5mm Hg and the fractions 180-300°C - were taken.

C. Blending

Precise oil No. 5 was prepared by the following blending:

75% by wt. of above mentioned fraction 180 - 300°C/ 5mm Hg.
5% by wt. of above mentioned fraction 300°C/5mm Hg.
19.8% by wt. of refined oil from 45 - 49% fraction of Niizu crude oil.
0.2% by wt. of refined rape seed oil.

VI. The specification and properties of precise oils are shown in Table III (B)22.

VII. A schematic diagram and flow sheets for the preparation of precise oils are shown in Figures 1(B)22, 2(B)22, and 3(B)22.

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Table I(B)22
PROPERTIES OF FRACTIONS

No.	Ranges of Fractions		Density (d_4^{15})	Flash Pt. (°C)	Viscosity(R.No.1)		Pour Pt. (°C)
	Vol. %	B.P.(°C) *2 760mm Hg			30°C	50°C	
1	29-33	250-335	0.900	132	49	38.5	-55
2	33-37	335-345	0.906	141	55	40.5	-52
3	37-41	345-360	0.914	151	69	46.5	-49
4	41-45	360-370	0.923	161	92.5	53	-45
5	45-49	370-380	0.931	171	138	64	-41
6	49-53	380-390	0.938	185	215	82	-36
7	53-57	390-410	0.942	193	372	119	-33
8	57-61	410	0.947	198	674	188	-30
9	61-65		0.953	209		304	-25
10	65-69		0.959	217		464	-20

*Calculated

Table II(B)22
FRACTION OF REFINED OIL AVAILABLE FOR EACH PRECISE OIL

	Available Fraction	
	Vol. %	B.P. (°C) /760mm Hg
Precise Oil No. 1	29 - 37	250 - 345
Precise Oil No. 2	33 - 41	335 - 360
Precise Oil No. 3	41 - 57	360 - 410
Precise Oil No. 4	41 - 57	360 - 410*

Refined rape seed oil....0.8% wt.
* 99.8% wt.

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Table III(B)22
SPECIFICATIONS AND PROPERTIES OF PRECISE OILS

	$d^{15}/_4$	Viscosity (Redwood No. 1)			Acid Value	Saponification Value	Pour Point (°C)	Evap. Loss wt.% 100°C 5 hrs
		10°C	30°C	50°C				
Precise oil No. 1	0.8895	131	62.2		0	0.12	-55	0.25
Specification	below 0.92	below 145	above 60		below 0.1	below 0.2	below -50	below 0.3
Precise oil No. 2	0.8992	246.2	90.2		0	0.15	-50	0.23
Specification	below 0.92	below 250	above 90		below 0.1	below 0.2	below -45	below 0.3
Precise oil No. 3	0.9169	542.6	160.1	65.6	0	0	-49	0.18
Specification	below 0.92	below 600	above 150	above 65	below 0.1	below 0.2	below -40	below 0.2
Precise oil No. 4	0.9060	508.8	152.6		0	0.22	-47	0.15
Specification	below 0.92	below 600	above 150		below 0.1	0.3~0.5	below -40	below 0.2
Precise oil No. 5	0.8938	457.6	134.5		0	0.54	-63	0.09
Specification	below 0.92	below 600	above 150		below 0.1	below 0.7	below -60	below 0.2

Note: Reaction was neutral in all cases.
There was no corrosion in any case.

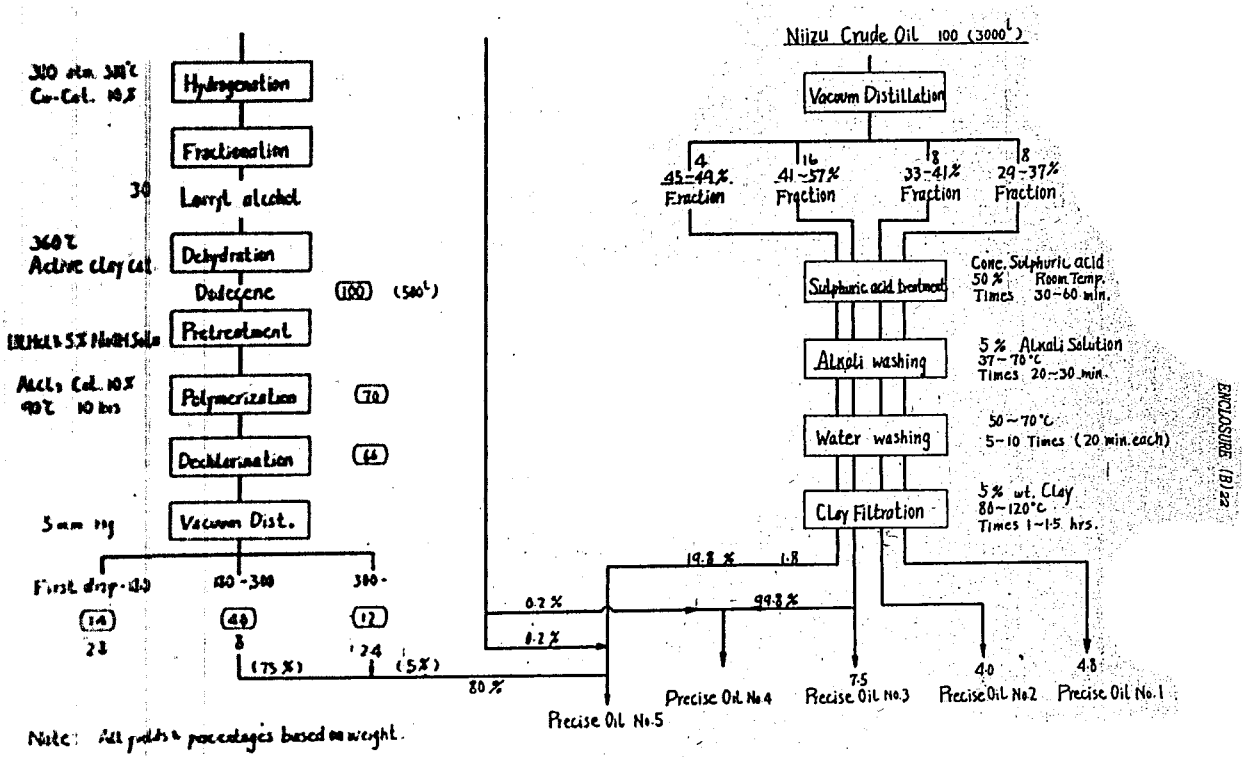

Figure 1(B)22

SCHEMATIC DIAGRAM FOR PREPARING PRECISE OILS

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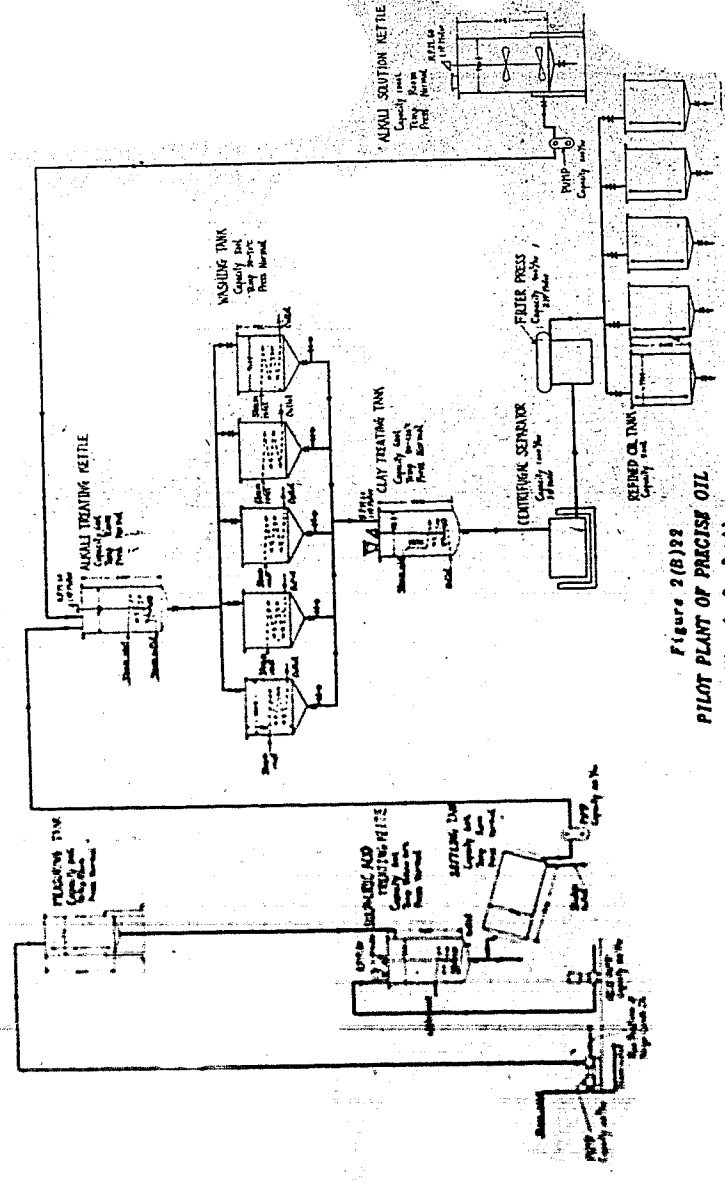

Figure 2(B)22
PILOT PLANT OF PRECISE OIL
(No. 1, 2, 3, 4)

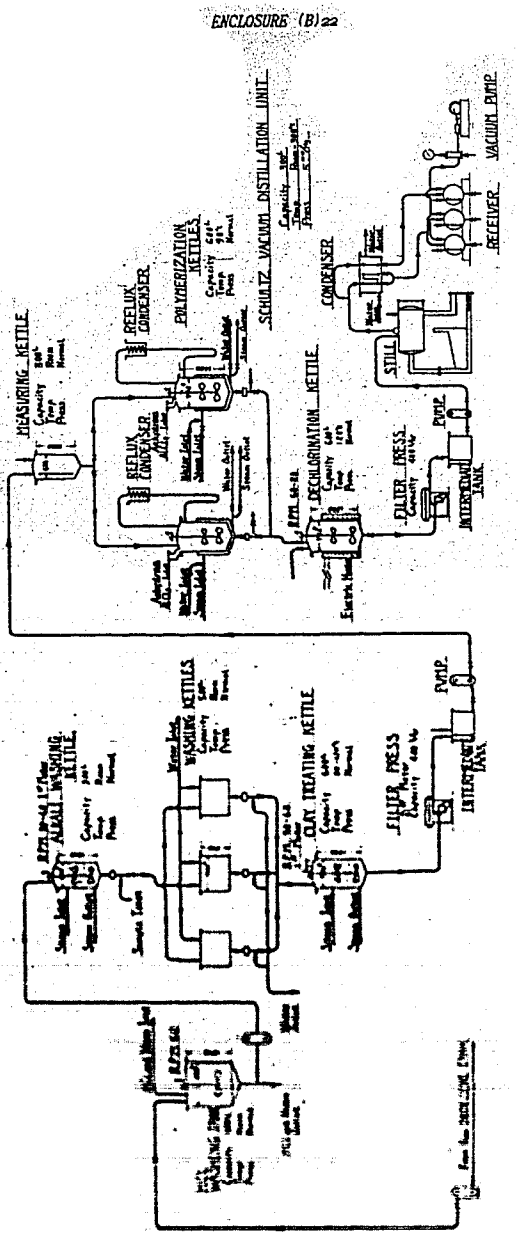

Figure 3(B)22
FLOW SHEET OF PILOT PLANT OF PRECISE OIL
(No. 5)

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