ENCLOSURE (B) 21

S T U D I E S O N P R E C I S E O I L S

by

CHEM. ENG. CAPT. DR. I. KAGEHIRA
NAVAL ENGINEER N. MATSUO
CHEM. ENG. LIEUT. I. HARA

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

1. No. 1, No. 2, No. 3, and No. 4 precise oils were prepared from refined mineral oils, by treating a suitable fraction of Niizu crude oil with 98% H_2SO_4. The properties of these oils are summarized in Table I(B)2. These oils were used practically.

2. No. 5 precise oil, which has a very low pour point was prepared by mixing the following:

a. A fraction boiling from 180°C to 300°C under a vacuum of 5mm Hg of the polymerized product of dodecene, the dodecene being prepared by the hydrogenation of lauric acid (80%)

b. A refined mineral oil, which was prepared from the fraction of 45 - [illegible] of Niizu crude oil (See Table II(B)29) (19.8%)

c. [illegible] rapeseed oil (0.2%).

Properties of No. 5 Precise Oil

Density 25/4	0.8278
Vis. in Redwood No. 1. sec	
at 100°C	457.6
at 300°C	154.5
Viscosity-index	101
Pour Point (°C)	-63
Acid Value	trace
Saponification Value	0.54
Evaporation Loss at 100°C for 5 hours(%)	0.09

3. Pre[illegible]ise Oils For Special Uses

a. A special precise oil, having a very low pour point, was ob[illegible]ed by mixing the following:

(1) The polymerized products of thermally cracked wax distillates, prepared by polymerization at 80°C for 10 hours in the presence of 5% (wt) aluminium chloride (33.5%)

(2) A refined mineral oil obtained from the distillate, cut from 29% to 37% of Niizu crude oil. (See Table II(B)29) (66.5%)

This oil was tested as an oil for working the flap or oleo of air-craft and its possible use below -40°C was recognized, but it was not put into practical application.

Properties of the Special Precise Oil

Density 25/4	0.8556
Vis. in Redwood No. 1, sec	
at 100°C	133.2
at 30°C	66.1
Pour Point (°C)	-67.5
Flash Point (°C)	108
Aniline Point (°C)	96.5
Acid Value	0.04
Saponification	0.45

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Increase of the weight and the volume of gum in the oil during 8 hours at 100°C followed by 24 hours at ordinary temperature.

Buna Gum Weight(%)	1.0
Natural Gum	30.3
Buna Gum Volume(%)	0
Natural Gum	47.4

b. A precise oil for special watches was prepared as follows: 20 parts of refined toluol and 100 parts of a thermally cracked wax distillate cut from 100°C to 230°C were polymerized in the presence of 3% aluminium chloride at 90°C for 3 hours and the reaction product, after being treated with 5% of dried acid clay at 200°C to be dechlorinated, was distilled under a vacuum of 5mm Hg.

The fraction which boils from 120°C to 300°C was used as a precise oil for special watches.

Properties of the Special Watch Oil

Density 25/4	0.8200
Vis. in Redwood No. 1, sec at 30°C	70
Pour Point (°C)	-65
Acid Value	0.02
Saponification Value	0.10
Iodine Value	4.00

4. A Precise Oil From Shark Liver Oil. Shark liver oil, which is characterized by a density below 0.9000, was used as raw material. The shark liver oil was distilled under vacuum of 5mm Hg, and the available fraction boiled at 235°C-245°C.

This fraction was rich in squalene ($C_{30}H_{50}$), which was washed with alkali and water.

The refined squalene fraction was hydrogenated with nickel catalyst, and the reaction product was treated by methanol to extract the higher alcohols in the original oil.

Properties of Shark Liver Oil

Yield from Shark Liver Oil	22.9%
Density 25/4	0.8100
Vis. in Redwood No. 1, sec at 30°C	110
Viscosity-Index	about 120
Pour Point (°C)	-55
Acid Value	0.02
Saponification Value	0.50
Iodine Value	10.00

I. INTRODUCTION

A. History of Project

The term of study: from April, 1939. to March, 1944. In Japan, there is a very low pour point crude oil in the NIIGATA district. This is

generally known by the name of Niizu crude oil and is of naphthenic character. Experiments on the manufacture of various precise oils, having low freezing points, were attempted, using this oil. The viscosity-index of this oil is poor(ca.-100), and the aniline point is low; i.e. 60-65°C.

Synthetic precise oils for special precise machines to be used at low temperatures were also studied.

1. In the case of Niizu crude oil, the suitable fraction was washed with concentrated H_2SO_4(98% once or, if necessary, several times for refining.

After refining one fraction or, if necessary, two or more fractions blended together were used to attain the required viscosity.

2. In the case of the synthetic precise oils, olefines were used. For example, dodecene ($C_{12}H_{24}$, which was obtained from cocoanut oil) or the distillates of thermally cracked waxes were polymerized, and either the mono-polymerization or co-polymerization product (whichever was more suitable) was taken.

In co-polymerization, the co-polymer used was toluol.

Polymerization reactions were carried out in the presence of anhydrous aluminium chloride as the catalyst under various conditions. Thus it was aimed to manufacture low freezing-point, high viscosity-index, precise oils by these procedures.

B. Key Research Personnel Working on Project

Naval Chem Eng. Capt. I. KAGEHIRA
Naval Engineer N. MATSUO
Naval Chem. Eng. Lt. I. HARA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

For washing the Niizu crude oil, common separatory funnels were used in which oil and H_2SO_4 were agitated. Polymerizations were carried out in a three-necked flask, furnished with one mechanical oil-sealed stirrer, thermometer and a reflux condenser.

For heating, oil-baths with an electrical heating apparatus were used.

B. Experimental Results

1. Vacuum Fractional Distillation of Niizu Crude Oil. The Niizu crude oil was fractionated under a vacuum of 5mm Hg into several fractions. Characteristics of the Niizu crude oil and the several fractions are tabulated below and in Table II(B)21.

Properties of Niizu Crude Oil

Density 25/4	0.945
Vis. in Redwood No. 1, sec	
- at 30°C	486
at 50°C	160
Flash Point (°C)	112
Pour Point (°C)	below -20

Sulphur Cont.(%)	0.477
Carbon Residue	5.25
Tar (%)	4.00
Water (%)	3.9

2. Manufacture of No. 1, No. 2, No. 3, No. 4 Precise Oil. According to the data (Table II(B)21), we used 3 fractions, cut 29%-37%, cut 33%-41%, and cut 41%-59%.

Refining of them took place as follows;

a. Washing twice with 25% vol. of conc. H_2SO_4(98%).

b. Washing with 100% vol. of 5% NaOH solution at 50°-70°C.

c. Washing with water until neutral.

d. Dehydration with 5% dried acid clay at 80-120°C. These procedures are shown diagrammatically in Figure 1(B)21. A summary of the properties of Precise Oils 1-4 and the Navy Dept. specifications for each is tabulated in Table III(B)21.

3. No. 5 Precise Oil

a. For the preparation of this oil, polymerization of olefines was first carried out. The raw olefine was dodecene. (Raw dodecene was not prepared here).

For polymerization, raw dodecene was refined as follows: Raw dodecene was washed with 10% by vol. of 1N HCl to remove aldehydes by oxidation, next with 50%-100% by vol. of 5% NaOH, then with water, and finally was dried by acid clay.

Generally, this refined dodecene was used in the manufacture of No. 5 precise oil. The characteristics of dodecene, obtained by the distillation of the refined dodecene, are shown in Table IV(B)21.

b. Polymerization Procedure: While maintaining dodecene at 80°C-90°C in the reaction vessel under good mechanical stirring, 10% (wt) of anhydrous $AlCl_3$ (in pieces) was slowly added. Maximum reaction temperature was about 120°C-140°C. For 8-10 hours, stirring was continued at 90°C. The color of the liquid changed rapidly as soon as the catalyst was added.

c. Dechlorination Procedure: The reaction product from the reaction vessel was taken out and 5% by wt of dried acid clay was added to it. The mixture was maintained at 200°C until all chlorine was removed, as indicated by the copper flame test.

d. Vacuum Fractional Distillation: The dechlorinated oil was distilled under a vacuum of 5mm Hg into various fractions, and the suitable fractions were used for the preparation of No. 5 precise oil:

Table V(B)21 indicates the characteristics of the fractions.

According to these data, the fraction from 180°C-300°C seemed suitable for the desired precise oil. Characteristics of this fraction are as follows:

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Density, 25/4	0.8216
Vis. in Redwood No. 1 sec	
at 100C	465
at 30°C	167
Viscosity-index	137.8
Pour point	-65°C

e. Blending: For producing No. 5 precise oil, 80% by volume of the polymerized dodecene fraction (boiling from 180°C-300°C, at 5mm pressure), 19.8% by volume of Niizu refined fraction of cut 45%-49%, and 0.2% rape seed oil were mixed.

The properties and the specifications of No. 5 precise oil are shown in Table VI (B)21.

Figure 3(B)21 indicates the steps involved in manufacturing the No. 5 precise oil from raw dodecene.

Precise Oils for Special Uses. A low freezing oil

a. A low-freezing oil for the flap or oleo of aircraft was obtained by mixing the polymerized products of thermally cracked distillates of waxes and a refined fraction of Niizu crude oil.

b. The polymerization of thermally cracked distillates of waxes was carried out as follows:

The 100°C-230°C fraction of cracked wax distillate was polymerized in the presence of 5% anhydrous $AlCl_3$ as the catalyst at 80°C for 10 hrs.

c. The 26%-29% fraction of Niizu crude oil was washed with 50% by vol. of conc. H_2SO_4 (98%) in the same manner, as in the case of No. 1, No.2, No. 3 or No. 4 precise oil.

d. These two components are mixed according to this ratio:

The polymerized oil	34.8% (vol)
The mineral oil	62.2% (vol)

e. Properties of each component and of the product are tabulated in Table 13.

The Special Watch Oil

a. A very low freezing-point precise oil for special watches, was obtained from the co-polymerization product of toluol and the distillate of thermally cracked waxes.

b. 100 parts of the 1000-230°C distillate of thermally cracked waxes and 20 parts of toluol were polymerized in the presence of 10% of anhydrous $AlCl_3$ at 90°C for 8 hrs. The catalyst had to be added slowly to maintain the temperature below the boiling point of toluol. This co-polymerization reaction was more vigorous than was the polymerization of dodecene.

c. The dechlorinating treatment was carried out in the same manner as for the No. 5 precise oil. The dechlorinated oil was fractionated under a vacuum of 5 mm Hg and the fraction out at 120°C-300°C was used for the special watch oil.

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The characteristics of the special watch oil are as shown below:

Density 25/4	0.8200
Vis. in Redwood No. 3, sec. at 30°C	70
Pour point (°C)	-65
Acid value	0.02
Saponification value	0.10
Iodine value	4.00

6. A Precise Oil from Shark Liver-Oil

a. It was observed in the literature, that squalene ($C_{30}H_{50}$) and squalane ($C_{30}H_{62}$), the hydrogenated product of the former, are very low-freezing compounds with freezing points of -70°C and -80°C respectively. Consequently, the completely or incompletely hydrogenated fraction of squalene from shark liver oil was used as a raw material for precise oils.

b. For this purpose, a shark liver oil from so-called "Aizame" was obtained. Its properties are listed below:

Density 25/4	0.8872
Refractive index n_D^{30}	1.4720
Vis. in Redwood No. 1, sec. at 30°C	135.1
Vis. in Redwood No. 1, sec. at 50°C	78.9
Acid value	36.3
Saponification value	148
Iodine value	197
Squalene cont. (%)	about 50%
Pour point (°C)	-16

c. For the separation of squalene from the glycerides, a vacuum fractional distillation was used. To prevent the cracking of the squalene fraction, it was desirable to introduce dried CO_2 gas into the vessel during the vacuum distillation, since squalene has six double bonds in the structure, and is affected by heat or polymerization agents.

The squalene fraction was distilled at 235°C-245°C under a vacuum of 5 mm Hg and the yield was 45% (wt) of the shark liver-oil. The product was washed with an equal volume of 10% solution of NaOH at 80°C-90°C.

Thus a fraction of refined squalene was obtained with yield of 40.5% of the shark liver-oil.

Properties of the product were as follows:

Density 25/4	0.8574
Vis. in Redwood No. 1, sec at 30°C	67
Acid value	0.07
Saponification value	2.71
Iodine value	351
Pour point (°C)	-67
Yield (%)	40.5

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d. Hydrogenation Procedure. To increase viscosity and stability, the squalene was subjected to high pressure hydrogenation at 180°C. The maximum pressure of hydrogen was 200 atm. and 5% of NiO was used as the catalyst. The characteristics of the hydrogenated product were as follows:

Density 25/4	0.8146
Acid value	0.21
Saponification value	0.91
Iodine value	9.8
Pour point (°C)	-20

e. Refining (methanol treating). The squalene was contaminated by the presence of higher alcohols. These higher alcohols were mainly selachyl alcohol, and some chimyl and batyl alcohols.

Selachyl alcohol $C_{21}H_{42}O_3$ B.pt. 236-239°C/5mm Hg
$(CH_3(CH_2)_7CH \quad CH(CH_2)_8OCH_2CH_2CHOHCH_2OH)$
Batyl alcohol $C_{21}H_{44}O_3$ melt. pt. 69°C.
Chimyl alcohol $C_{19}H_{40}O_3$ melt. pt. 60-60.5°C.

In the hydrogenated squalene fraction, these alcohols (mainly hydrogenated selachyl alcohol and the so-called batyl alcohol) crystallized out and the cloud point of the hydrogenated squalene fraction was raised.

These higher alcohols were removed by washing the hydrogenated squalene fraction with 200% by vol. of anhydrous methanol. The squalene was available for many uses and had the following properties:

Yield for shark liver-oil	22.9
Density 25/4	8.8100
Vis. in Redwood No.1, sec at 30°C	110
Pour point, (°C)	-55
Acid value	0.02
Saponification value	0.50
Iodine value	10.00
Aniline point, (°C)	120

It was intended to use this refined squalene fraction for the manufacture of No.2 precise oil and the oil for the flap or oleo of aircraft by mixing with a refined mineral oil from Niizu crude (No. 1 precise oil).

This was not done in actual application and no data for such mixture was available.

III. CONCLUSIONS

A summary table is given in Table VIII(B)21 which shows the use, compositions and flow characteristics of the precise oils discussed in this paper.

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Table I(B)21
CHARACTERISTICS OF PRECISE OILS

	No.1 Precise oil	No.2 Precise oil	No.3 Precise oil	No.4 Precise oil
Fraction of Niizu crude oil used for the preparation of precise oils	29%-37%	33%-41%	41%-57%	41%-57%
Calculated boiling point (°C)	250-345	335-360	360-410	360-410
Composition of precise oils (°C)	250-345	335-360	360-410	99.8% vol. of this fraction 0.2% vol. of rape seed oil
Properties:				
Density 25/4	0.8895	0.8992	0.9169	0.9060
Vis. in Redwood No. 1 sec. at 10°C	131	246.2	562.6	508.8
Vis. in Redwood No. 1 sec. at 30°C	62.2	90.2	160.1	152.6
Calculated viscosity index	-	-	18.4	-31.3
Pour point (°C)	-55	-50	-49	-47
Acid value	0.01	0.02	0.02	0.03
Saponification value	0.12	0.15	0.15	0.22
Evaporation loss at 100°C for 5 hrs. (%)	0.25	0.23	0.15	0.15

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Table II(B)21
PROPERTIES OF FRACTIONS OF NIIZU CRUDE OIL

No.	Fraction of distillation (%)	Boiling temp. (°C)	Density (25/4)	Flash point	Vis. in Redwood No. 1, sec.		Pour point (°C)
					at 30°C	at 50°C	
1	29 - 33	250-335	0.900	132	41	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	350-370	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	410-423	0.947	198	674	188	-30
9	61 - 65	423-435	0.953	209		304	-25
10	65 - 69	435-440	0.959			464	-20

Table III(B)21
NAVAL SPECIFICATIONS AND THE PROPERTIES
OF NO. 1, NO. 2, NO. 3, NO. 4, PRECISE OILS

	$d^{25}/4$	Vis. in Redwood No. 1, sec.		Pour point (°C)	Acid value	Saponification value	Evaporation loss (%)*
		at 100°C	at 30°C				
No. 1 Precise Oil	0.8895	131	62.2	-55	0.01	0.12	0.25
Special	0.92 >	145 >	60 <	-50 >	0.1 >	0.2 >	0.3 >
No. 2 Precise Oil	0.8992	246.2	90.2	-50	0.02	0.15	0.23
Special	0.92 >	350 >	90 <	-45 >	0.1 >	0.2 >	0.3 >
No. 3 Precise Oil	0.9149	462.6	150.1	-49	0.02	0.15 >	0.15
Special	0.92 >	600 >	150 <	-40 >	0.1 >	0.2 >	0.2
No. 4 Precise Oil	0.9060	508.8	152.6	-47	0.03	0.22	0.15
Special	0.92 >	600 >	150 <	-40 >	0.1 >	0.3-0.5	0.2 >

*After 5 hrs at 100°C.

Note: In the case of No. 4 precise oil, 0.2% (wt) rape seed oil was added as the oiliness improved to the Blim's refined fraction.
Reaction was neutral in all cases.
There was no corrosion.

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Table IV(B)21
CHARACTERISTICS OF REFINED DODECENE

	Refined dodecene	Beilstein's data
Boiling point	210°C-212°C	212°C
Yield from cocoanut oil	11.2%	
Density	d_4^{25} 0.7681	d_4^{20} 0.7590
Refractive index	n_D^{20} 1.4342	n_D^{20} 1.4270
Acid value	0.12	0
Saponification value	0.12	0
Iodine value	93.5	141.2

Table V(B)21
PROPERTIES OF POLYMERIZED DODECENE FRACTIONS

Fraction/5mm	Yield, (wt %)		Density (25/4)	Vis. in Redwood No. 1, sec. at 30°C	Pour Point (°C)	Iodine value
1st drop-140°C	14.7		0.7615	-	-37	7.40
140°C-160°C	1.7	18.4	0.7896	35.3	-52	8.98
160°C-180°C	2.0		0.7983	41.0	-60	12.12
180°C-200°C	4.7		0.8089	52.1	-70	14.67
200°C-220°C	9.6		0.8148	68.5	-71	16.42
220°C-240°C	13.2	59.0	0.8217	95.7	-70	17.09
240°C-260°C	5.7		0.8305	176	-62.5	17.53
260°C-280°C	12.1		0.8360	294	-57	17.72
280°C-300°C	13.7		0.8392	437	-56	21.74
300°C-18	18.2		0.8508	325.9	-38.5	21.34

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Table VI(B)21
NAVAL SPECIFICATIONS AND PROPERTIES OF NO. 5 PRECISE OIL

	$d^{25}/_4$	Vis. in Redwood No. 1, sec.		Pour point (°C)	Acid value	Saponification value	Evaporation loss(%)
		at 10°C	at 30°C				
No. 5 Precise oil	0.8338	457.6	154.5	-63	trace	0.54	0.09
Specification	0.02 >	600 >	150 <	-60 >	0.1 >	0.7 >	0.2 >

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

Table VII(B)21
PROPERTIES OF COMPONENTS AND THE SPECIAL PRECISE OIL

	The polymerized oil	The mineral oil	The mixed product (special precise oil)
Density(25/4)	0.8336	0.8611	0.8556
Flash point (°C)	175.5	117	108
Vis. in Redwood No. 1, sec. at 10°C	1701.1	52.6	133.2
Vis. in Redwood No. 1, sec. at 30°C	527.8	40.5	66.1
Pour point (°C)	-43	below-70	-67.5
Aniline point (°C)	137	67	96.5
Acid value	0.13	0.09	0.04
Saponification value	0.20	0.28	0.45
Increase of weight and volume of gum in the oil during 8 hrs. at 100°C. Followed by 24 hrs. at ord. temp.			
Weight			
Buna gum Natural gum	-4.4% plus 4.5%	plus 4.5% plus 68.2%	plus 1.0% plus 30.3%
Vol.			
Buna gum Natural gum	-0.6 13.6	8.6 143.2	0 47.4

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Table VIII(B)21
SUMMARY OF PRECISE OILS

Oil	Uses	Composition	Vis. in Redwood No.1, sec. at 30°C	V.I.	Pour point (°C)
No. 1 Precise oil	Watches and meters of aircraft	Straight distillate of Niizu crude 29%-37%	62.2	-	-55
No. 2 Precise oil	Watches and meters of aircraft	Straight distillate of Niizu crude 33%-41%	90.2	-	-50
No. 3 Precise oil	Magnetic dynamo and motor in aircraft	Straight distillate of Niizu crude 41%-57%	160.1	-18.4	-49
No. 4 Precise oil	Precise machines of the marine torpedo	Straight distillate of Niizu crude (41%-57%) .... 99.8% Rape seed oil 0.2%	152.6	-31.3	-47
No. 5 Precise oil	Precise machines of the aero-torpedo	Distillate 180°C -300°C/5mm of dodecene polymer .... 80 % Straight distillate of Niizu crude (41%-57%) .... 19.8% Rape seed oil 0.2%	154.5	101.39	-63
Special Precise oil	The flap or oleo of aircraft (Experimental)	Polymerized product of thermally cracked waxes .... 33.5% Straight distillate of Niizu crude (29%-37%) 67.5%	66.1	-	-67.5
Special Watch oil	Time limit bombs of aircraft	Distillate 120°C-300°C 5mm of Co-polymerized product of thermally cracked waxes and toluol	70	-	-65
Precise oil from shark liver-oil	Watches, meters and the flap or oleo of aircraft (not used)	The refined, hydrogenated product of distillate 235° -245°C/5mm of shark liver-oil	110	120	-55

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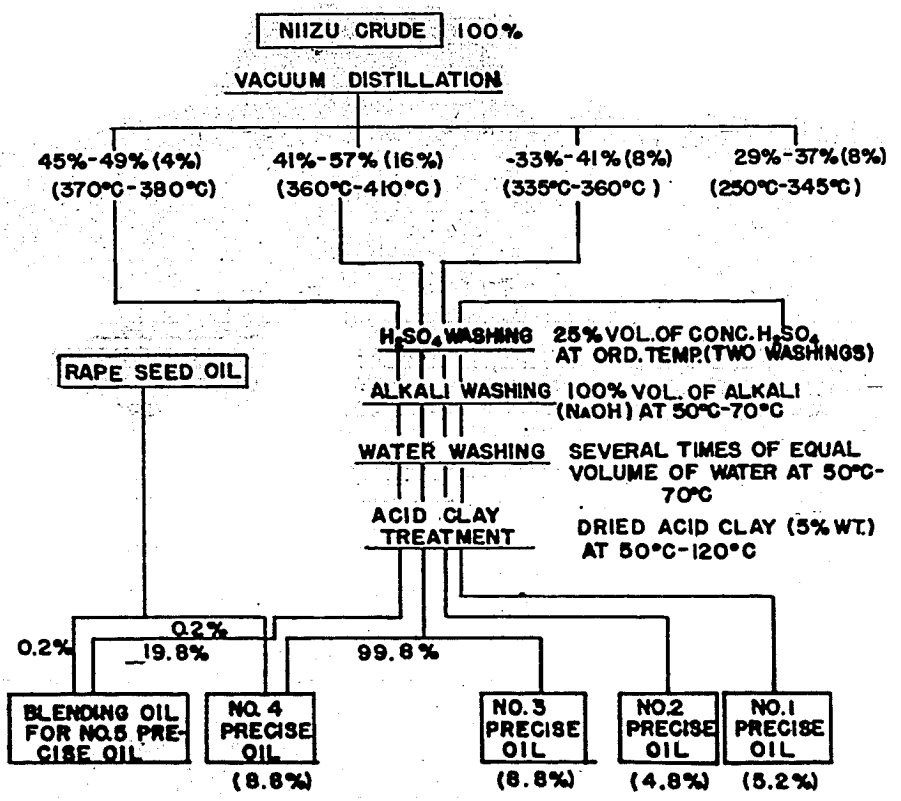

Figure 1(B)21

MANUFACTURE OF PRECISE OILS FROM NIIZU CRUDE

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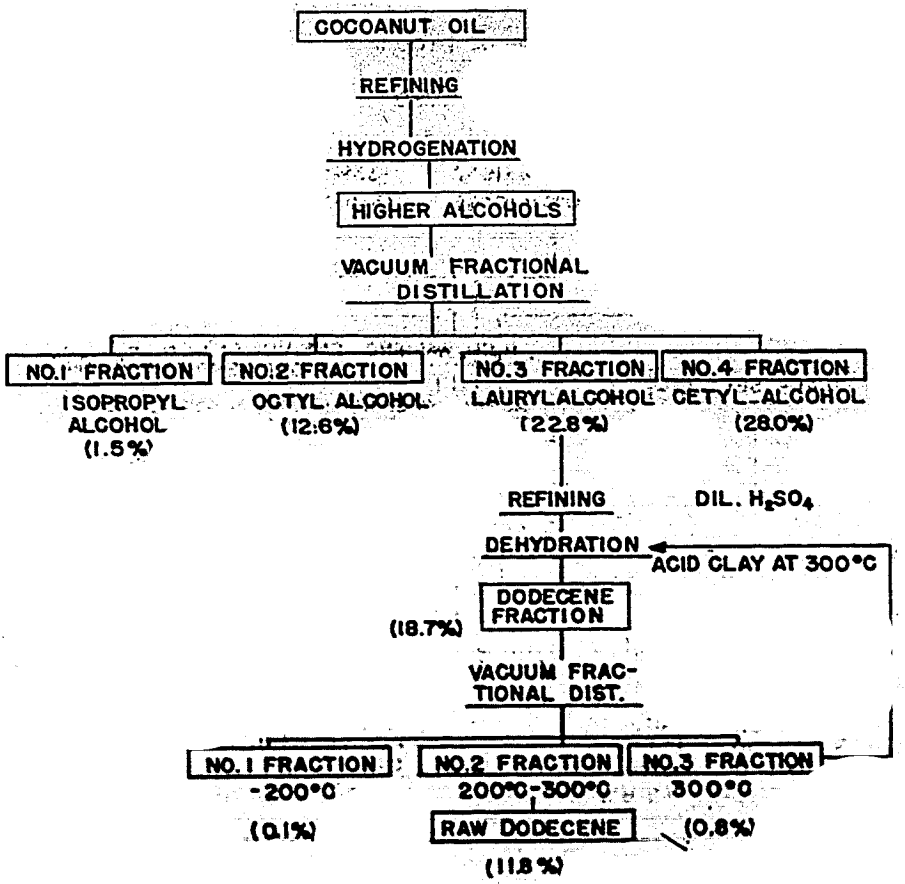

Figure 2(B)21
PREPARATION OF DODECENE

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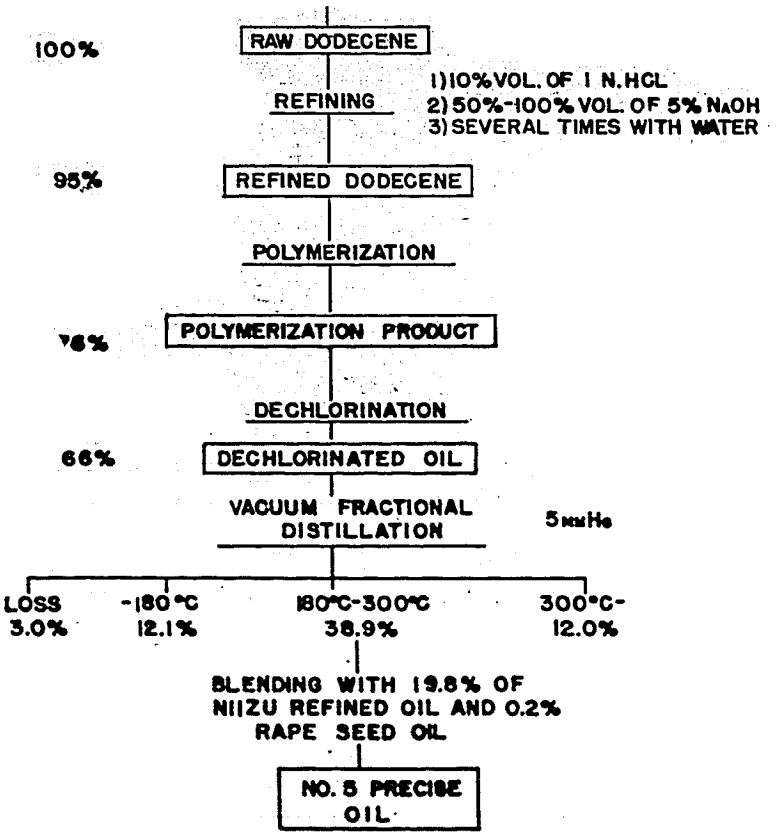

Figure 3(B)21
STEPS IN MANUFACTURE OF NO. 5 PRECISE OIL FROM RAW DODECENE