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From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.

Subject: Target Report - Japanese Fuels and Lubricants, Article 8 - Naval Research on Lubricants.

Reference: (a)"Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Subject report, covering lubricant research by Japanese Navy outlined by Targets X-09, X-10, and X-38(N) of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, Lieut. W. H. Millet, USNR, with the assistance of Ens. E. R. Dalbey, as interpreter and translator.

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Captain, USN

RESTRICTED

X-38(N)-8

JAPANESE FUELS AND LUBRICANTS - ARTICLE 8
NAVAL RESEARCH ON LUBRICANTS

"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945
FASCICLE X-1, TARGETS X-09, X-10, AND X-38(N)

FEBRUARY 1946

U.S. NAVAL TECHNICAL MISSION TO JAPAN

SUMMARY

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS-ARTICLE 8
NAVAL RESEARCH ON LUBRICANTS

Japanese naval research pertaining to lubricating oils has been investigated. The scarcity of Japanese crude oils having characteristics suitable for the manufacture of aircraft engine lubricants necessitated the use of imported crude oils for this purpose. As this supply was depleted, it became necessary to consider non-petroleum sources. The synthesis of lubricating oils from shale oil, paraffin wax, fatty oils, Fischer-Tropsch liquid, rubber, and other sources was studied at the First Naval Fuel Depot and other research laboratories. In applying these lubricants to practice, the use of oxidation inhibitors, oiliness agents, and other additives was frequently necessitated, in view of service performance limitations. Hence, additive studies were included as an essential part of the Navy's research program.

Perhaps the most important phase of lubricant research included in this report is the fundamental study of the relationship between structure and lubricant characteristics made by Dr. I. KAGEHIRA and co-workers. This research indicated that structures in which saturated cyclohexane rings are joined in the "para"-position either by single bonds or by paraffinic chains, are the most suitable for lubricating oils. These theories were reflected in the synthetic lubricant research conducted at the First Naval Fuel Depot.

It is believed that this report presents a broad picture of the lubricant requirements of the Japanese Navy during the war and includes detailed information on many special products peculiar to naval use.

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The Report

LIST OF ENCLOSURES

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture.
Third Naval Fuel Depot, TOKUYAMA.
First Naval Technical Depot, YOKOSUKA.
Army Fuel Research Institute, FUCHU.
Miike Synthetic Oil Company, OMUTA, Kyushu.
TEIKOKU NENRYO K. K. (Imperial Fuel Co.), Ube Plant, UBE.
NIHON HATSUDOKIYU K. K. (Japanese Motor Oil Co.), UBE.
Kyoto Imperial University, KYOTO.

Japanese Personnel Interviewed at the First Naval Fuel Depot:

I. KAGEHIRA, Ph. D., Chemical Engineering Captain, Japanese Navy, Head of Section of Inspection and Planning, First Naval Fuel Depot, (a chemist of outstanding ability specializing in synthetic lubricants).
N. MATSUO, Naval Engineer, Head of Lubricants Section, First Naval Fuel Depot.
A. WAKANA, Chemical Engineering Lt. Comdr., Japanese Navy, Head of Lubricant Additive Section, First Naval Fuel Depot.
T. DAN, Chemical Engineering Lt. Comdr., Japanese Navy, Head of Grease Section, First Naval Fuel Depot.
T. FUJIMOTO, Chemical Engineering Lieutenant, Japanese Navy, Head of Lubricant Testing Section, First Naval Fuel Depot.

Research Assistants of the First Naval Fuel Depot whose names are included in individual Japanese reports.

Other Japanese Personnel Interviewed:

T. KONDO, Engineering Captain, Japanese Navy, Head of Aviation Engine Testing Section, First Naval Technical Depot, YOKOSUKA.
I. WATANABE, Engineering Rear Admiral, Japanese Navy, Superintendent of Third Naval Fuel Depot, TOKUYAMA.
I. MOTOYOSHI, Engineering Captain, Japanese Navy, Chief Engineer of Third Naval Fuel Depot, TOKUYAMA.
N. TAKEI, Chief Engineer of Miike Synthetic Oil Company, OMUTA, Kyushu.
C. KITA, Professor of Chemistry (Retired), Kyoto Imperial University, (an outstanding research chemist specializing in catalysts for the Fischer-Tropsch synthesis).
A. IBUKI, Professor or Bio-Chemistry, Kyoto Imperial University, Kyoto.
S. NOMURA, Head of the Nomura Office, TOKYO, (one of the leading petroleum executives of Japan).

Referenced Japanese Reports:

"Technical Notes on Research Work" prepared by the Army Fuel Research Institute, FUCHU. 2 September 1944.

INTRODUCTION

At no time during the war did Japan's supply of lubricating oil become as critical as did the supply of fuel of all types. In spite of this fact, however, a substantial portion of the hydrocarbon research activity of the Japanese Navy was devoted to the synthesis of lubricants from substitute sources.

This report summarizes the findings of the Petroleum Section of the U. S. Naval Technical Mission to Japan relative to lubricant research conducted by the Japanese Navy at the First Naval Depot, OFUNA. It includes studies on petroleum refining, the synthesis of lubricants, and data relative to lubricating oil additives and greases. The information from OFUNA has been supplemented by that obtained from other laboratories, commercial plants, and naval installations.

Detailed reports of the lubricant research projects investigated at the First Naval Fuel Depot have been prepared in English by the technical personnel of the Depot and are included in this report as Enclosure (B)1 to (B)37, inclusive. A summary of these reports has been prepared in English by Chemical Engineering Captain I. KAGEHIRA and is submitted herewith as Enclosure (A).

Since all of the research files of the First Naval Fuel Depot were burned in August, 1945 by order of the Director of the Depot, it was necessary to summon the Japanese personnel and reconstruct this information from laboratory notebooks, laboratory apparatus, and pilot-plant equipment. The preparation of these reports and drawings continued for a period of nearly three months, during which time each Japanese author was frequently interrogated and was assisted in the organization and translation of his report. This material, which is submitted as Enclosures (A) and (B), constitutes an integral part of this report and, although it may include minor errors in construction introduced in the translation by the Japanese authors, it does serve as an accurate indication of the quality and extent of the lubricant research conducted by the Japanese Navy.

THE REPORT

Part I
REFINING OF LUBRICATING OILS

The principal Japanese crude oils are those obtained from the AKITA and NIIGATA districts. These crudes are of a highly naphthenic nature and, in general, are not suitable sources of aviation engine lubricants. Oils refined from Niizu crudes (NIIGATA) are characterized by exceptionally low pour points and negative viscosity indices, whereas most of the Akita oils have high wax contents and the viscosity-indices of the refined oils are less than 50. One exception is Omonogawa crude from AKITA which gives the best lubricating oil yield of any Japanese crude oil,- a yield 2% or less (based on total crude) of 85-90 viscosity-index lubricating oil.

Oha crude produced in SAKHALIN was of a more paraffinic nature than the Japanese crudes discussed above, and from this crude a limited amount of aviation lubricating oil of from 90 to 95 V.I. was produced by solvent extraction with treating yields from 0.3 to 5% of total crude, depending upon the degree of treatment and type of treating process utilized (Enclosure (B)4).

The small amount of domestic crudes available, coupled with the low yield of refined products, rendered the production of aircraft oils from these sources quite inadequate, and, in order to meet this situation, Japan imported huge reserves of crude oil and finished products from the United States before the war. These crude oils constituted the charging stocks for the Japanese refineries producing the high viscosity-index oils needed as aircraft engine lubricants.

Two of Japan's largest oil refineries, the Second and Third Naval Fuel Depots, located at YOKKAICHI and TOKUYAMA, respectively, were owned and operated by the Japanese Navy. These two plants had a combined refining capacity of approximately 27,000 barrels of crude oil per day which represented one quarter of Japan's total refining capacity. All research activity pertaining to the processes utilized at these refineries was concentrated at the First Naval Fuel Depot, OFUNA. At first, the Ofuna research was directed towards solvent refining techniques for both Japanese and imported crude oils. However, as the stock of imported crudes diminished, the research emphasis was shifted to the synthesis of lubricants from various non-petroleum sources.

A comprehensive picture of solvent refining studies at the First Naval Fuel Depot is presented in Enclosures (A) and (B)4 to (B)8, inclusive. The first process developed consisted of a combined deasphalting-dewaxing operation using propane, followed by Duo-sol solvent extraction. This so-called "Navy" process was utilized at both naval refineries but considerable difficulty with the propane dewaxing operation was encountered in practice. The process was later modified to incorporate the use of Barisol dewaxing after solvent treating.

There were three pilot plants at OFUNA used in connection with these studies. One of these pilot plants, built in TOKUYAMA in 1937 and transfered to OFUNA in 1939, was designed to study the combined propane deasphalting-dewaxing process. In conjunction with this unit there was a single-stage phenol-cresol extraction pilot plant at OFUNA. Each of these units had a capacity of 10 liters of charge per hour. In 1944 an acetone-benzol dewaxing pilot plant, having a capacity of 20 liters of charge per hour, was built.

Another refining process which was studied was one in which amyl alcohol was used for the deasphalting-dewaxing operation and furfural was used for solvent extraction. This method was particularly attractive to the Japanese in view of amyl alcohol as a by-product of alcohol fermentation and the suitability of furfural for naphthenic oils. However, it was never put into commercial operation.

A report on the inspection of the Third Naval Fuel Depot at TOKUYAMA is submitted as Enclosure (F) of Article 10 of this series. This refinery had two propane deasphalting, Duo-sol extraction plants, each with a capacity of 160 kiloliters of charge per day. The capacity of the Barisol dewaxing unit was 30 kiloliters of product per day.

During the war the aircraft engine lubricants refined in this equipment were obtained from topped Rhodessa, Osage, and Avalu crudes. The lubricating oil production in 1944 was 4120 kiloliters of aircraft engine oil, 4550 kiloliters of cylinder oil, and 1950 kiloliters of bearing oil.

While the lubricating oil treating data presented in detail as enclosures in this report disclose no new techniques, this material is included to show the nature of the Japanese stocks and to serve as a background for evaluating their overall lubricant position.

An interesting report entitled, "The Petroleum Industry in Japan" by I. AOKI and G. NARA has been written through the co-operation of S. NOMURA of the Nomura Office, TOKYO, for the Petroleum Section of the U. S. Naval Technical Mission to Japan. This report is submitted as Enclosure (D) of Article 10 of this series. The report discusses the history and recent developments in the Japanese petroleum industry. The characteristics of the various Japanese crude oils, Japanese crude oil production, and a discussion of the major refining equipment in Japan is included.

Part II
SYNTHESIS OF LUBRICATING OILS

A. FUNDAMENTAL CONSIDERATIONS

All research activity of the First Naval Fuel Depot pertaining to synthetic lubricants fell under the jurisdiction of Dr. I. KAGEHIRA; who held a specialist's commission as Captain in the Japanese Navy. For the past sixteen years Dr. KAGEHIRA has been studying the effect of molecular structure on the properties of lubricating oils. He has been particularly interested in the synthesis of pure compounds of naphthenic or mixed naphthenic-paraffinic type prepared by the hydrogenation of aromatic compounds and has studied the relationship of the ring structure of these products to their viscosity, stability, and related properties.

Dr. KAGEHIRA has concluded that the most desirable structure for lubricants of this type is that of a saturated compound in which cyclohexane rings are joined by single bonds in the para position. Applying his theories, several promising lubricants have been synthesized in the laboratory by completely hydrogenating such compounds as the condensation product of one mole of diphenylmethane with two moles of cetene or one mole of dibenzyl benzene with one mole of cetene. The lubricants thus prepared are characterized by high viscosity indices and satisfactory oxidation stability. Detailed discussions of the various studies which have been made are given in Enclosures (A), (B)1 and (B)2. In this connection, it is of interest that the theories of this research are reflected in the overall synthetic lubricant program of the Japanese Navy.

B. SOURCES OF SYNTHETIC LUBRICANTS

As Japan's accumulated reserves of imported crude oil stocks diminished, it became increasingly imperative that additional sources of lubricant supplies be developed. The Japanese Navy pioneered this development, and a discussion of the principal sources investigated is presented herewith.

1. Shale Oil. A large supply of the kerosene and gas oil fractions obtained from shale was available from the South Manchurian Railway plant at FUSHUN, Manchuria. The synthesis of lubricating oils by first refining these fractions and then polymerizing in the presence of aluminum chloride was studied at the First Naval Fuel Depot. Satisfactory aircraft lubricants were obtained in 10% yield but the process was applied only to the manufacture of **aerial** torpedo lubricants (Enclosures (B)3 and (B)19).

2. Paraffin Wax. Since 1942, high viscosity index aircraft lubricants, obtained by the polymerization of cracked paraffin wax from Sanga Sanga and Pendopo crude oils using aluminum chloride catalysts, had been commercially produced by the Fuel Depot at BALIKPAPAN, South Borneo. The product was inferior in respect to oxidation stability and a study of modifications of the process was undertaken at the First Naval Fuel Depot in 1940. It was found that an improved product of greatly increased stability could be obtained by condensing the cracked wax distillate with aromatic compounds, sulfur, or combinations thereof. Stable aircraft oils were also prepared by polymerizing the cracked wax distillates with different topped crude oils. The utilization in this process of the wax obtained from Barison dewaxing plants was investigated but the results were not promising. Laboratory data and a discussion of the project are presented in Enclosure (B)10 and (B)11.

Commercially, this process for manufacturing aircraft lubricating oils was in operation at the Balikpapan Fuel Depot and at the Second Naval Fuel Depot, YOKKAICHI. The Nippon Oil Company also manufactured small quantities of a similar product at its Yokohama refinery. A paraffin wax, melting at 50°C, was cracked in a reconstructed Cross vapor-phase unit of 30 kiloliters per day capacity. The reaction conditions and the properties of the product are given below:

Reaction Conditions

Cracking Temperature	550-570°C.
Cracking Time	4 sec
Polymerization Temperature	60 - 80°C.
Polymerization Time	8 - 10 hours
Catalyst	$AlCl_3$ (3-4%)
Dechlorination Catalyst	$Ca(OH)_2$, (2-3%) Clay, (4-5%)
Dechlorination Temperature	270°C.

Properties of Product

Reaction	Neutral
Neutralization Number	0.41
Flash Point	260°C.
Pour Point	28°C.
Viscosity, SUS, at 210°C	129
Viscosity Index	108
Carbon Residue	0.63%
Ash	0.012%
British Air Ministry Oxidation	
Viscosity Ratio	1.60
Carbon Residue Ratio	1.41
Neutralization Number	1.25

3. Fatty Oils. Polymerization in the presence of aluminum chloride of the olefines obtained by the dry distillation of sodium soaps of coccanut oil and related fatty oils was investigated at the First Naval Fuel Depot. The method could only be applied to non-drying or hydrogenated oils since unsaturated fatty oils yielded low viscosity-index products, (Enclosure B-12, 13 and 14). A commercial unit applying this process was under construction at the Sixth Naval Fuel Depot, FORMOSA, but it was destroyed by bombardment prior to completion.

Under the jurisdiction of the Army, the Japanese Vegetable Oil Company, (Nippon Yushi K. K.) constructed a hydrogenation plant at AMAGASAKI, for the synthesis of 7000 kiloliters per year of aircraft oils from soya bean oil. The hydrogenating units of this plant were destroyed by an explosion which occurred during the initial test run and these units never rebuilt. Dr. Y. NAGAI, of Tokyo Imperial University, had studied this process for many years. Extensive pilot plant and laboratory tests had been conducted by the Army at the Army Fuel Research Institute, FUCHU, prior to the construction of the plant at AMAGASAKI. The original process consisted of the polymerization of soya bean oil, hydrocracking of the polymerized oil in the presence of molybdenum trisulfide catalyst, hydrogenation of the resultant oil in the presence of nickel catalyst, and vacuum topping to yield a lubricating oil of the desired viscosity. The research at FUCHU was directed towards the simplication of the process and the following conditions were established as those which were to be utilized at the AMAGASAKI plant:

Polymerization

(Soya bean oil thermally polymerized)

Temperature	330-340°C.
Pressure	750 mm
Time	24 hours
Yield	90%

Hydrocracking

(Liquid phase hydrocracking using a flowing catalyst)

Temperature	320-360°C.
Pressure	150 atmospheres
Oil Velocity	1/4 Vol/hr/vol. of reaction tube.
Hydrogen Velocity	2000 vol/hr/vol. of reaction tube.
Catalyst	Cu:Ni:Acid Clay(1:1:1) 3-5% as metallic oxide

Vacuum Distillation

(In presence of 20% clay.)

No accurate data of the physical and chemical properties and service characteristics of this lubricant were available. A 16,435 kilometer non-stop test flight in MANCHURIA using the lubricant manufactured in the pilot plant has been reported.

Other processes utilizing fatty acids for the synthesis of lubricating oils were studied by commercial companies but none were applied to large scale production.

4. Fischer Liquid. A promising source of raw material for the synthesis of lubricating oils is the product of the Fischer-Tropsch coal liquefaction

process. This liquid is of a highly paraffinic nature and should yield a stable and high viscosity-index lubricating oil. No research in regard to this problem was undertaken by the Navy, but other laboratories have made initial investigations of methods by which this liquid might be utilized for the production of lubricating oils.

The Miike Synthetic Oil Company, OMUTA, was the most productive Fischer-Tropsch plant in Japan, and in 1941 they were ordered by the Army to concentrate on the construction of a lubricating oil polymerization plant which was to utilize the product of a U.O.P. Dubbs catalytic cracking plant under construction at the time. When the war ended, neither of these units had been completed.

The process which was to be put into operation at OMUTA was first, to prepare a highly unsaturated gasoline by the vapor phase cracking of the heavier oil fractions from the Fischer-Tropsch synthesis. This cracked distillate, having an end point of 250°C., was then to be charged to a polymerizer with 3% anhydrous aluminum chloride and maintained with agitation at 60°C. for 8 hours, or 80°C. for 7 hours. The product was to be settled, dechlorinated, purified with active clay (3 hours at 150°C, 5% by weight of clay), filtered, and topped. A light lubricating oil and an aircraft lubricating oil were to be obtained from the product. Small scale pilot plant tests indicated that these oils would have the following chemical and physical properties:

	Aircraft Lubricating oil	Light Lubricating oil.
Specific Gravity, 15/4°C.	0.85-0.87	0.82-0.83
Flash Point, °C.	240	145
Pour Point, °C.	20	25
Neutralization Number	0.05	0.06
Viscosity (S.U.S.)		
at 100°F.	1550	104
at 210°F.	125	34
Viscosity Index	107	54
Carbon Residue, %	0.08	
Ash, %	0.003	

According to Dr. KITA of Kyushu Imperial University, Fischer liquid prepared by means of an iron catalyst should be easily adapted to the synthesis of lubricating oils, since this product is higher in unsaturates and can be more readily polymerized than the product obtained using cobalt catalysts. More complete information pertaining to Dr. KITA's work on Fischer-Tropsch catalysts and the Miike Synthetic Oil Company is presented in Article 7 of this series, Enclosures (D) and (G), respectively.

5. Rubber. Rubber was one of the few types of hydrocarbons readily available to Japan during the first years of the war, hence it is only natural that it should have been considered as a source of fuels and lubricants. During 1943 and 1944 the First Naval Fuel Depot studied various methods by which aircraft engine lubricants might be obtained from rubber. The methods studied were:

a. Polymerization of the isoprene fraction of cracked rubber distillate.

b. Copolymerization of cracked rubber distillate with 2.54 volumes of the cracked distillate of paraffin wax.

c. Hydrocracking of a rubber-paraffinic hydrocarbon paste in a continuous hydrocracking pilot plant.

Both the copolymerization and hydrocracking methods yielded products of high viscosity index and satisfactory oxidation stability but neither process was applied to large scale units. Details of the research are described in Enclosure (B)15.

It is of interest that several companies prepared automotive lubricants from rubber on a commercial scale. Since the product could not be used as prepared because of poor oxidation stability, it was blended with mineral oil before use. Five plants utilized a process consisting of the following steps:

a. Shredded rubber dissolved in kerosene or comparable solvent (210°C. for 30 hours).

b. Rubber polymerized using acid clay catalyst (222°C. for 8 hours).

c. Filtration.

d. Topping and distillation of light oil.

e. Blending.

The combined monthly capacity of these plants was 3550 kiloliter of product. The name, location and capacity of each factory is tabulated below:

Name of Plant	Location	Capacity (kl/mo)
Nippon Sekiyu K. K.	AKITA	830
Nippon Sekiyu K. K.	NIIGATA	500
Showa Sekiyu K. K.	NIIGATA	370
Toa Nenryo K. K.	SHIMIZU	1500
Teikoku Nenryo Kogyo K. K.	UBE	350

6. Other Sources. Two other possible sources of synthetic lubricant were investigated at the First Naval Fuel Depot during the last few months of the war. These two sources were brown coal tar and pine root oil. It was planned to study the products obtained by polymerizing selected fractions of the dry distillation product of each of these materials in the presence of aluminum chloride. In the short time that was spent on these studies, no significant data had been obtained.

Part III
LABORATORY STUDIES ON FUNDAMENTAL LUBRICANT PROPERTIES

A. Oiliness

A considerable amount of research was carried on during the war at the First Naval Fuel Depot in regard to oiliness agents for lubricating oils, particularly for diesel engine lubricants and aircraft engine oils both petroleum and synthetic types.

A number of oiliness test machines were constructed for this purpose and it was concluded that Stanton's pendulum-type tester was the most suitable for routine work. Also a special machine, closely resembling the Almen Machine, was installed at the First Naval Fuel Depot in 1944, to carry out tests in regard to master rod bearing failures in Japanese aircraft engines. While no practical results were obtained due to poor design features, a description of this apparatus is included in this report in view of the use of magneto-striction to measure torque instead of the hydraulic means used in the Almen Machine. (Enclosure (B)30.)

This oiliness research work indicates that the Japanese investigator recognized the value of such test variables as bearing metal combinations, rubbing speed and test temperatures on oiliness determinations, but the applicability of such variables was not considered in selecting oiliness agents for practical engine tests.

The most interesting oiliness research carried out at the First Naval Fuel Depot was a systematic study to find the relation between the chemical structure and the oiliness properties of lubricants based on static friction determinations in a modified Deeley Machine using steel on steel surfaces. It was observed that in the case of hydrocarbons, cyclic compounds were better than chain compounds with the same number of carbon atoms. while compounds in which six-membered rings are combined with single bonds were better than those in which the rings were combined in condensed form (Enclosure (B)27). Fundamental studies on the oiliness characteristics of stearic acid, benzene, and their derivitives indicated that the NH_2 and COOH groups were the most effective, whereas other groups containing oxygen and nitrogen atoms were comparatively less effective. (Enclosure (B)28.)

Another interesting oiliness study related to the use of soya bean phosphatides. Research work based on kinetic friction determinations for steel on steel at low rubbing speeds and at room temperature indicated that the soya been phosphatides were effective as oiliness agents and that the higher the acid value the better the oiliness characteristics. (Enclosure (B)29.)

B. Anti-Oxidants

1. First Naval Fuel Depot, OFUNA. Research work of the First Naval Fuel Depot in regard to anti-oxidants fell in two categories, namely anti-oxidants for lubricants from petroleum sources and anti-oxidants for lubricants made synthetically. In these laboratory studies the means for evaluating oxidation stability was the use of the British Air Ministry Oxidation Test, wherein increase in viscosity and Conradson Carbon after air-blowing in the absence of metal catalysts is determined. Some of these tests were paralleled by oxygen absorption tests conducted in the Warburg Bio-chemical Oxidation Apparatus described below. A fundamental weakness of the laboratory oxidation data obtained is the lack of adequate study of the formation of organic acids and supporting engine test results.

The lubricants prepared synthetically and discussed in detail in Part II of this report were usually deficient in oxidation stability and the inhibitors suitable for natural oils were not, as a rule, suitable for the synthetic oils. For example, for aircraft engine oil produced from petroleum, tricresyl phosphite was the best anti-oxidant investigated, whereas for synthetic aircraft engine oil prepared from paraffin wax or Fischer-Tropsch condensate, copper soaps were the most effective. (Enclosure (B)23.)

One of the most interesting laboratory findings was the improved oxidation stability of aircraft engine, compressor, and turbine oils when utilizing soya bean phosphatides (Enclosure (B)29).

2. Kyoto Imperial University, KYOTO. During the period 1944-45, Professor A. IBUKI of the Kyoto Imperial University conducted research relative to the oxidation of pure straight chain and cyclic compounds. In this work he used methyl oleate and tetralin as being typical, respectively, of unsaturated straight chain compounds and ring compounds.

Oxidation was studied by the use of the Warburg Bio-chemical Oxidation Apparatus in which the oxygen absorption of 0.5 grams of oil is indicated by change in pressure. The test is conducted at 50°C. for a period of 120 minutes and the millimoles of O_2 absorbed are measured.

Name of Inhibitor	Absorption in cu.mm. of O_2 by 0.5 gram methyl oleate with .1% (weight) of Inhibitor
b-naphthylamine	5.0
a-naphthylamine	11.0
a-naphthol	12.0
b-naphthol	17.5
Phenol	19.5
Aniline	41.0
No inhibitor	52.5
Cyclohexanol	63.0
	Tetralin
Phenol	5.0
Aniline	13.5
No inhibitor	18.8

These data are of a preliminary nature and no conclusions have been drawn by Dr. IBUKI.

3. Article 10 of this series, Enclosure (D), presents data relative to the oxidation characteristics of a blend of synthetic lubricant prepared from soya bean oil with 5% of naphthenic base oil and 0.1% of an organic salt (formula unknown). According to laboratory tests, this oil possessed superior oxidation stability characteristics when compared to typical aircraft engine lubricants manufactured in America. No comparative engine data were available.

4. Pour Point Depressants. The synthesis of "Paraflow" was studied and a most effective product was obtained by condensing naphthalene and chlorinated wax in the presence of aluminum chloride. A significant finding was that it was necessary to control the reaction by the addition of small quantities of water. The need for water was accidentally discovered and was not mentioned in the U.S. patent on "Paraflow". This pour point depressant differed somewhat in physical properties from "Paraflow", but it was effective in depressing the pour points of oils and was manufactured on a commercial scale throughout Japan. (Enclosure (B)35).

Part IV
ENGINE LUBRICANTS

A. Aircraft Engine Oils

1. Mineral Oils. In Japan there was a sufficient supply of imported aircraft engine oil until about 1943, consisting principally of Texaco Oil No. 120. However, it then became necessary for the Japanese Navy to use oil designated as "K-120-K" which was prepared in Japan from Phillips Osage crude treated in the Duo-Sol plant at TOKUYAMA. Full-scale aircraft engine tests (conducted at the First Technical Depot, YOKOSUKA) indicated that "K-120-K" was not equal in service performance to Texaco Oil No. 120 and, accordingly, full-scale tests were made at the Mitsubishi, Nakajima and Aichi Companies. The oil was compounded with 2% by weight of both tricresyl phosphate and tricresyl phosphite (this compounding was chosen in view of laboratory research oxidation and stability tests discussed in Enclosure (B)23) Results of the engine tests were not conclusive, but indicated sufficient improvement on master rod bearing and piston ring condition to justify its practical use in combat planes during July and August 1945. There is no information in regard to the practical results

obtained with compounded "K-120-K" oil used during the last two months of the war. (Enclosures (B)25 and (B)26.)

As discussed in Part III, Section B, laboratory data are presented in Enclosure (B)29 relative to the improved oxidation stability of aircraft engine oils by the use of soya been phosphatides as additive agents. A small amount of laboratory data are also presented on the simultaneous use of a phosphatide and tricresyl phosphate in aircraft engine oils of both the natural and synthetic types. No engine test data relative to the use of these compounds are available.

2. Synthetic Oils. For synthetic aero engine oils prepared from paraffin wax or Fischer-Tropsch Oil, as discussed in Part II, B, of this report, it was found that the anti-oxidants most suitable for petroleum oils were not suitable, but that copper soaps were markedly effective. Again there is no supporting engine data for the synthetic oil so compounded. (Enclosure (B)23.)

3. Viscosity Index Improvers. Japanese naval aircraft engine oil "K-120-K" was produced from Mid-Continent crude by solvent extraction at the Third Naval Fuel Depot to meet the minimum viscosity index requirement of 90. In order to improve the viscosity index, iso-butylene polymers were prepared following the method of the Standard Oil Company of New Jersey and were blended with aircraft engine oil No. 80 purchased from the Texas Oil Company. This raised the viscosity from 80 S.U.S. to 121 S.U.S. at 210°F and the viscosity index from 94 to 101. In single cylinder aircraft engine tests it was indicated that wear with the blended oil was somewhat greater than that obtained with natural petroleum oils, and it was concluded that it was necessary to improve the heat stability of the polymer engine oil blend before it could be satisfactorily used in aircraft engines. (Enclosure (B)33.)

4. Reclaiming. In view of the increasing shortage of aircraft engine lubricants in the latter part of the war and the difficulty of transporting used lubricants from the airfields to the refineries for re-refining, a portable unit, which could be fabricated at the airfields from materials on hand, was developed for reclaiming used lubricating oil. The unit consisted essentially of a tank with a perforated plate in the bottom covered with a sheet of paper. The oil was placed in this tank and the ashes of wood, grass, or roots were added, using 15% of ashes by weight. The oil was heated to 130°C and drawn through the paper into another tank using a vacuum system. Analyses of the used and reclaimed oil in one case showed reduction in the ash content from .2 to .01% and in acid rate of from 7 to 20 liters per hour by this apparatus.

showed reduction in the ash content from .2 to .01% and in acid value from .26 to .08. Reclaimed oil could be produced at the rate of from 7 to 20 liters per hour by this apparatus.

B. Marine and Aero-Tropedo Engine Lubricants

During the period of 1938 to 1943 research was carried out at the First Naval Fuel Depot to develop lubricants particularly suited for marine and aero-torpedo engines. Significant results included the following:

1. Marine Torpedo Engines. For marine torpedo engines the lubrication requirements were judged to be similar to those of aircraft engines, and aircraft engine oil prepared from Oha crude by solvent extraction (Part I, this report), and having a viscosity-index of 99 and a pour point of -14°C, gave excellent results.

2. Aero-Torpedo Engines. Aero-torpedo engines operate at a much lower temperature than those of marine torpedos and consequently, require special

lubricants. A synthetic oil prepared from crude shale oil by the polymerization method (Part II, Section B-1) was found to be satisfactory in practical service tests. This product had a viscosity-index of 92 and a pour point of -32.

For still lower temperature conditions of operation, a synthetic oil prepared by the polymerization of a fraction of cracked wax distillate (Part II, Section B-2 of this report), compounded with 1½% aluminum oleate, gave satisfactory results. Its viscosity-index was 112 and its pour point, -46°C. The aluminum oleate was added to prevent the oil from being washed out by sea water in the aero-torpedo engine at the end of its run on trial shots. This product was tested and approved by the Naval Aeronautical Arsenal, YOKOSUKA, in 1943 for use under all conditions of temperature.

C. TURBINE OILS

Turbine oils were, in general, prepared from Japanese crudes. These turbine oils had high pour points unless dewaxed and the capacity of the dewaxing plants in Japan was insufficient for treating turbine oils, since the plants were chiefly used for the production of aircraft engine lubricants. For this reason, pour point depressants were manufactured as discussed in Part III, C, of this report, and added to turbine oils, depressing their pour points from approximately 15°C to below 0°C. This method was applied on a commercial scale.

No other additives such as oxidation inhibitors or rust-proof compounds were used with turbine oils and no information in regard to service performance characteristics of turbine oil was obtained.

D. DIESEL ENGINE OILS

1. Straight Mineral Oils. Prior to the war, turbine oils had been mainly used for marine diesel engine lubrication in the Japanese Navy, but this type of oil, except that prepared from Oha crude, was not found satisfactory from the viewpoint of cylinder wear. When aircraft engine oil No. 00 (produced by the Texas Oil Company) was used as a diesel engine lubricant, cylinder wear was decreased to about one-fifth that obtained with the turbine oil, but the carbon and lacquer deposits on the pistons were excessive. Lubricating oil prepared from Oha crude by vacuum distillation, phenol extraction, dewaxing and acid clay treating gave good results in engine tests and did not require the use of an additive, but a treating yield of only 0.3% was obtained. (Enclosure (B)20.)

2. Compounded Oils (Laboratory Tests). In 1942 and 1943 a series of laboratory tests were conducted to determine additives suitable for use in submarine diesel engine lubricating oils. These compounds were studied from the standpoint of oiliness, oil stability, and dispersion or peptizing of carbon deposits. It was found that calcium phenyl stearate was the most effective from the standpoint of detergency and dispersion of carbon deposits and that lecithin (soya bean phosphatide) and tricresyl phosphate were the most effective as oiliness agents and anti-oxidants. The detergency tests were made by washing a piece of flannel stained with soot, with gasoline containing 2% of each additive, whereas the laboratory dispersion test consisted in measuring, by means of a photometer, the translucency of white oil to which had been added oil sludge and one of the several additives being investigated.

As a result of this laboratory work, it was concluded that calcium phenyl stearate was suitable as an additive for high viscosity aero-type engine oils intended for use as diesel engine lubricants, whereas lecithin and tricresyl phosphate were beneficial as additives for low viscosity-index oils when used in diesel engines. (Enclosure (B)29.)

3. Compounded Oils (Engine Tests). No actual engine data were obtained on diesel engine lubricating oils either straight or compounded. It was reported, however, that practical tests in diesel engines of turbine oils

compounded with lecithin (the active constituent of soya bean phosphatide) showed this additive was not sufficiently effective to render this oil stock satisfactory as a diesel engine lubricant. It was further reported that diesel engine tests showed that the use of calcium phenyl stearate did not sufficiently reduce the carbon deposition characteristics of aircraft engine oil No. 80.

Part V
SPECIAL OILS

A. "PRECISE" OILS

The term "precise oil" is applied by the Japanese Navy to such types of lubricants as instrument oils and hydraulic oils. Specifications for five different grades of these oils were established by the Japanese Navy in 1943. All but one of them consisted of highly refined and selected fractions of Niizu crude oil obtained from the NIIGATA district in northwestern HONSHU.

The refined product was highly naphthenic and, although it had an exceptionally low pour point, difficulties were encountered in practice which were attributed to the low viscosity index (-100) and low aniline point (60-65°C.) of these oils. It was reported that, in service, rubber softening and swelling of packings was frequently encountered. Several explosions had occurred because of the bursting of rubber hose and all rubber fittings had to be renewed frequently. During the war the First Naval Fuel Depot was actively engaged in developing synthetic lubricants which would surmount the difficulties encountered with mineral oil. A comprehensive picture of this development is presented in Enclosures (A), (B)21, and (B)22.

Four precise oils synthesized from non-conventional sources were developed by the Navy at the First Naval Fuel Depot. The method by which each was prepared may be briefly stated as follows:

1. Number 5 Precise Oil

   a. 80% of a fraction of polymerized dodecene boiling from 180°C. to 300°C. at a pressure of 5 mm of mercury.

   b. 19.8% of a selected fraction of refined Niizu crude oil.

   c. 0.2% of rapeseed oil.

2. Special Precise Oil

   a. 33.5% of the polymerized product of thermally cracked paraffin wax distillate.

   b. 66.5% of a selected fraction of refined Niizu crude oil.

3. Special Watch Oil. The fraction boiling from 120°C. to 300°C. of the polymerization product of a mixture of 20 parts of toluol with 100 parts of a thermally cracked wax distillate.

4. Precise Oil from Shark Liver Oil. Squalene, obtained from shark liver oil distillate, was hydrogenated in the presence of a nickel catalyst.

Details of the methods of preparation and the properties of the products are given in Enclosure (B)21. The Number 5 precise oil has been used since 1943 as an instrument oil for aerial torpedoes and the special watch oil was utilized in time bomb mechanisms. The other two oils did not progress beyond the experimental stage, but were to be utilized as hydraulic oils.

B. HYDRAULIC OILS

The Japanese Navy used two hydraulic oils in addition to the "precise oils" described above. One was a highly refined fraction of Niizu crude oil, and the other was a butanol-castor oil mixture. No research on either of these oils was conducted at the First Naval Fuel Depot during the war.

C. ESTERIFIED OILS

Although the Japanese Navy conducted no research on this type of lubricant, it is of interest that the Japanese Army did use esterified oils as automotive lubricants. Enclosure (D) outlines the information obtained from the Japanese Motor Oil Company (Nihon Hatsudokiyu K. K.) pertaining to the manufacture of these oils. Of particular interest is the low temperature lubricating oil prepared by blending 87 volumes of refined butyl ricinoleate with 13 volumes of polymerized soya bean oil. The lubricant was manufactured for the use of the Army in Manchurian operations, but production was stopped early in 1944 since there was no appreciable military activity in that area.

D. ANTI-CORROSIVE CYLINDER OIL

A cylinder oil for aircraft engines which served as a rust preventive was developed at the First Naval Fuel Depot in 1943. Details of the manufacture of this product are given in Enclosure (B)39. The composition (wt. %) of the oil is as follows:

Refined rapeseed oil	75
Aluminum stearate	10-12
Triethanol amine	5
n-Butanol	10-8

E. ELECTRIC CABLE INSULATING OILS

In 1944 the preparation of polyisobutylene to be used as an insulating oil was studied at OFUNA. The reaction was carried out at a temperature of -150°C. and a polymer having an average molecular weight of 170,000 was obtained. The process was not applied commercially. The method of preparation follows that described in U. S. Patents and is outlined in Enclosure (B)34.

Part VI
GREASES

Research work conducted at the First Naval Fuel Depot on lubricating greases, primarily for aircraft use, was undertaken in 1938 using natural mineral oil stocks. In 1943, due to the increasing shortage of oil stocks, the research on greases from petroleum sources was paralleled with studies of synthetic lubricating oils as substitutes. Generally speaking, natural lubricants from Japanese crude oil consisted of aromatic hydrocarbons which have good soap solubility, characteristics compared to paraffinic hydrocarbons. Synthetic paraffinic-type oils were less desirable due to solubility characteristics, particularly the high viscosity grades. When using synthetic lubricating oils, it was found that for calcium or soda soap greases, condensation products of paraffinic and aromatic hydrocarbons were suitable.

Prior to 1938, special greases for aviation engines and auxiliary parts were imported chiefly from the United States and up until that time, practically no research had been carried out in Japan along these lines.

The procedure adopted in 1938 was first, to install modern grease manufacturing equipment, including the latest electrically heated experimental grease kettles and milling machines of the three-roll type. The second step was to manufacture greases whose characteristics matched those of imported greases found to be satisfactory in service. After matching these greases in small equipment, experimental products were manufactured at the First Naval Fuel Depot in equipment of pilot plant size.

1. Magneto Grease. A grease for aircraft engine magnetoes was developed whose service performance matched that of Bosch Magneto Grease manufactured in the United States. The Japanese grease was composed of a soda soap of castor oil with an excess of soda and was prepared at a temperature of 230°C. Quick cooling was used and was followed by milling to provide a smooth texture. For manufacturing magneto grease from synthetic oils and castor oil soap, it was found necessary to specify the viscosity and maximum aniline point of the synthetic oils in view of solubility considerations.

2. Rocker Arm Grease. Two experimental greases having satisfactory service performance characteristics were developed. Both of these greases contained a mixture of sodium oleate and sodium stearate soaps and a small amount of glycerine. There is no information in regard to the manufacture of this lubricant using synthetic oils.

3. Controllable Pitch Propeller Grease. A satisfactory product was made by using a mixture of aluminum stearate, aluminum oleate, and lead oleate soaps, plus a small amount of glycerine, compounded with approximately 90% of viscous lubricating oil stock. Friction tests in a machine resembling the Timken Lubricant Test Machine showed that the presence of lead oleate imparted friction reducing properties.

4. Liquid Grease for Framework of Aero-Torpedoes. A grease containing 7% aluminum stearate and 0.2% calcium stearate and 92.8% of cylinder stock gave excellent results for the prevention of corrosion of engine parts. The role of the calcium stearate in this product was to modify the plasticity of the aluminum stearate.

5. Special Grease for Preventing Corrosion of the Interior of Compressed Air Cylinders of Aero-Torpedes. Up until 1943, heavy cylinder oil was found unsatisfactory in adhesiveness and in anti-freezing characteristics. A product overcoming these deficiencies was prepared by heating 12% aluminum stearate and 0.36% calcium stearate with cylinder stock, followed by milling.

6. Sea Water-Proof Grease. This product was prepared as an anti-corrosive, anti-wash compound to be used on machine guns mounted on submarines. A satisfactory composition consisted of 13% aluminum stearate and 87% heavy lubricating oil.

7. Special Greases. A minor amount of work was done on special greases such as alcohol-proof greases and greases that were resistant to concentrated nitric acid. (Enclosure (B)36, Part III.)

Part VII
LUBRICANT SPECIFICATIONS JAPANESE NAVY

Official specifications of lubricants used by the Japanese Navy during the war period are included as an Enclosure to Article 1 of this series.

ENCLOSURE (A)

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SUMMARY OF LUBRICANTS RESEARCH PROGRAM AT THE FIRST NAVAL FUEL DEPOT, OFUNA

by

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Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (A)

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (A)

I. AERO ENGINE OILS

Of all sorts of lubricating oils, aero engine oils are subjected to the most severe conditions, i.e. high temperatures and high pressures. Hence they must have high oxidation stability and a low rate of change of viscosity with varying temperature. These requirements have led to the use of mineral oils in place of castor oil, and oils prepared from paraffin base crude oil (Pennsylvania crude oil) has been said to be the best. Extensive studies have been carried out in regard to the chemical composition of lubricating oils derived from petroleum, and it has been concluded that lubricating oils are, in general, composed mainly of cyclic hydrocarbons with paraffinic side chains. However, practically nothing was known concerning the relation of ring structure to the viscosity, the oxidation stability and the other properties of cyclic hydrocarbons.

Thus, the author has studied these fundamental problems since 1929. He came to the conclusion that a saturated compound in which cyclohexane rings combine by single bonds in the para position, such as per hydro- 1, 4-diphenyl benzene ($C_6H_{11}\cdot C_6H_{10}\cdot C_6H_{11}$), is the best and that a condensed ring compound containing a naphthalene ring, such as tetrahydro-anthracene, tetrahydro-phenanthrene or hexahydro-pyrene, is suitable for a lubricating oil (Enclosure (B)1).

Based on these conclusions, in 1940 diphenylmethane and dibenzylbenzene were prepared by condensing benzene with benzyl-alcohol in the presence of aluminium chloride and, after these hydrocarbons were condensed with cetylchloride or cetene, the condensation products were hydrogenated. The hydrogenated products had a high viscosity index and a low Conradson's carbon. They were, therefore, suitable as aero engine oils and proved the correctness of the above conclusion. The properties of typical examples of hydrogenated products are shown in Table I(A), (Enclosure (B)2).

Shale kerosene or gas oil is the most important potential source of synthetic aero engine oils in Japan, since the production is large and it consists mainly of olefinic and aromatic hydrocarbons. From both types of hydrocarbons a suitable aero engine oil is obtainable by condensation. Since this raw material contains 20-30% of acidic, basic and highly unsaturated compounds as impurities, studies have been carried out since 1937 relative to the pre-refining methods, and the polymerization of the pre-refined oil. It was found that it was best to treat the raw material with 2% by weight of hydrochloric acid gas and 50% by weight of 20% caustic soda solution and then to condense the pre-refined oil in the presence of 10% of aluminium chloride at 60°C-80°C, for 10 hours. A satisfactory aero engine oil was thus produced with a yield of 10% by weight of the raw material, (Enclosure (B)3).

At the same time, since 1937 solvent extraction methods applicable to the preparation of aero engine oils from Japanese crude oil were investigated. (Enclosures (B)4, (B)5, (B)6, (B)7, (B)8, and (B)9). As solvent extraction methods the propane-phenol and the amyl alcohol-furfural processes were adopted. In the former process, the operating conditions of dewaxing especially were surveyed and it was found that it was best to treat the deasphalted oil in 3 volumes of liquid propane at (-)40°C with a cooling rate of 1°C-5°C per minute. In the latter process, the operating conditions in each treating stage were studied. It was found best to treat the residual oil of the petroleum crude with 3 volumes of amyl alcohol at -20°C for deasphalting and dewaxing and to extract the deasphalted and dewaxed oil with 3-4 volumes of furfural at 80°C-100°C. Results of the former process were utilized in the industrial plants at the Second and Third Naval Fuel Depots, where aero engine oils were produced from imported crude oils, since the production of crude oils in Japan was slight and the yield of the product from them was only about 5% by weight of the crude oil.

ENCLOSURE (A)

An ample supply of this oil could not be obtained by the process mentioned above. So other surveys were made and synthetic aero engine oils from the following raw materials was undertaken; from paraffine wax in 1940, fatty oil and rubber in 1943, and brown coal tar and pine root oil in 1945. Olefinic hydrocarbons would be obtained from paraffine wax by thermal cracking in the vapour phase and from fatty oil by the dry-distillation of its alkali soap which would yield a suitable oil by condensation with aromatic hydrocarbons or sulphur. In the latter case, the sulphur compounds formed in the condensation product would serve as the anti-oxidants. The condensation products from the paraffin wax contained some highly unsaturated compounds derived from diolefins formed during the thermal cracking of the paraffin wax. By removing these highly unsaturated compounds with organic solvents, the comparatively poor oxidation stability of the product would be improved. High fractions of brown coal tar consist mainly of aromatic hydrocarbons of naphthalene, diphenyl, phenanthrene etc., and those of pine root oil consist mainly of condensed ring compounds such as abietin and abietic acid. These could be utilized as the source of aromatics, based on the author's systematic research on the synthesis of lubricating oils. Rubber will form cyclic compounds by heating, and if this reaction is carried out in the presence of hydrogen to reduce the highly unsaturated nature of the product, suitable aero engine oils will be obtained.

Superior oils with a very high oxidation stability, as indicated by the viscosity ratio of 1.1-1.3 in the British Air Ministry Oxidation Test, were obtained from paraffin wax by condensing 10%-20% of aromatic hydrocarbons (benzene, naphthalene, anthracene, etc.) or 0.1% of elementary sulphur or both with the cracked distillate of paraffin wax. If the cracked wax was condensed with the residual oil of a petroleum crude oil as the aromatic hydrocarbon, the viscosity ratio of the product was 1.5-1.6. Blending the condensation product of the cracked wax with 10%-20% of a natural oil such as Texaco airplane oil #120 or an acid treated distillate of Niizu, Selia or Milli crude oil, the resulting oil had a viscosity ratio of 1.3-1.6. Solvent extraction with 1.5 volumes of a phenol-cresol mixture greatly improved the oxidation stability of the condensation product of the cracked wax, the viscosity ratio being lowered from 2.07 to 1.4. The above synthetic method was applied on an industrial scale at the Second Naval Fuel Depot. (Enclosure (B)10 and (B)11)

The following procedures were applied in obtaining synthetic oils from fatty oils; the dry distillation of sodium soap, purification of the dry distilled oil by distillation with 10% by weight of solid caustic soda, and polymerization of the purified oil or condensation of the purified oil with naphthalene or other aromatic hydrocarbons in the presence of aluminium chloride. In the case of the coconut oil, a good oil was produced with a yield of 20% by weight. This method can only be applied to non-drying oils or hydrogenated fatty oils, since unsaturated fatty oils yield low viscosity index products. Another survey on the pre-refining method of dry-distilled oil showed that ketones formed in the dry distillation of sodium soap had to be removed by treating with anhydrous sodium hydroxide and that if water formed in this process were removed from the reaction zone, the amount of solid caustic soda required could be reduced from 10% to 1%. (Enclosures (B)12, (B)13 and (B)14)

A desirable oil was prepared by the hydrocracking of rubber in a solution of 5 volumes of a paraffinic hydrocarbon such as Fischer oil under high pressure of hydrogen in the presence of nickel at 300-350°C, for 15 hours. (Enclosure (B)15)

Research on brown coal tar and pine root oil as sources of aero engine oils had shown no important results at the termination of war. (Enclosures (B)16 and (B)17)

ENCLOSURE (A)

Research was conducted on a method of reclaiming aero engine oils, and a simple method, which yielded a satisfactory oil by filtering in the presence of wood ashes at 100-130°C, was established. This method was actually used at several air stations. (Enclosure (B)18)

Studies on the anti-corrosive cylinder oil of aero engines were carried on and a suitable oil was obtained, used in practice. (Enclosure (B)37)

II. TORPEDO ENGINE OILS (Enclosure (B)19)

A mixture of a steam cylinder oil and a rape oil was used for marine torpedo engines, but the formation of the oil sludge was observed to be comparatively large. Since the operating conditions of marine torpedo engines resembled those of aero engines, preparation of the oil from Oha crude oil by the propane-phenol process has been studied since 1938, and a refined mineral oil with a viscosity at 210°F of 92 S.U.S., a viscosity index of 99, a Conradson's carbon of 0.55 and a pour point of (-)14°C was obtained. This refined mineral oil was successful in engine tests, however, a mixture of 80% of aero engine oil #100 and 20% of aero engine oil #80 was actually used, owing to the insufficient supply of Oha crude oil.

For aero torpedo engines, a very low pour point oil with a high viscosity index was needed. From studies on the preparation of aero engine oils from shale gas oil, this was considered to be a readily obtainable source. The practical application of the product was verified by studies on its preparation by condensation of the pre-refined oil and on engine tests of the product. Since 1942, the raw material used was produced and obtained from FUSHUN in South Manchuria.

The aero torpedo engine oil prepared from shale gas oil, however, was inferior in respect to pour point and unsatisfactory for use in the coldest zones. For this purpose, the synthesis of a product from the cracked distillate of paraffin wax was studied and an oil was prepared by condensing a fraction of the cracked wax boiling from 100°C to 230°C and adding 1.5% by weight of aluminium oleate to the condensation product. The product had a viscosity at 210°F of 96 S.U.S., a viscosity index of 112, a Conradson's carbon of 0.08% and a pour point of -46°C. The oil proved to be satisfactory in actual use either in cold or tropical zones.

III. CYLINDER OILS FOR MARINE DIESEL ENGINES (Enclosure (B)20)

In general, turbine oils were used for marine Diesel engines in the Japanese Navy. Piston ring and cylinder wall wear was comparatively high. This wear was considered to be due to the insufficiency of the oil viscosity. Hence, an oil having a viscosity at 210°F of 72 S.U.S., a viscosity index of 99 and a Conradson's carbon of 0.05 was prepared from a fraction of Oha crude oil boiling from 250°C to 300°C at a vacuum of 5 mm Hg by the propane-phenol process. This oil was proved to be satisfactory as a Diesel cylinder oil in 1940, yet it was not actually supplied since the yield was so small, 0.3% to the original crude oil.

In 1941, other tests on the utilization of aero engine oil #80 for Diesel cylinders were conducted, but no satisfactory results were obtained.

IV. PRECISE OILS (Enclosures (B)21 and (B)22)

Together with the progress in aircraft, torpedoes and other machineries, accessory precise machines have also developed and improvements in the properties of precise oils were necessary to insure satisfactory operation. Important properties required of precise oils are: high oxidation stability, high viscosity index, low pour point and also, in the case of aircraft hydraulic apparatus, high aniline point.

Based on the possibility of obtaining low pour point oils from Niizu crude oil, the manufacture of lubricating oils to be used for the precise machines of aircraft and marine torpedoes was studied since 1938, applying a sulphuric acid treatment to the distillates of Niizu crude oil (using 50% by weight of 98% sulphuric acid to the raw material). In the case of a precise oil for the marine torpedo (No.4 precise oil) 0.2% of a rape oil was blended with a refined distillate. The main properties of products are shown in Table II(A).

In the case of aero torpedo precise machines, a very low pour point oil was needed. For this requirement no satisfactory oil was obtainable from Niizu crude oil. Considering that the average molecular weight of the precise oil is approximately 400 and that the polymers of olefinic hydrocarbons have very low pour point, the polymerization of dodecene was studied in 1940. An oil was prepared by blending a fraction of the polymerized product of dodecene boiling from 180°C to 300°C under a vacuum of 5mm Hg, a refined mineral oil prepared from a fraction of 45%-49% of Niizu crude oil, and a rape oil in the ratio of 80:19.8:0.2. The product had a Redwood No.1 viscosity at 10°C of 457.6 and at 30°C of 154.5 seconds, a viscosity index of 101, a pour point of (-)63°C, and proved satisfactory in engine tests. Hence from that time this product was actually used.

In 1943 there was a demand for a special watch oil with a very low pour point. This requirement was easily satisfied with an oil synthesized by condensing 100 parts of a thermally cracked distillate of paraffin wax with 20 parts of toluene in the presence of aluminium chloride at 90°C for 8 hours and then distilling under 5mm Hg of vacuum to cut a fraction boiling from 120°C to 300°C. The product thus synthesized had a viscosity at 30°C of 70-Redwood No.1 seconds and a pour point of (-)65°C.

As another source, shark liver oil may be utilized, since it contains the squalene fraction. Since 1943 studies were made on the seperation of squalene by vacuum distillation and on its hydrogenation. A product suitable for use in various precise machines was obtained. The viscosity of the oil at 30°C was 110 Redwood No.1 seconds and the pour point was (-)55°C.

At the same time, No.1 precise oil used for the oleos and flaps of aircraft was found to be inferior in regard to rubber swelling and low temperature freezing character. Considering that an oil of paraffinic nature has excellent anti-rubber-swelling and low temperature freezing characteristics, a blended oil of 33.5% of a condensation product of thermally cracked wax and 66.5% of a refined mineral oil prepared from a fraction of 29%-37% Niizu crude wax and 66.5% of a refined mineral oil prepared from a fraction of 29%-37% Niizu crude oil, was prepared. This blended oil was satisfactory, yet it was not developed sufficiently to be put into practice.

V. ADDITIVE AGENTS FOR LUBRICATING OILS

With the increase of horsepower in aero engines, lubricating oils are exposed to higher and higher temperatures and pressures. Under these severe conditions, a mere hydrocarbon oil will not be satisfactory from the standpoint of oxidation stability and oiliness, and additive agents will become necessary to improve these properties.

Considering the above, since 1940 studies have been made on anti-oxidants and oiliness carriers for aero engine oils. Referring to the literature, phenolic compounds, metallic soaps and amine compounds may be said to be representative of anti-oxidants. On the other hand, natural mineral oils, synthetic oils and

ENCLOSURE (A)

castor oil are used as aero engine oils and the effective anti-oxidant for an individual oil may differ due to differences in chemical structure. For natural oils, tricresyl phosphite was found to be the best antioxidant and tricresyl phosphate was found to have nearly the same retarding effect on oxidation. (Enclosures (B)23, (B)24, (B)25, and (B)26) In this respect, the soya-bean phosphatides were also effective on natural aero engine oils. (Enclosure (B)29) For synthetic oils, tricresyl phosphite, triphenyl phosphite, copper oleate, tin oleate, chromium oleate, and their mixtures were tested as anti-oxidants, and copper oleate was found to be the best for synthetic oils prepared from sweated waxes, Fischer oil, or diphenyl-methane series hydrocarbons. The viscosity ratio after the British Air Ministry Oxidation Test of an oil with a small amount of copper oleate was decreased from over two for the original to 1.5. For castor oil, p,p'-dioxydiphenylamine, thiodiphenylamine and phenyl-b-naphthylamine were tested and the former compound was found to be the best one. Among them, a mixture of tricresyl phosphite and tricresyl phosphate was actually used in natural oils. (Enclosure (B)23)

A systematic survey was made to find the relation between the chemical structure and the oiliness of lubricants, and it was observed that in the case of hydrocarbons, cyclic compounds were better in respect to oiliness than paraffinic compounds with the same number of carbon atoms, while a compound in which six-membered rings combined with single bonds was better than one in which the rings were combined in condensed form. (Enclosure (B)27) In the case of polar compounds, the $-NH_2$ and $-COOH$ groups were most effective on the oiliness, the $-OH$ group was next, and other groups containing oxygen or nitrogen atoms were comparatively less effective. (Enclosure (B)28) Soya bean phosphatides were also tested and found to be effective not only on the oiliness but also on the oxidation stability of aero engine, compressor and turbine oils. (Enclosure (B)29). Studies on the method of testing oiliness were also carried out and a simple pendulum oiliness tester suitable for routine testing was obtained. (Enclosures (B)30 and (B)31)

For diesel engine cylinders, a turbine oil has been generally used in the Japanese Navy and recently an aero engine oil #80 was tested for its availability. In the former case, the wear of piston rings and cylinder walls was high, and soya bean phosphatides were tested to decrease this wear, but no positive results were obtained. When aero engine oil #80 was used, the wear was much smaller, but the carbon deposit in cylinders was greater. In 1942 calcium phenylstearate was tried in engine tests as a means of decreasing the carbon deposition but no desirable effect was observed. (Enclosure (B)32)

Yields of aero engine oils from Japanese crude oil meeting the viscosity index specification were small, being of the order of 5% to the original crude. If a suitable viscosity index improver was found, yields of aero engine oils would be increased by adding a small amount of it to the low viscosity index oil. For this purpose, in 1942 an isobutylene polymer was prepared by polymerizing isobutylene at (-)40°C in the presence of aluminium chloride and topping off the fraction up to 250°C under 5mm Hg of vacuum. The product was observed to be unsatisfactory in engine tests from the view point of the heat stability of oil. (Enclosure (B)33). In extending these studies a suitable high frequency insulating material with an average molecular weight of 170,000 was obtained by polymerizing isobutylene in liquid ethylene at (-)150°C in the presence of an ethylchloride solution of aluminium chloride. (Enclosure (B)34).

Turbine oils were, in general, prepared from Oha or other Japanese crude oils. These turbine oils had high pour points unless dewaxed, and the capacity of dewaxing plants in Japan was insufficient for treating turbine oils, since these plants were chiefly used for the production of aero engine oils. Hence, an attempt to prepare a suitable pour point depressant was made, and studies on the preparation of a compound similar to "Paraflow", which was observed to be the best additive for this purpose, were carried out. Experimental results showed that a satisfactory depressant could be obtained by the condensation of naphthalene and chlorinated wax in the presence of 5% of aluminium chloride at 50°C-100°C for 3 hours. The reaction was controlled by the additon of small quantities of water, which was not mentioned in the U. S. Patent on "Paraflow". The product readily depressed the pour point of typical turbine oils from (+)15°C to below 0°C. This method was applied on a commercial scale. (Enclosure (B)35)

VI. GREASES

Studies on greases were meagre and almost all special greases used in Japan were imported until recently. Considering these conditions and the availability of greases for various machineries, studies on the preparation of special greases were begun in 1939. There was a demand that greases should possess certain properties, and it was desired to utilize the water-repellent nature of calcium soap, the high temperature and speed withstanding nature of sodium soap, the water-repellent and the high temperature withstanding character of aluminium soap, and the extreme load carring property of lead soap, and to select a suitable oil for each grease.

With these ideas in mind, a magneto grease was first studied and was prepared by mixing 78.7% of a refrigerating oil with 22.3% of the sodium soap of castor oil containing an excess of caustic soda at 230°C. The product had a consistency at 25°C of 254, a dropping point of 175°C, and a good heat stability, and was used successfully in practice. (Enclosure (B)36, Part I.)

Next, a controllable pitch propeller grease was studied and was prepared by mixing 91.6% of a solvent refined mineral oil having a viscosity at 210°F of of 133.4 S.U.S. and a viscosity index of 88, 6.48% of aluminium stearate, 0.72% of aluminium oleate, 0.8% of lead oleate, and 0.4% of glycerine. The product was an excellent grease with a consistency at 10°C of 347, a dropping point of 40°C and good heat stability. (Enclosure (B)36, Part I.)

For the rocker arms of aero engines, a satisfactory grease was obtained by mixing 91.2% of a solvent refined mineral oil having a viscosity at 210°F of 95 S.U.S. and a viscosity index of 67 with 3% of sodium stearate, 3% of sodium oleate, 1% of calcium oleate and 0.8% of glycerine at 150°C. The product had a consistency at 25°C of 360, a dropping point of 119°C, good heat stability and a water-repellent nature. (Enclosure (B)36, Part I.)

Preparation of the above mentioned greases from synthetic lubricating oils was also studied and condensation products prepared from olefinic and aromatic hydrocarbons were observed to be only suitable for the preparation of greases. (Enclosure (B)36, Part II.)

In 1943, greases for the frame work of aero torpedo engines and for the anti-corrosion of air chambers of aero torpedoes were investigated, because of the lack of satisfactory lubricants for these uses. The former grease was made by mixing 92.79% of a synthetic oil from Shale gas oil having a viscosity at 210°F of 61.9 S.U.S., a viscosity index of 85 and a pour point of (-)36°C with 7% of aluminium stearate and 0.21% of calcium stearate at 150°C. The product obtained proved to be satisfactory in engine tests and had a consistency at (-)40°C of 284, a viscosity at 210°F of 1036 S.U.S., and good heat stability. (Enclosure (B)36, Part I.) Changing the mixing ratio of the synthetic oil, aluminium stearate and calcium stearate to 87.64%, 12% and 0.36%, respectively, a satisfactory grease was obtained as an anticorrosive lubricant for the compressed air chambers of aero torpedoes, having a consistency at 25°C of 226, a dropping point of 90°C and good heat stability. (Enclosure (B)36, Part I.)

ENCLOSURE (A)

Recently a sea-water-repellent grease to be used in submarines was studied and was prepared by mixing a refined heavy mineral oil, having a viscosity at 210°F of 141 S.U.S. and a viscosity index of 15, with 13% of aluminium stearate. Practical tests showed the product to be satisfactory. The consistency at 25°C and the dropping point of the product were 310 and 88°C respectively. (Enclosure (B)36, Part I.)

Alcohol proof and concentrated nitric acid proof greases were studied in 1945. For the former a mixture of 90% of petrolatum and 10% of aluminium stearate and for the latter a petrolatum was observed to be suitable for the purpose, but no practical tests had been performed by the termination of war. (Enclosure (B)36, Part III.)

Table I(A)
AERO ENGINE OILS SYNTHESIZED FROM DIPHENYLMETHANE SERIES HYDROCARBONS

	Synthetic Oil	Properties of Oil				
		Viscosity		Conradson's Carbon (wt.%)	After the British Air Ministry Oxidation Test	
		S.U.S. at 210°F	Index		Viscosity Ratio	Conradson's Carbon (wt.%)
1	Completely hydrogenated product of condensation product of one mol. diphenylmethane and two mols. cetene.	90.6	121	0.13		
2	Completely hydrogenated product of condensation product of one mol. dibenzylbenzene and one mol. cetene.	136.6	108	0.11	2.2	0.7
3	(2)+0.5% by weight of copper oleate.				1.4	0.6
4	(2)+0.1% by weight of copper oleate.				1.44	

ENCLOSURE (A)

Table II(A)
PROPERTIES OF PRECISE OILS

		Name of Precise Oil			
		No. 1	No. 2	No. 3	No. 4
Fraction of Niizu Crude Oil used. (%)		29-37	33-41	41-57	41-57
Boiling Range of Fraction at 760mm Hg (calculated) (°C)		250-345	335-360	360-410	360-410
Application		Various precise machines in air craft.	Various precise machines in air craft.	Air-craft magneto	Precise machine in marine torpedo
Properties of Oil	Viscosity in Redwood No.1 Sec. at 10°C	131	246.2	562.6	508.8
	at 30°C	62.2	90.2	160.1	152.6
	Pour Point (°C)	-55	-50	-49	-47

RESTRICTED

ENCLOSURE (B)

ENCLOSURE (B) 1

ON THE SYNTHESIS OF LUBRICATING OILS

Reference NavTechJap Document No. ND 26-0009.14 ATIS No. 4580

by

CHEM. ENG. CAPT. I. KAGEHIRA

Research Period: 1929-1938

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

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ENCLOSURE (B)1

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)1

I. INTRODUCTION

Extensive studies have been carried out in regard to the chemical composition of lubricating oils derived from petroleum oils.(1) The results of these studies show that lubricating oils are, in general composed largely of cylic hydrocarbons expressed as C_nH_{2n-2}, C_nH_{2n-4} etc. The relation between the structure and the viscosity of hydrocarbons has also been studied, but mainly for aliphatic compounds.(2)

Practically nothing is known concerning the relation of ring structure to the viscosity and other properties of cyclic compounds.

Thus, the author intended to conduct a systematic survey of the relationship between the structures and the lubricating properties of cylic compounds in order to synthesize better lubricating oils. Various hydro-aromatic hydrogenated bezene, diphenyl, 1,3 - or 1,4 - diphenyl bezene, naphthalene, anthracene, phenanthrene, acenaphthene and pyrene, by the reduction of corresponding aromatic compounds at high temperatures and pressures in the presence of reduced nickel.

The chemical stability of hydroaromatic compounds was discussed from the point of view of their reduction mechanism. The physical properties such as boiling point, specific gravity, specific and molecular refraction and viscosity of these compounds were determined, and the relation between the molecular volume and visocity, and molecular structure were surveyed.(3)

With these results, a new method for the synthesis of superios lubricants has been proposed.

II. THE CHEMICAL STABILITY OF HYDROAROMATIC COMPOUNDS VIEWED FROM THE STANDPOINT OF REDUCTION MECHANISM

The aromatic hydrocarbons which were uaws in the experiment were benzene, diphenyl, 1,3 - or 1,4 - diphenyl benzene, naphthlene, anthracene, phenanthrene acenaphthene and pyrene, and they were all found to be chemically pure; their physical constants are shown in Table I(B)1. These compounds were completely or partially reduced by hydrogen at high pressure in the presence of reduced nickel, the reaction products being purified by distillation or recrystallization, and identified by elementary and chemical analysis.

The conditions and results of reduction are shown in Table II(B)1. In the case of the reduction of benzene, diphenyl and diphenyl benzene, the reaction took place easily at about 200°C. and completely hydrogenated compounds were formed

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(1) C. Engler, Das Erdol, Bd. I, S. 382-387; C. F. Mabery, J. Amer. Chem. Soc., 30 (1908), 992; J. Ind. Eng. Chem., 5 (1923), 1233; A. E. Dunstan, J. Inst. Petr. Tech., 4 (1918), 191; 7 (1921), 417; Chem. Met. Eng., 28 (1923), 289; M. Bestuschew, Erdol u. Teer, 7 (1931), 159, 191, 205; A Sachv n U. R. Wirabiaz, Erdol u. Teer, 9 (1933), 170, 187, 202, 220; B. J. M ir & C. E. Willingham, J. Ind. Eng. Chem., 28 (1936), 1452.

(2) W. R. Wiggins, J. Inst. Petr. Tech., 22 (1936), 305; H. B. L. Evans J. Inst. Petr. Tech., 241 (1938), 38, 321, 537.

(3) Dr. I. KAGEHIRA, The Report of Imperial Naval Fuel Depot, No. 128, June, 1938.

quantitatively. Hydrogenation of diphenyl at 250°C. and the restriction of the absorption of hydrogen to three mols, however, resulted in the formation of phenylcychohexane, owing, perhaps to the catalytic oxidation of the dicychohexyl formed directly from diphenyl:

$$C_6H_{11}-C_6H_{11}\ \underline{\hspace{5cm}}\ C_6H_5-C_6H_{11}$$

Analogous phenomena were observed in the case of hydrogenation of diphenylbenzene which was reduced to the hexa-hydro or the dodecahydro compound by restricting the absorption of hydrogen at 140 - 180°C. However, in the reduction of diphenylbenzene, it was observed that the meta isomer was partially reduced easily, while the para isomer was not.

Naphthalene, on reduction at 200°c., yielded tetra-hydro-naphthalene which was converted into a decahydro compound at 160°c. In the reduction of phenanthrene, the tetrahydro compound was formed at 170°c. and was reduced to the octahydro compound at 180°c., which was converted into a perhydro compound at 160°c.

Anthracene, on the other hand, behaved differently from phenanthrene in the reduction. It was reduced to the perhydro compound in one reaction step, while by restricting the absorption of hydrogen, it could be partically reduced.

In the reduction of acenaphthene at 200 c a decahydro compound was formed. The hydrogenation at higher temperatures (270°C), however, produced tetrahydroacenaphthene due to the reverse reaction which occurs in the decahydro compound and which is favoured by high temperature. The hydrogenation of pyrene was the most difficult of these hydrocarbons. A hexahydro compound was first formed at 300°c and the hexahydro compound was reduced to the decahydro compound at 170°c, which was by further catalytic reduction at 240°c. converted into perhydro-pyrene.

As will be seen from the previous observations, aromatic hydrocarbons may be divided into two groups from the point of view of catalytic reduction. Some can be reduced completely by one experimental condition as was noticed in the case of benzene, diphenyl or diphenylbenzene, but in the case of the other group to which naphthalene, phenanthrene, anthracene, acenaphthene and pyrene belong, complete reduction can be achieved only through two or more reaction steps, with changes in the experimental conditions especially in the reaction temperature.

In the case of the reduction of anthracene or acenaphthene, however, the completely reduced compounds were obtained in one step with changes in the experimental condition, but the reduction velocity differed markedly from that of diphenyl. Analogous phenomena were also seen in the comparison of the reduction of benzene to that of linolic acid.(4) Thus, these facts indicate that anthracene or acenaphthene are compounds of a series to which diphenyl does not belong.

reduction of benzene to that of linolic acid.(4) Thus, these facts indicate that anthracene or acenaphthene are compounds of a series to which diphenyl does not belong.

Reaction differences in the reduction of isomers is noteworthy. For example, in the case of diphenyl benzene, it is more difficult to reduce the para

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(4) S. KOMATSU, Bull. Chem. Soc., Japan, 56 (1935).

ENCLOSURE (B)1

isomar to the partially hydrogenated compound than the meta isomer. These differences in reaction were also observed in the reduction of anthracene and phenanthrene; in the former, benzene rings are combined in the para position and in the latter in the meta position.

If the partial reduction of the above-mentioned compounds can be attributed to the ununiform distribution of energy in the molecule, it may be considered that the molecule, in which the energy distribution is uniform, will be completely hydrogenated in one easy reaction step.

In view of these considerations, it may be predicted that the hydro-aromatic compounds, obtained by hydrogenation, will behave differently towards oxidation, the inverse reaction of reduction. Thus, a hydro-aromatic compound, derived from an aromatic molecule in which the distribution of energy is ununiform, would sustain easily partial oxidation, while a compound derived from an aromatic molecule in which the distribution of energy is uniform would be difficult to oxide.

The latter compouns, therefore, would be well suited for a lubricating oil. In other words, it may be claimed that a compound which is to be suitable as a lubricating oil consists of such molecules as those in which the distribution of energy is uniform, such as perhydro-diphenyl or diphenylbenzene.

These principles show that some partially hydrogenated compounds would also be useful as lubricating oils, sunce the partially hydrogenated compound may be considered to be in the same energy state as the completely hydrogenated product of diphenyl benzene.

III. MOLECULAR VOLUME OF HYDROAROMATIC COMPOUND

In view of the hydrogenation reaction, hydroaromatic compounds have been classfied into two groups:

A. Hydro compounds of benzene, diphenyl and 1,3 - or 1,4 - diphenyl benzene.

B. Hydro compounds of naphthalene, anthracene, phenanthrene, acenaphthene and pyrene.

Also, differences between para and meta isomers have been observed.

These differences may be considered in light of their molecular volumes. As shown in Table III(B)1, in the case of the first group, the difference of molecular volume between the neighbouring saturated compounds decreases with the increase of molecular weight, while this difference increases in the case of the second group.

The effect on the molecular volume of a benzene ring which is observed by comparing the molecular volumes of saturated compounds with those of partially hydrogenated compounds, is also shown to decrease with an increase in molecular weight in the case of the first group but is nearly constant in the case of the second group, as shown in Table IV(B)1

The effect on the molecular volume of the naphthalene ring is almost constant in every case of the second group. This analogous to the effect of the benzene ring (see TableV(B)1.

As shown in Table VI(B)1 the difference of molecular volume between pare and meta isomers could not be practically observed.

IV. VISCOSITY OF HYDROARMOMATIC HYDROCARBONS

Dunstan and Wilson(5) proposed in viscosity formular for a liquid as follows: log = (1/B) X (M-A) in which is the viscosity of the liquid, M is the molecular weight, A is a specific constant depending on the particular series to which the liquid belongs, and B is a general constant.

By applying the viscosities of benzene solutions of the hydroaromatic compounds used in this experiment to ISHIKAWA's viscosity formular for binary mixtures,(6)

$$\frac{\frac{k_2a_2}{k_1a_1}}{(1-Z_m) \qquad \frac{(k_2a_2)}{k_1a_1} \; Z_m}$$

in which 1, 2 and are viscosities of benzene, hydroaromaric compound and their mixtures respectively, Z_m is the molar fraction of the liquid, k_1 and k_2 are the characteristic "field constants" of benzene and the hydroaromatic compound, and a_1 and a_2 are the degrees of association of benzene and the hydromatic compound, respectively, the author determined the degrees of association and concluded that the viscosity of a liquid depends not only on the molecular weight and molecular association but may also depend on another factor namely on the structure of the molecule.(7)

A. Effect of Ring Form.

Comparing the viscosities of saturated compounds of the two groups classified according to reduction mechanism and change of molecular volume, the effect of ring form on viscosity is considered, the viscosity being compared with the ratio of the viscosity difference to the molecular weight difference.

The difference of viscosity ratio between cyclohexane and dicyclohexyl is 0.03, and between dicyclohexyl and perhydro-1,3-diphenyl benzene is 0.83. In the case of the second group, the difference between cyclohexane and decahydronaphthalene is 0.04, between decahydronaphthalene and perhydro-anthracene 0.11, between decahydronaphthanlene and decahydro-acenaphthene0.13 and between decahydroacenaphthene and perhydro-pyrene 0.32. The compounds of the first group show a much greater increase of viscosity with increase of molecular weight than do these of the second group. The results are shown in Table VII(B)1

Analogous results were obtained in comparing the viscosity of 0.1M benzene solutions of these compounds in the same manner, as shown in Table VIII(B)1.

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(5) A. E. Dunstan & R. W. Wilson, J. Chem. Soc., 91 (1907) 90.

(6) T. ISHIKAWA, Bull. Chem. Soc., Japan, 4 (1929), 288.

(7) I. KAGEHIRA, the Report of Imperial Naval Fuel Depot, No. 97, August, 1935.

In view of these results, from the standpoint of viscosity, it may be concluded that compounds of the homologous series to which perhydro-diphenyl or diphenylbenzene belong, are the most suitable and that such a compound as perhydro-pyrene will be also useful as lubricating oils.

B. Effect of Benzene Ring

In the first group, to which hydro-diphenyl or -diphenylbenzene belongs, the viscosities of the saturated compounds are greater than the unsaturated in which the molecules have a benzene ring, while in the second group, with one exception, the unsaturated compound is more viscous than the corresponding saturated compound (see Table IX(B)1) However, in benzene solutions, the unsaturated compounds are more viscous than the saturated compounds in every case (See Table X).

C. Effect of Naphthalene Ring

The compounds which have naphthalene ring are crystalline at ordinary temperatures, so their viscosities in benzene solution were compared.

As may be seen in Table XI, the ratio of the viscosity of an unsaturated compound in which the molecule has a naphthalene ring to that of the corresponding saturated compound is almost the same in each case.

The difference between the effect on viscosity of the naphthalene ring and the benzene ring may be determined from the results shown in Tables X(B)1 and XI(B)1; the naphthelene ring increases the viscosity more than the benzene ring.

This fact suggests that compounds in which the molecule has a naphthalene ring, such as hexahydro-pyrene, will be useful as lubricating oils.

D. Effect of Isomerization

The effect on viscosity of isomerization may be observed by comparing hydro-1,4 - to the corresponding hydro -1,3- diphenylbenzene or hydro-anthracene to the corresponding hydrophenanthrene (See Table XII(B)1. The para compound is more viscous than the meta compound. Therefore, the compounds in which the cyclohexane rings combine in the para position, whould be more useful as lubricating oils.

V. SYNTHESIS OF LUBRICATING OILS

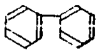
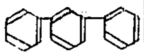
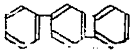
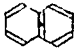
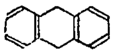
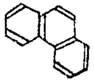
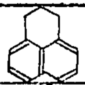
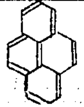
A systematic investigation of the relation of molecular structure to the chemical stability and the viscosity of hydroaromatic compounds has suggested that saturated compounds in which the molecules consist of cyclohexane rings combined by single bonds in the para position, such as perhydro-1,4 -diphenylbenzene, will have the best characteristics for use in the synthesis of lubricating oils.

If the relation between the viscosities of cyclohexane, dicyclohexyl and perhydro-1,3-diphenylbenzene is extended to higher compounds of the same series, the viscosity of dicyclohexyl-dicyclohexyl (C_6H_{11}-C_6H_{10}-C_6H_{10}-C_6H_{11}) would be in the order of 20-30 poise at 25°c. (See table VII(B)1, which is of the proper range for aero lubricating oils.

It is generally recognized that the change of viscosity with temperature of paraffine hydrecarbons is the least of all types of hydrocarbons. Hence, a cyclic compound which has a long paraffinic chain might be expected to be of the proper viscosity and be less susceptible to change in viscosity with changing temperature.

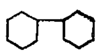
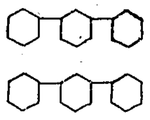
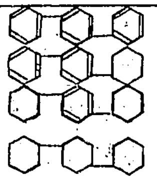
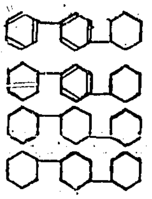
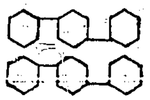
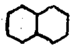
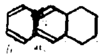
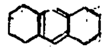
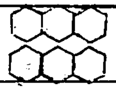
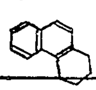
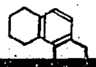
The author's surveys, therefore, suggest a new method of synthesizing lubricating oils to be used for automobiles or aero-engines, where constancy of viscosity with varying temperatures and high oxidation stability are required.

TABLE I(B)1
AROMATIC HYDROCARBON

Aromatic Hydrocarbon	Structural formula	Emprical formula	Appearance	Boil Pt. (°C)	Melt. Pt. (°C)	Picrate	
						Appearance	Malt. Pt. (°C)
Benzene		C_6H_6	Colorless liquid	80- 80.5			
Diphenyl		$C_{12}H_{10}$	White Thin Plates	248- 249	68.5-69.5		
1,3,-diphenyl benzene		$C_{18}H_{14}$	White needles		85.5-86.5		
1,4-diphenyl benzene		$C_{18}H_{14}$	White thin plates		211.5- 212		
Naphthalene		$C_{10}H_8$	White granular	212.5-213.5	80 - 81	Pale Yellow needles	150-150.5
Anthracene		$C_{14}H_{10}$	White thin plates		212.5-213.5	Red needles	139-140
Phenanthrene		$C_{14}H_{10}$	White thin Plates		97-98	Orange yellow thin plates	141-142
Acenaphthene		$C_{12}H_{10}$	White needles	266.5-267.5	93-94	Orange red	160.8-161.8
Pyrene		$C_{16}H_{10}$	Yellow tetrahedral crystals		148-149	Red needles	222-223

ENCLOSURE (B)1

TABLE II(B)1
THE CONDITIONS AND RESULTS OF HYDROGENATION OF AROMATIC AND PARTIALLY HYDROGENATED COMPOUNDS

Aromatic compound	Amount used in experiment (gr.)	Reaction temperature (°C)	Initial pressure of hydrogen at 0°C (atm.)	Hydrogen absorbed		Reaction time (hr-min.)	Reaction Products								
				Obs.	Calc.		Hydroaromatic compound	Structural formula	Yield (wt.%)	Boil. pt. (°C)	Melt. pt. (°C)	Density (25/4)	Refractive index (25 D)	Molecular refraction Obs.	Molecular refraction Calc.
Benzene	100	200	76	182	168	5-15	Cyclohexane		96	80-80.5		0.7741	1.4235	26.67	27.70
Diphenyl	40	250	75	91	92	11- 0	Phenylcyclohexane		93	234-236		0.943;	1.5313	52.56	51.82
Diphenyl	65	200	95	115	98	3-45	Dicyclohexyl		94	231-233		0.8836	1.4777	53.20	53.22
1,3-diphenylbenzene	62	140	113	36	34	1- 0	Hexahydro-1,3-diphenylbenzene		95	176-178/2.6mm		1.0102	1.5798	77.78	75.82
1,3-diphenylbenzene	75	150	119	85	83	1-45	Dodecahydro-1,3 diphenyl-		100	176-178/2mm		0.9742	1.5425	78.31	77.32
Dodecahydro- 1,3-diphenylbenzene	36	150	102	18	18	2-30	Perhydro-1,3-diphenylbenzene Perhydro-1,3-diphenylbenzene		46 52	182-184/5mm 182-184/5mm	 625-630	0.9443	1.5176	79.61	78.72
1,4-diphenylbenzene	100	180	103	76	61	7- 0	1,4-diphenylbenzene Hexahydro-1,4-diphenylbenzene Dodecahydro-1,4-diphenylbenzene Perhydro-1,4-diphenylbenzene		25 49 18 small quantity	 178-180/1.5mm	 745-75.5 96-97				
1,4-diphenylbenzene	50	170	108	53	53	2- 0	Hexahydro-1,4-diphenylbenzene Dodecahydro-1,4-diphenylbenzene Perhydro-1,4-diphenylbenzene Perhydro-1,4-diphenylbenzene		small quantity 87 3 3	 178-180/1.8mm	 96-97 48-49 162-163				
1,4-diphenylbenzene	50	220	108	85	80	6-30	Perhydro-1,4-diphenylbenzene Perhydro-1,4-diphenylbenzene		36 46	130-134/2.5mm	48.5-49.5 162-163				
Naphthalene	100	200	91	71	67	13- 0	Tetrahydro-naphthalene		91	201.5-203.5		0.9683	1.5392	42.79	42.58
Tetrahydro-naphthalene	100	160	91	119	67	7- 0	Dodecahydro-naphthalene		97	189-191		0.8906	1.4784	43.82	43.87
Anthracene	50	200	100	32	24	3-15	Tetrahydro-anthracene				101.5-102.5				
Anthracene	50	200	99	48	48	2-15	Octahydro-anthracene				72-73				
Anthracene	100	270	98	198	167	19-15	Perhydro-anthracene Perhydro-anthracene		84 14	139-141/11mm	 89-90	0.9383	1.4990	60.14	60.25
Phenanthrene	50	170	95	26	25	7 - 0	Tetrahydro-phenanthrene			160-162/10.9mm		1.0706	1.6260	60.[illegible]	57.92
Tetrahydro-phenanthrene	72	180	90	40	36	2 -15	Octahydro-phenanthrene			159-160/12mm		1.0167	1.5620	59.38	58.85

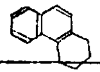
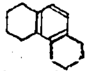
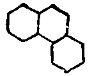
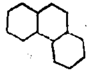
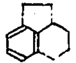
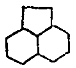
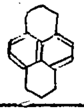
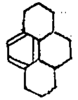
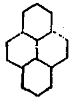
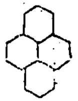
Naphthalene	100	200	91	71	67	13- 0	Tetrahydro-naphthalene		91	201.5-203.5		0.9683	1.5392	42.79	42.58
Tetrahydro-naphthalene	100	160	91	119	67	7- 0	Dodecahydro-naphthalene		97	189-191		0.8906	1.4784	43.82	43.67
Anthracene	50	200	100	32	24	3-15	Tetrahydro-anthracene				101.5-102.5				
Anthracene	50	200	99	48	48	2-15	Octahydro-anthracene				72-73				
Anthracene	100	270	98	198	167	19-15	Perhydro-anthracene Perhydro-anthracene	 	84 14	139-141/11mm	89-90	0.9383	1.4990	60.14	60.25
Phenanthrene	50	170	95	26	25	7 - 0	Tetrahydro-phenanthrene			160-162/10.9mm		1.0706	1.6260	60.12	57.92
Tetrahydro-phenanthrene	72	180	90	40	36	2 -15	Octahydro-phenanthrene			159-160/12mm		1.0167	1.5620	59.38	58.85
Tetrahydro-phenanthrene	65	210	102	81	82	8 - 0	Perhydro-phenanthrene			132-134/10.7mm		0.9502	1.5020	59.69	60.25
Octahydro-phenanthrene	15	160	77	3	9	16 -30	Perhydro-phenanthrene								-
Acenaphthene	100	270	102	62	57	3 -20	Tetrahydro-acenaphthene		96	245-247		1.0065	1.5550	50.42	49.62
Acenaphthene	100	200	94	168	142	9 - 0	Dodecahydro-acenaphthene		103	235-237		0.9462	1.5020	51.20	51.06
Pyrene	65	320	82	39	39	5 -30	Hexahydro-pyrene		100		131-132				
Hexahydro-pyrene	50	170	96	62	62	11 -15	Dodecahydro-pyrene		100	158-160/3mm		1.0497	1.5742	66.71	65.88
Decahydro-pyrene	70	240	107	40	40	40 -45	Perhydro-pyrene		20	144-148/4mm		0.9835	1.5230	67.63	67.29
							Perhydro-pyrene		71		86.8-87.8				

TABLE III(B)1
EFFECT OF RING FORM ON MOLECULAR VOLUME

	Cyclohexane	Dicyclohexyl	Perhydro-1,3-diphenyl benzene	
Empirical formula	C_6H_{12}	$C_{12}H_{22}$	$C_{18}H_{32}$	
Diff.		C_6H_{10}	C_6H_{10}	
Mol. Wt.	84	166	248	
Spec. grav (25/4)	0.7741	0.8836	0.9443	
Mol. vol (at 25°C)	109	188	263	
Diff.		79	75	
	Cyclohexane	Decahydro-naphthalene	Perhydro-anthracene	
Empirical formula	C_6H_{12}	$C_{10}H_{18}$	$C_{14}H_{24}$	
Diff.		C_4H_6	C_4H_6	
Mol. Wt.	84	138	192	
Spec. grav. (25/4)	0.7741	0.8906	0.9383	
Mol. vol. (25°C)	109	155	205	
Diff.		46	50	
		Decahydro-naphthalene	Decahydro-acenaphthene	Perhydro-pyrene
Empirical formula		$C_{10}H_{18}$	$C_{12}H_{20}$	$C_{16}H_{26}$
Diff.			C_2H_2	C_4H_6
Mol. Wt.		138	164	218
Spec. grav (25/4)		0.8906	0.9462	0.9835
Mol. vol. (25°C)		155	174	222
Diff.			19	48

ENCLOSURE (B)1

TABLE IV(B)1
EFFECT OF BENZENE RING ON MOLECULAR VOLUME

	Cyclohexane	Benzene	Dicylohexyl	Phemylcyclohexane	Perhydro-1,3-diphenylbenzene	Decahydro-1,3-diphenylbenzene		
Empirical formula	$C_6 H_{12}$	$C_6 H_6$	$C_{12} H_{22}$	$C_{12} C_{16}$	$C_{18} H_{16}$	$C_{18} H_{26}$		
Diff	H_6		H_6		H_6			
Mol. Wt.	84	78	166	160	248	242		
Spec. Grav ($^{25}/4$)	0.7741	0.8740	0.8836	0.9431	0.9443	0.9741		
Mol. Vol. (25°C)	109	89	188	170	263	249		
Diff.	20		18		14			
			Decahydro-naphthalene	Tetrahydro-naphthalene	Perhydro-phenanthrene	Octahyaro-phenanthrene		
Empirical formula			$C_{10} C_{18}$	$C_{10} C_{12}$	$C_{14} H_{24}$	$C_{14} H_{18}$		
Diff.			H_6		H_6			
Mol. Wt.			138	132	192	186		
Spec. Grav ($^{25}/4$)			0.8906	0.9683	0.9502	1.0167		
Mol Vol (25°C)			155	136	202	183		
Diff.			21		19			
					Perhydro-acenaphthene	Tetrahydro-acenaphthene	Perhydro-pyrene	Decahydro-pyrene
Empirical formula					$C_{12} H_{20}$	$C_{12} H_{14}$	$C_{16} H_{26}$	$C_{16} H_{20}$
Diff.					H_6		H_6	
Mol. Wt.					164	158	218	212
Spec. Grav. ($^{25}/4$)					0.9462	1.0065	0.9835	1.0497
Mol. Vol. (25°C)					174	157	222	202
Diff.					17		20	

ENCLOSURE (B)1

TABLE V(B)1
EFFECT OF NAPHTHALENE RING ON MOLECULAR VOLUME

		Decahydro-naphthalene	Naphthalene	Perhydro-anthracene	Tetrahydro-anthracene	Perhydro Phenanthrene	Tetrahydro-phenanthrene
Benzene solution of o.1 molar fraction	Mol wt.	84	83	90	89	90	89
	Spec. Grav.(25/4)	0.8744	0.8975	0.8856	0.9041	0.8888	0.9031
	Mol Vol.(25°C)	96	92	101	98	101	98
	Diff.	4		3		3	

		Decahydro-acenaphthene	Acenaphthene	Perhydro-pyrene	Hexahydro-pyren
Benzene solution of o.1 molar fraction	Mo. Wt.	87	86	92	insoluble
	Spec. Grav.(25/4)	0.8850	0.9129	0.8932	
	Mol. Vol.(25°C)	98	94	103	
	Diff.	4			

ENCLOSURE (B)1

TABLE VI(B)1
EFFECT OF ISOMERISATION ON MOLECULAR VOLUME

		Hexahydro-		Dodecahydro-		Perhydro	
		1,3-diphenyl-benzene	1,4-diphenyl benzene	1,3-diphenyl-benzene	1,4-diphenyl-benzene	1,3-diphenyl-benzene (liquid)	1,4-diphenyl benzene (M.P.485-495°C)
	Mol. Wt.	236	236				
	Spec. Grav(25/4)	0.9849	0.9846				
	Mol. Vol.(80°C)	240	240				
Benzene solution of o.1 molar fraction	Mol. Wt.	94	94	95	95	95	95
	Spec. Grav.(25/4)	0.9083	0.9088	0.8992	0.8959	0.8926	0.8865
	Mol. Vol.(25°C)	103	103	105	106	107	107
		Tetrahydro-		Octahydro-		Perhydro-	
		phenanthrene	anthracene	phenanthrene	anthracene	Phenanthrene	anthracene
	Mol. Wt.					192	192
	Spec. Grav (25/4)					0.9502	0.9388
	Mol. Vol.(25°C)					202	205
Benzene solution of o.1 molar fraction	Mol. Wt.	89	89	90	90	90	90
	Spec. Grav (25/4)	0.9031	0.9041	0.9053	0.9050	0.8898	0.8856
	Mol. Vol.(25°C)	98	98	98	98	101	101

ENCLOSURE (B)1

TABLE VII(B)1
EFFECT OF RING FORM ON VISCOSITY

	Cyclohexane	Dicyclohexy	Perhydro-1,3-diphenyl benzene		
Empirical formula	C_6H_{12}	$C_{12}H_{22}$	$C_{18}H_{22}$		
Mol. Wt.	84	166	248		
Diff.	82	82			
Viscosity in poise at 25°C	0.008991	0.031467	0.614263		
Vis. ratio	1	3.5	68.3		
Vis. diff.	2.5	64.8			
Vis. ratio Diff/M.W.diff.	0.03	0.83			
	Cyclohexane	Decahydro-naphthalene	Perhydro-anthracene		
Empirical formula	C_6H_{12}	$C_{10}H_{18}$	$C_{14}H_{24}$		
Mol. Wt.	84	138	192		
Diff.	54	54			
Viscosity in poise at 25°C	0.008991	0.026526	0.080397		
Vis. ratio	1	2.9	8.9		
Vis. ratio diff.	1.9	6.0			
Vis. ratio diff/M.W.diff.	0.04	0.11			
			Decahydro-naphthalene	Decahydro-acenaphthene	Perhydro-pyrene
Empirical formula			$C_{10}H_{18}$	$C_{12}H_{20}$	$C_{16}H_{26}$
Mol. Wt.			138	164	218
Diff.			26	54	
Viscosity in poise at 25°C			0.026526	0.058821	0.21215
Vis. ratio			2.9	6.2	23.6
Vis. ratio diff			3.3	17.4	
Vis. ratio diff/M.W.diff.			0.13	0.32	

TABLE VIII(B)1
EFFECT OF RING FORM ON VISCOSITY

		Cyclohexane	Dicyclohexy	Perhydro-1,3-diphenyl benzene	
Benzene solution o.1 molar	Mol. Wt.	79	87	95	
	Diff.		8	8	
	Viscosity in poise at 25°C	0.005909	0.007085	0.009388	
	Vis. ratio	1	1.2	1.59	
	Diff.		0.2	0.39	
	Vis. ratio diff/M.W.diff.		0.025	0.049	
		Cyclohexane	Decahydro-naphthalene	Perhydro-anthracene	
Benzene solution o.1 molar	Mol. Wt.	7.9	84	90	
	Diff.		5	6	
	Viscosity in poise at 25°C	0.005909	0.006738	0.07722	
	Vis. ratio	1	1.14	1.32	
	Diff.		0.14	0.18	
	Vis. ratio diff./M.W.diff.		0.032	0.03	
			Decahydro-naphthalene	Decahydro-acenaphthene	Perhydro-pyrene
Benzene solution o.1 molar	Mol. Wt.		84	87	92
	Diff.			3	5
	Viscosity in poise at 25°C		0.006738	0.007268	0.008075
	Vis. ratio		1.14	1.23	1.37
	Diff.			0.09	0.14
	Vis. ratio diff./M.W.diff			0.03	0.028

ENCLOSURE (B)1

TABLE IX(B)1
EFFECT OF BENZENE RING ON VISCOSITY

	Cyclohexane	Benzene	Dicyclohexyl	Phenyl-cyclohexane	Perhydro-1,3-diphenyl benzene	Dodecahydro-1,3-diphenyl benzene		
Empirical formula	C_6H_{12}	C_6H_6	$C_{12}H_{22}$	$C_{12}H_{16}$	$C_{18}H_{32}$	$C_{18}H_{26}$		
Mol. Wt.	84	78	166	160	248	242		
Diff.	6		6		6			
Viscosity in poise at 25°C	0.008991	0.006096	0.031467	0.025713	0.614263	0.319378		
Vis. ratio	1	0.7	1	0.8	1	0.5		
Diff.	-0.3		-0.2		-0.5			
			Decahydro-naphthalene	Tetrahydro-naphthalene	Perhydro-phenanthrene	Octahydro-phenanthrene		
Empirical formula			$C_{10}H_{18}$	$C_{10}C_{12}$	$C_{14}H_{24}$	$C_{14}H_{18}$		
Mol. Wt.			138	132	192	186		
Diff.			6		6			
Viscosity in poise at 25°C			0.026526	0.020215	0.076323	0.12511		
Vis. ratio			1	0.8	1	1.6		
Diff.			-2		+0.6			
					Decahydro-acenaphthene	Tetrahydro-acenaphthene	Perhydro pyrene	Decahydro-pyrene
Empirical formula					$C_{12}H_{20}$	$C_{12}H_{14}$	$C_{16}H_{26}$	$C_{16}H_{20}$
Mol. Wt.					162	158	218	212
Diff.					6		6	
Viscosity in poise					0.058821	0.059731	0.21215	0.54961
Vis ratio					1	1.0	1	2.6
Diff.					+0.0		+1.6	

ENCLOSURE (B)1

TABLE X(B)1
EFFECT OF BENZENE RING ON VISCOSITY

	Cyclohexane	Benzene	Dicyclohexyl	Phenyl-cyclohexane	Perhydro-1,3-diphenyl-benzene	Dodecahydro-1,3-diphenyl-benzene	Perhydro-1,4-diphenyl-benzene	Dodecahydro-1,4-diphenyl-benzene
Viscosity of o.1 mol. benzene solution in poise at 25°C	0.005909	0.006096	0.007085	0.007204	0.009388	0.009414	0.009485	0.009656
Vis. ratio	1	1.03	1	1.02	1	1.00	1	1.02
			Dodecahydro-naphthalene	Tetrahydro-naphthalene	Perhydro-phenanthrene	Octahydro-phenanthrene	Perhydro-anthracene	Octahydro-anthracene
Viscosity of o.1 mol. benzene solution in poise at 25°C			0.006738	0.006894	0.007665	0.008047	0.007792	0.008070
Vis. ratio			1	1.02	1	1.05	1	1.05
					Decahydro-acenaphthene	Tetrahydro-acenaphthene	Perhydro pyrene	Decahydro-pyrene
Viscosity of o.1 mol. benzene solution in poise at 25°C					0.007268	0.007517	0.008073	0.008696
Vis. ratio					1	1.03	1	1.08

ENCLOSURE (B)1

TABLE XI(B)1
EFFECT OF NAPHTHALENE RING ON VISCOSITY

	Dodecahydro-naphthalene	Naphthalene	Perhydro-anthracene	Tetrahydro-anthracene	Perhydro-phenanthrene	Tetrahydro-phenanthrene		
Viscosity of o.1 mol. benzene solution in poise at 25°C	0.006738	0.007105	0.007722	0.008191	0.007665	0.008159		
Vis. ratio	1	1.05	1	1.06	1	1.06		
					Decahydro acenaphthene	Acenaphthene	Perhydro-pyrene	Hexahydro-pyrene
Viscosity of o.1 mol. benzene solution in poise at 25°C					0.007268	0.007756	0.008073	insoluble
Vis.ratio					1	1.07		

TABLE XII(B)1
EFFECT ON ISOMERISATION ON VISCOSITY

	Hexahydro-		Dodecahydro-		Perhydro-	
	1,3-diphenyl benzene	1,4-diphenyl benzene	1,3-diphenyl benzene	1,4-diphenyl benzene	1,3-diphenyl benzene (liquid)	1,4-diphenyl benzene (M.P.485-49.5°C)
Viscosity in poise at 80°C	0.043384	0.048899			0.057706	0.067687
Vis. ratio	1	1.13			1	1.17
Viscosity of o.1 mol. benzene solution in poise at 25°C	0.009603	0.009975	0.009414	0.009656	0.009388	0.009485
Vis. ratio	1	1.04	1	1.03	1	1.01
	Tetrahydro-		Octahydro-		Perhydro-	
	phenanthrene	anthracene	phenanthrene	anthracene	phenanthrene	anthracene
Viscosity in poise at 25°C					0.076323	0.086397
Vis. ratio					1	1.05
Viscosity of o.1 mol. benzene solution in poise at 25°C	0.008159	0.008192	0.008047	0.008070	0.007665	0.007722
Vis. ratio	1	1.00	1	1.01	1	1.01

ENCLOSURE (B) 2

STUDIES ON SYNTHESIS OF AERO-ENGINE OIL BY CONDENSATION METHOD

by

CHEM. ENG. CAPT. DR. I. KAGEHIRA
LIEUT. COMDR. A. WAKANA

Research Period: 1938-1940

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)2

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)2

SUMMARY

Dibenzyl-diphenylmethane was prepared by the condensation of benzene and benzyl alcohol in the presence of aluminium chloride at 60-80°C for five hours. The hydrogenated product had a viscosity index of -139, viscosity of 118 S.U.S. at 210°F, and a Conradson's carbon residue of 0.002%.

Diphenylmethane series hydrocarbons, prepared by the condensation of benzyl alcohol and benzene in the presence of $AlCl_3$ were condensed with cetene and then hydrogenated. The product thus obtained had a viscosity index of more than 100, Conradson's carbon of 0.1%, and freezing point below-20°C, but the oxidation stability as indicated by the viscosity ratio of 2.2 in the British Air Ministry Oxidation Test was not good. This defect was easily remedied by adding 0.1% of copper-oleate, which reduced the viscosity ratio from 2.2 to 1.4.

An aeroengine oil of similar nature was also obtained by reduction of the condensation products of olefines with diphenyl-methane series hydrocarbons which were formed by the interaction of benzene and formalin in the presence of concentrated sulphuric acid.

I. INTRODUCTION

Although extensive chemical studies on lubricating oils derived from the petroleum oils have been carried out, practically nothing is known concerning the relation between chemical structure and the viscosity and other properties of cyclic compounds. The authors, therefore, from 1927 to 1942, have undertaken the present study relative to the relation of chemical structures of cyclic compounds to lubricating properties.

II. DETAILED DESCRIPTION

Prior to this study, one of the authors, I. KAGEHIRA*, derived an idea from the systematic investigation of the relation between the molecular structure and the chemical and physical properties of hydroaromatic compounds, that a molecule in which cyclohexane rings combine by single bonds in the para position, such as perhydro-1, 4-diphenyl benzene, (C_6H_{11}-C_6H_{10}-C_6H_{11}), should have good lubricating qualities. Table I(B)2 shows the data for this series of hydrocarbons.

If this idea is extended to dicyclohexyl, its viscosity would be assumed to be of the order of 20-30 poises at 25°C. (See Table I(B)2).

Therefore, compounds of the diphenylmethane series, $C_6H_{11}(CH_2)$-C_6H_{11}, have been synthesized by the method of Huston and Friedmann** as follows:

4.5kg of benzyl alcohol were added drop by drop to a benzene solution (18kg) of $AlCl_3$ (0.614kg) while agitating for 15 hours at 30°C. The reaction products were obtained by distilling off the solvent, and fractionating. For each frac-

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* I. KAGEHIRA, the report of Imperial Naval Fuel Depot, No.128 June, 1938. (Reference Nav Tech Jap Document No. ND26-0007-77)
** R. C. Huston and T. E. Friedmann, J. Amer. Chem. Sec., 38, 1916, 2527.

tion the properties were determined and are shown in Table II(B)2. From these it ~~was~~ considered that fraction 1 was composed mostly of benzene, fraction 2 was diphenyl methane, fraction 3 was dibenzylbenzene, and fraction 4 was dibenzyldiphenylmethane. These fractions were hydrogenated under high pressure of hydrogen at 200°C in the presence of reduced nickel, and the properties of the reduced compounds were determined and are given in Table III(B)2. Tetracosahydro-dibenzyldiphenylmethane was observed to have a viscosity comparable with commercial aircraft lubricating oils and to have a very low Conradson's carbon, although its viscosity index was extremely poor. Also, a large increase in viscosity and decrease in viscosity index was obtained when dibenzyldiphenylmethane was completely hydrogenated.

It has been observed that the diphenylmethane series of hydrocarbons can be prepared by the condensation of benzene and formalin in the presence of concentrated sulphuric acid.***

It is a generally known fact that the change of viscosity with temperature of paraffin hydrocarbons is the lowest of all types of hydrocarbons, and therefore, a cyclic compound which has a long paraffinic side chain might be expected to be of adequate viscosity and less susceptible to change of the viscosity with temperature. In this connection, L. A. Mikeska**** has synthesized various high viscosity index compounds by reduction of the condensation products of aromatic hydrocarbons and fatty acids.

Based on these facts, the authors prepared the hexadecyl derivative of dicyclohexyl methane, $C_6H_{11}(CH_2)C_6H_{10}-C_{16}H_{33}$. The results are shown in Table IV(B)2. One mol. of cetylchloride was condensed at 50°C, in the presence of 5% aluminium chloride, with one mol. each of diphenylmethane, dibenzylbenzene or dibenzyldiphenylmethane and the products were hydrogenated at 200°C in the presence of reduced nickel under high pressure hydrogen and then purified by fractionation.

The crude reaction products, as will be seen in Table IV(B)2, show viscosities at 210°F of 49, 74 and 77 S.U.S., viscosity indices of 136, 109 and 108, and Conradson's carbon values of 0.04, 0.14 and 0.21, respectively. The substances, purified by distillation, which correspond to the hexadecyl derivatives, dodecahydrodiphenylmethane, octadecahydro dibenzylbenzene and tetracosahydrodibenzyldiphenylmethane, have S.U.S. viscosities of 97, 197 and 260., viscosity indices of 98, 90 and 86, and Conradson's carbon values of 0.05, 0.20, 0.39, respectively.

Instead of cetylchloride, one or two moles of cetene were used for the condensation, and the reaction products which were obtained in a similar manner as in the above case, showed almost the same results. These results are shown in Table V(B)2.

The synthetic compounds prepared as mentioned above did not have good stability as measured by the viscosity ratio of the British Air Ministry Oxidation Test (Table V(B)2). This defect was easily improved by adding 0.1% of copper oleate, which decreased the viscosity ratio from 2.2 to 1.4 (Table V(B)2).

III. CONCLUSIONS

Some homologous series of dicyclohexyl, dicyclo hexylmethane and hexadecyl dicyclohexylmethane were synthesized and their chemical and physical properties were studied in comparison with those of the natural lubricating oils derived

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*** C. Ellis, the Chemistry of Synthetic Resins, Vol. 1, p. 263.
**** L. A. Mikeska, J. Ind. Eng. Chem., 28 (1936) 970.

ENCLOSURE (B)2

from petroleum.

Since the synthetic compounds are superior in chemical stability and viscosity index, they may be used in a proper way in an automobile and aero engine which require a lubricating oil of constant viscosity with varying temperature and of high stability for oxidation.

Table I(B)2
VISCOSITY RATIOS

	Cyclohexane	Dicyclohexyl	Perhydro-1. Diphenylbenzene
Experimental Formula	C_6H_{12}	$C_{12}H_{22}$	$C_{18}H_{22}$
M.W.	84	166	248
Viscosity in Poises at 25°C	0.008991	0.031467	0.614263
Ratio of Viscosity to C_6H_{12}	1	3.5	68.3
Vis. Ratio Diff.	2.5	64.8	

Table II(B)2
CONDENSATION PRODUCTS

Fraction	Yield (gm)	Properties of Fractions			
		d_4^{25}	n_D^{25}	Mol. Refr.	
				Found	Calc.
1 -200°C	14.520	0.8756	1.5023	26.32	26.31
2 -170°C/5mm	4.007	1.0042	1.5763	55.42	55.03
3 170-250°C/5mm	1.185	1.0467	1.6024	84.64	83.76
4 250-290°C/5mm	353	1.0683	1.6170	114.04	112.48
5 Residue	185				

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Table III(B)2
HYDROGENATION PRODUCTS

Compound	B.P.	d_4^{25}	n_D^{25}	M.R.		Viscosity in Poises	Viscosity in S.U.S.		Viscosity Index	Conradson's Carbon
				Found	Calc.	at 25°C	100°F	210°F		
Dodecahydrodiphenyl-methane	224-244.5°C/745mm	0.8723	1.4747	58.07	57.83	0.04914	-	-	-	-
Octadecahydrodibenzyl benzene	169-173/2.2 mm	0.9127	1.4940	88.19	87.96	0.9499	-	-	-	-
Tetracosahydrodibenzyl diphenylmethane	240-280°C/5mm	0.9492	1.5206	119.38	118.09	-	6773	117.8	-139	0.002

Table IV(B)2
LUBRICATING OIL SYNTHESIZED FROM DIPHENYLMETHANE SERIES HYDROCARBONS AND CETYLCHLORIDE

	Raw Materials and Reaction Products	Yield Theo. (%)	Boiling Pt. (°C)	M. Pt. (°C)	Density d_4^{25}	n_D^{25}	Viscosity in S.U.S.		Viscosity Index	Conradson's Carbon (%)	Four Pt. (°C)
							at 100°F	at 210°F			
1	Cesylchloride	-	165~169°C/5mm	-	0.8596	1.4479	-	-	-	-	-
2	Diphenylmethane	-	110	26	1.0010	1.5752	-	-	-	-	-
3	p-Dibenzylbenzene	-	214	84~86	-	-	-	-	-	-	-
4	Dibenzylbenzenemethane	-	<70~272	-	1.0691	1.6203	263	47.6	62	-	-
5	Condensation product of 1 and 2	90	-	-	0.8928	1.5085	122.4	44.3	154	3.8	-16
6	Condensation product of 1 and 3	81	-	-	0.9214	1.5260	210.3	52.6	141	5.75	-18
7	Condensation product of 1 and 4	75	-	-	0.9298	1.5290	203.5	51.0	137	7.35	-21
8	Completely hydrogenated product of 5	100	-	-	0.8612	1.4770	188.5	49.2	136	0.04	-16
9	Completely hydrogenated product of 6	100	-	-	0.8787	1.4862	616.0	74.0	109	0.14	-20
10	Completely hydrogenated product of 7	100	-	-	0.8777	1.4815	671.3	77.0	108	0.21	-26
11	The fraction over 230°C/5mm of 8	54	230	-	0.8861	1.4901	1160.0	97.0	98	0.05	-10
12	The fraction over 230°C/5mm of 9	71	230	-	0.8966	1.4957	4228.5	197.4	90	0.20	-5
13	The fraction over 230°C/5mm of 10	67	230	-	0.8950	1.4900	72000	260	86	0.39	-5

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Table V(B)2
LUBRICATING OIL SYNTHESIZED FROM DIPHENYLMETHANE SERIES HYDROCARBONS AND CETENE

	Raw Materials and Reaction Products	Yield Theo. (%)	B.P. (°C)	M.P. (°C)	d_4^{25}	n_D^{25}	Viscosity in S.U.S.		Viscosity Index	Conradson's Carbon (%)	Pour Pt, (°C)	After the British Air Ministry Oxidation Test		
							100°F	210°F				Vis. Ratio	Conradson's Carbon	Acid Value
1	Cetene	-	280-283°C/755mm	-	0.7785	1.4407	-	-			-11			
2	Diphenylmethane	-	100°C/5mm	26	1.0010	1.5752								
3	Dibenzylbenzene	-	214°C/5mm	84-86	-	-								
4	Condensation product of one mol.of (1) & one mol.of (2)	81	-	-	0.8955	1.5055	125	45.6	162	-	10			
5	Condensation product of two mol.of (1) & one mol.of (2)	97.6	-	-	0.8750	1.4941	307.9	60.8	136	091	+3			
6	Condensation product of two mol.of (1) & one mol.of (3)	90.3	-	-	0.9096	1.5150	475.4	71.7	125	-	-4			
7	The fraction of over 230°C 5mm of (5)	51.7	230°C/5mm	-	0.9070	1.5122	380.9	62.0	120	-	-5			
8	The fraction of over 230°C 5mm of (6)	86.1	230°C/5mm	-	0.8788	1.4944	486.6	74.0	128	1.04	+4			
9	The fraction of over 230°C 5mm of (7)	79.2	230°C/5mm	-	0.9044	1.5113	813.3	91.2	117	-	-4			
10	Completely hydrogenated product of (5)	82.7	-	-	0.8651	1.4808	754.5	90.6	121	0.13	+4			
11	Completely hydrogenated product of (6)	75.9	-	-	0.8750	1.4872	1756.4	136.6	108	0.11	-4	2.2	0.7	2.6
12	(11)+0.5% wt. Copper oleate											1.40	0.6	1.3
13	(11)+0.1% wt. Copper oleate											1.44		
14	(11)+0.05% wt Copper oleate											1.88		
15	(11)+0.5% wt. Chrome oleate											2.10		
16	(11)+0.5% wt. Iron oleate											2.56		
17	(11)+0.5% wt. Tin oleate											3.00		
18	(11)+0.5% wt. Triphenylphosphate											2.0		

ENCLOSURE (B) 3

STUDIES ON THE PREPARATION OF AEROENGINE OILS FROM SHALE OIL

by

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Research Period: 1937-1943

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Prepared for and Reviewed with Authors by
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December 1945

ENCLOSURE (B)3

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)3

SUMMARY

Studies were conducted on the synthesis of a superior aero-engine oil from a kerosene or gas oil fraction of shale oil. Investigations were made especially on the pre-refining method of oil, also on the optimum conditions of polymerization of pre-refined oil and the method of recovering $AlCl_3$ from its sludge. Results obtained were as follows:

1. A kerosene or gas oil fraction contains about 20-30% of basic, acidic and highly unsaturated compounds and it is necessary to remove these compounds before the polymerization to synthesize an aero-engine oil. It was found that the best results were obtained by pre-refining of the raw material with HCl gas and NaOH solution and polymerization of the pre-refined oil. By this method, about 10% of a superior aero-engine oil from a kerosene or gas oil fraction of shale oil was obtained.

   The optimum conditions for each procedure are given in Figure 1(B)3.

2. Basic, acidic and highly unsaturated compounds were almost completely removed by treating with NaOH solution and concentrated sulphuric acid. It was difficult to prepare an excellent aero-engine oil by this pre-refining method, but it is suitable for the synthesis of a mobile oil. Actually, these studies were utilized in the preparation of aero-torpedo-engine oil. The optimum conditions of each procedure are shown in Figure 2(B)3.

3. The recovery of aluminium chloride from its sludge was accomplished by distilling off oil from the sludge at 390°C, coking the distillation residue at 500-600°C for 1-3 hours and, finally, the chlorination of the cokes at 800°C. The theoretical yield of aluminium chloride recovered was about 80% and its activity was almost the same as that of $AlCl_3$ obtained from the market.

I. INTRODUCTION

A. History

Shale oil was one of the important raw materials for preparing aero-engine oils in Japan, but it contains about 20-30% of acidic, basic and highly unsaturated compounds. These compounds must be removed before its polymerization to prepare aero-engine oils from shale oil. The authors studied especially the preliminary purification of higher fractions of shale oil with HCl gas and caustic soda solution or caustic soda solution and sulphuric acid, and also the optimum conditions of polymerization of pre-refined oil and the recovery of $AlCl_3$ from its sludge.

B. Key Research Personnel

Chem. Eng. Lt. Comdr. N. IIMURE
Chem. Eng. Lieut. M. MAEDA

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II. DETAILED DESCRIPTION

A. Raw Materials

The kerosene and gas oil fraction of shale oil, used as the raw materials for this research project, were obtained from FUSHUN in South Manchuria, and were prepared as described in Figure 3(B)3. Their properties are shown in Table I(B)3.

B. Procedures and Results

Studies were carried especially on the pre-refining method of acidic, basic and highly unsaturated compounds contained in the raw materials, and also on the optimum conditions of polymerization of pre-refined oil and the recovering of $AlCl_3$ from its sludge. The procedures and the results are described as follows:

1. Pre-refining Raw Materials

a. Hydrochloric Acid Caustic Soda Method. Hydrochloric acid reacts with highly unsaturated and basic compounds and changes them to oil-insoluble matter, except in the case of mono-olefines or aromatics. Caustic soda reacts with acidic compounds, forming a soap. Utilizing these behaviors, hydrochloric acid gas and caustic soda were used as the pre-refining agents. Results obtained were as follows:

(1) Hydrochloric Acid Gas Treatment. A gas oil fraction of shale oil was treated with various amounts of hydrochloric acid gas by introducing it into the oil, at 34-45°C and then separating the oil part and the sludge. The hydrochloric acid absorbed in the oil was determined by the increase in weight of oil. The results obtained are given in Table II(B)3.

From these results it was observed that the greater part of acidic and basic compounds and all asphaltic compounds were removed by 2% of HCl gas absorbed.

When the gas oil fraction was treated with the separated sludge before the HCl gas treatment, the removal of basic compound was completely accomplished by 3% of HCl gas as shown in Table III(B)3.

(2) Alkali-Treatment. All the basic and asphaltic compounds and most of the acidic compounds in the gas oil fraction could be removed as sludge by pre-treatment with hydrochloric acid sludge and 3% of hydrochloric acid gas, but 1 - 2% of the acidic compounds still remained.

To remove the residual acidic compounds, a gas oil fraction treated with 3% of HCl gas, was washed at various temperatures with 20% NaOH solution. Results obtained are shown in Table IV(B)3.

These results showed that the higher the temperature and the amount of NaOH solution, the lower the content of acidic compounds in the treated oil. Next, the effect of the amount of 20% NaOH solution on the content of acidic compounds of treated gas oil was examined, and the following results were obtained (See Table V(B)3).

From the results in Table IV(B)3 and V(B)3, it appears that the acidic compounds in a gas oil could be almost completely removed by treating with 50% of 20% NaOH solution at 80°C. Properties of the refined kerosene and gas oil obtained by the above mentioned method are shown in Table VI (B)3.

b. <u>Caustic Soda - Sulphuric Acid Method</u>. By treating with concentrated caustic soda solution at comparatively high temperature, the acidic compounds are converted to soap, and the unstable nitrogen compounds and highly unsaturated compounds polymerize to higher molecules. If the product obtained by the alkali treatment is washed with hot water to remove the remaining free alkali and treated with sulphuric acid, the unstable nitrogen and highly unsaturated compounds should be almost completely removed. Working on this assumption, the authors studied the optimum conditions of alkali and sulphuric acid treatment.

A gas oil fraction of shale oil was used as the raw materials and the degree of the removal of acidic, basic and highly unsaturated compounds was judged by the ease of separation of sludge and the yield and specific gravity of the refined product. The results obtained were as follows:

(1) <u>Necessary Amount of Caustic Soda Solution</u>. A gas oil was washed with various amounts of 10% NaOH solution at 80°C for 20 minutes and allowed to stand for 20 minutes. The separated oil was washed with an equal volume of hot water and filtered with 3% of $CaCl_2$.

Results obtained are given in the Table VII (B)3.

From these results it was observed that 15% - 20% of 10% NaOH solution was required in the treatment of a gas oil.

(2) <u>Effect of Temperature on the Alkali-Treatment</u>. A gas oil was treated with 15% by weight of 10% NaOH solution at various temperatures. Results are given in the Table VIII (B)3 and it was observed that the suitable treating temperature was about 60°C.

(3) <u>Necessary Amount of Concentrated H_2SO_4</u>. A gas oil treated with 15% by weight of 10% NaOH solution and washed with an equal volume of hot water three times, was used as a sample. The sample was treated with various amounts of 98% H_2SO_4 at temper tures below 45°C for 10 minutes with vigorous agitation and allowed to stand for 30 minutes. The separated oil was filtered with 5% of acid clay and distilled in vacuum to cut a gas oil fraction (boiling from first drop to 300°C, the calculated temperature at 760 mmHg).

Results obtained are given in the Table IX (B)3 and it was observed that the necessary amount of H_2SO_4 to be used was 6%.

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2. Polymerization of Pre-refined Oil.

a. Polymerization of the pre-refined oil obtained by treatment with HCl gas and NaOH.

Studies were carried out on the effect of temperature and time in the polymerization process on the properties of the final product. The raw material used was prepared by treating a gas oil fraction with hydrochloric acid sludge, 2% of HCl gas and 50% of 20% NaOH solution and distilling up to 300°C. Procedures taken for this study were as follows:

The pre-refined gas oil was subjected to polymerization in the presence of $AlCl_3$ and after standing for 24 hours, the sludge was separated. The polymerized product was treated with 5% of acid clay, 10% NaOH solution and hot water, and distilled in vacuum. Three cuts were obtained; the diesel oil fraction (up to 350°C at 760mm Hg), the light lubricating oil fraction (350 - 450°C at 760mm Hg) and the aero-engine oil fraction (450°C over at 760mm Hg). Results obtained are as follows:

(1) The effects of the polymerization temperature on the yield of an aero-engine oil fraction are given in the Table X(B)3. It was observed that the polymerization proceeded incompletely at lower temperatures and that cracking partially occurred at higher temperature. The optimum temperature for polymerization was 80 - 100°C from the view point of the yield of aero-engine oil.

(2) The effect of reaction time on the polymerization is shown in Table XI(B)3 and it was observed that the longer the reaction time, the higher the yield but the lower the viscosity index of aero-engine oil fraction. From the view point of viscosity index of product, the suitable reaction time should be 10 hours.

(3) The amount of catalyst ($AlCl_3$) used should be the most important factor in the polymerization. Hence, the raw material was subjected to polymerization in the presence of various amounts of $AlCl_3$ at 80°C for 10 hours and the properties of the products and its aero-engine oil fraction was examined in detail. Results obtained were tabulated in Table XII(B)3. From these results, it was observed that a superior aero-engine oil was prepared by polymerization in the presence of 10% or more of $AlCl_3$.

b. Polymerization of Pre-refined Oil Prepared by Treatment With Caustic Soda Solution and Sulphuric Acid.

Raw material used for the polymerization was prepared from the gas oil fraction by treating with 20% by weight of 10% NaOH solution and 6% of 98% H_2SO_4 and distilling to 300°C. The raw material was polymerized by the same procedure as described in the section (b) - (1). Results obtained are given below.

Yield for Product of Polymerization (wt%)	10.3
Properties	
Density (15/4)	0.9041
Viscosity in S.U.S. at 210°F	111.9
Viscosity Index	77

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Pour Point	-19.5
Conradson's Carbon (%)	0.49

Comparing with the results shown in Tables XII(B)3, it was concluded that the hydrochloric acid gas - caustic soda method was a better pre-refining process than the caustic soda-sulphuric acid method from the view point of preparing an aero-engine oil in high yield and with superior properties.

C. Recovery of $AlCl_3$ from its Sludge

Aluminium chloride sludge separated with a yield of about 20% by weight in the polymerization stage. It consisted of 5% aluminium, 17.5% chlorine and 72.6% oil. Its mean molecular weight was 296, and the composition of sludge could be indicated as 2.88 parts $AlCl_3$ and 1.51 parts oil. From an economical point of view, the recovery of $AlCl_3$ from the sludge is an important problem. The authors, therefore, adopted a method, consisting of the distillation of the oil, coking the distillation residue and chlorinating the cokes. The optimum conditions of each procedure were studied and also the activity of recovered $AlCl_3$ as the polymerization catalyst. Results obtained were as follows:

1. Distillation of Aluminium Chloride Sludge. An aluminium chloride sludge was distilled in a three-necked flask at 375°C - 390°C. Results obtained are tabulated in Table XIII(B)3.

2. Coking of Residue. The residue obtained by the distillation of aluminium chloride sludge was subjected to coking in a porcelain tube at 500°C - 800°C by electrical heating. Results obtained are shown in Table XIV(B)3 and it was observed that coking the residue prepared by the distillation of aluminium chloride sludge should be carried out at 500°C - 600°C for 1 - 3 hours, from the point of view of higher yield of cokes and larger content of chlorine in the cokes.

3. Chlorination of Cokes. Cokes were subjected to chlorination in a porcelain tube electrically heated at 600 - 800°C by treating with chlorine gas. The results obtained are shown in Table XV(B)3. It was observed that the higher the chlorination temperature the larger the yield of recovered $AlCl_3$.

4. Activity of Recovered Aluminium Chloride as the Polymerization Catalyst. The activity of recovered aluminium chloride was determined by comparing the iodine values of the polymerized products of pre-refined gas oil fractions when recovered $AlCl_3$ and when commercial grade $AlCl_3$ was used.

The results obtained are shown below. From these results, it may be concluded that the activity of recovered $AlCl_3$ is a little less than that of the commercial material but that it may be compensated by using a little more catalyst.

Yield of Pre-refined Oil for Gas Oil (wt%)	71.0
Properties of Pre-refined Oil	
Density (15/4)	0.8251
Iodine Value	57.0

$AlCl_3$ Used for Polymerization	Iodine Value of Polymerized Products
5% of commericial catalyst	28.0
5% of recovered catalyst	42.7
7% of recovered catalyst	25.0

III. CONCLUSIONS

The kerosene or gas oil fraction in shale oil contains about 20 - 30% of basic, acidic and highly unsaturated compounds and these must be removed before polymerizing for the preparation of an aero-engine oil. Hence, studies were conducted pertaining to the pre-refining method and it was found that a method consisting of treating with hydrochloric acid gas and concentrated caustic soda solution was the best as the pre-refining method for the preparation of an aero-engine oil and a method consisting of treating with caustic soda solution and concentrated sulphuric acid was suitable for the preparation of a mobile oil or a generally used lubricating oil. Actually, these studies were utilized in the preparation of the aero-torpedo engine oil from shale gas oil.

The scheme of these procedures is given in Figures 1(B)3 and 2(B)3.

Table I(B)3
PROPERTIES OF THE KEROSENE AND GAS OIL FRACTIONS OF SHALE OIL

		Kerosene Fraction	Gas Oil Fraction
Properties	Boiling Point (°C)	180 - 250	200 - 300
	Density (15/4)	0.8217	0.8607
	Flash Point (°C)	60.5	73.0
	Pour Point (°C)	-28.5	-13.0
	Iodine Value	90.6	63.1
Composition of Fraction	Acidic Compound (%)	3.4	8.8
	Basic Compound (%)	2.8	4.6
	Neutral Oil (%)	93.8	86.6
Composition of Neutral Oil	Unsaturates (%)	27.6	
	Aromatics (%)	13.8	
	Naphthenes (%)	0.0	
	Paraffines (%)	58.6	

Table II(B)3
ANALYSIS OF HYDROGEN CHLORIDE TREATED PRODUCT OF GAS OIL FRACTION

Composition of Oil Separated (wt %)	HCl Gas Absorbed in the Oil (wt %)							
	0	0.5	0.75	1.0	1.5	2.0	3.0	5.4
Acidic Compound	7.32	3.77	3.17	5.64	1.10	1.32	1.78	0.52
Basic Compound	6.53	5.83	4.37	5.79	1.66	0.51	0.78	0.60
Asphaltic Compound	14.85	3.48	3.27	1.53	0.10	0	0	0
Neutral Oil	71.30	86.92	89.19	87.04	97.14	98.17	98.44	98.80

Table III(B)3
ANALYSIS OF PRODUCT OF GAS OIL FRACTION TREATED WITH HYDROCHLORIC ACID SLUDGE BEFORE HYDROCHLORIC ACID TREATMENT

	HCl Gas Absorbed in the Oil (wt %)				
	1	2	3	4	5
Oil Separated (wt %)	82.9	85.3	82.9	85.8	85.9
Composition of Oil Separated (wt %)					
Acidic Compound	1.62	1.22	0.59	0.26	
Basic Compound	0.36	0.15	0	0	
Neutral Oil	98.12	98.63	99.41	99.74	

Table IV(B)3
EFFECT OF TREATMENT WITH 20% NaOH SOLUTION ON THE CONTENT OF ACIDIC COMPOUNDS IN GAS OIL AT VARIOUS TEMPERATURES

	Amount of 20% NaOH Solution (%)			
		5	10	15
Content of Acidic Compounds in the Treated Oil	at 30°C	1.56	0.70	0.84
	at 50°C	1.92	0.76	0.80
	at 80°C	1.44	0.64	0.50

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Table V(B)3
EFFECT OF 20% NaOH SOLUTION ON THE CONTENT OF ACIDIC COMPOUND IN GAS OIL FRACTION*

	Amount of 20% NaOH Solution		
	30	50	100
Yield of Treated Oil (wt % for HCl Treated Oil)	86.7	84.5	83.3
Content of Acidic Compounds in the Treated Oil	0.32	0.32	0.12
Content of Basic Compounds in the Treated Oil	0.36	0.28	0.12

*Temperature of treating. 80°C

Table VI(B)3
PROPERTIES OF REFINED KEROSENE AND GAS OIL FRACTION AFTER TREATMENT WITH 3% HCl GAS AND 50% OF 20% NaOH SOLUTION AT 80°C

	Kerosene		Gas Oil	
	Raw Material	Refined Oil	Raw Material	Refined Oil
Density (15/4)	0.8217	0.8136	0.8607	0.8308
Pour Point (°C)	-28.5	-28.0	-13.0	-11.0
Conradson's Carbon (wt %)	0.19	0.07	0.83	0.12
Content of Acidic Compounds (wt %)	2.8	0.48	8.8	0.4
Content of Basic Compounds	3.4	0.40	4.8	0.4

Table VII(B)3
EFFECT OF AMOUNT OF NaOH SOLUTION IN TREATING SHALE GAS OIL

-	Amount of 10% NaOH Solution used (wt %)				
	5	10	15	20	25
Refined Oil Yield (wt %)	95.0	92.5	91.0	92.0	91.5
Density (15/4)	0.8490	0.8471	0.8459	0.8453	0.8457
Separation of Oil	*	easy	easy	easy	easy

*A small amount of tarry matter remained in the oil.

ENCLOSURE (B)3

Table VIII(B)3
EFFECT OF TEMPERATURE ON ALKALI TREATMENT

	Treating Temp.(°C)				
	20	35	45	60	80
Refined Oil Yield (wt %)	91.0	91.5	90.5	92.5	91.5
Density (15/4)	0.8447	0.8452	0.8450	0.8468	0.8459
Separation of Oil	**	*	*	easy	easy

*Soft tarry matter separated.
**Hard tarry matter separated.

(See page 72 for Table IX(B)3.)

Table X(B)3
EFFECT OF TEMPERATURE ON POLYMERIZATION*

	Product of Polymerization		Aero-Engine Oil Fraction	
Reaction Temp. °C	Mean M.W.	Iodine Value	Yield (wt %)	Mean M.W.
50	275	42.9	12.4	731
80	281	33.5	20.2	720
100	282	22.7	18.2	623
130	258	23.5	9.6	640

Note: In each case, reaction time, eight hours, and 5% $AlCl_3$ (wt) were used.

Table IX(B)3
EFFECT OF AMOUNT OF 98% H_2SO_4 IN TREATING SHALE GAS OIL

98% H_2SO_4 Used (wt %)	Treating Temperature (°C)	Separation of Sludge and Oil	Property of Sludge	Yield of Product for Raw Material (wt %)	Filtered Product			Fract. Boiling from 1st Drop to 300°C of Filt. Prod.		
					Yield for Raw Material (%)	Density (15/4°C)	Iodine Value	Density (15/4)	Iodine Value	Yield of Filtered Product (wt %)
2	24	easy	hard	96.0	92.0	0.8380	61.7	0.8353	61.2	85.0
4	37.5	easy	hard	89.7	80.7	0.8290	63.1	0.8257	62.1	85.2
6	39.0	easy	soft	82.0	77.4	0.8280	62.0	0.8251	61.1	84.7
8	41.0	easy	soft	88.7	83.3	0.8252	61.8	0.8231	64.1	85.1
10	43.0	easy	soft	89.4	82.7	0.8250	60.1	0.8254	61.7	85.3

Table XI(B)3
EFFECT OF REACTION TIME ON POLYMERIZATION*

Reaction Time (hr)	Product of Polymerization		Fraction of Product										
			Diesel Oil Fraction (~350°C)	Light Lubricating Oil Fraction (350~450°C)					Aero-Engine Oil Fraction (450°C~)				
	Yield (wt %)	Iodine Value	Yield (wt %)	Yield (wt %)	Density (15/4)	Viscosity in S.U.S. at 210°F	Viscosity Index	Pour Point (°C)	Yield (wt %)	Density (15/4)	Viscosity in S.U.S. at 210°F	Viscosity Index	Pour Point (°C)
10	87.3	23.2	57.4	22.6	0.8892	43.4	76	-45	14.6	0.9032	126.6	81	-26
20	86.1	11.7	59.6	21.3	0.8885	43.1	64	-49	17.7	0.9053	127.4	79	-27
30	86.1	14.9	60.0	18.3	0.8897	42.0	55	below -50	18.8	0.9051	118.1	73	-27

*In each case, reaction temperature, 80°C, and 5% $AlCl_3$ (wt) were used.

ENCLOSURE (B)3

Table XII(B)3
EFFECT OF AMOUNT OF $AlCl_3$ ON POLYMERIZATION

Conditions of Polymerization		$AlCl_3$ used (wt %)	12	10	7	5
		Reaction Temp(°C)	80	80	80	80
		Reaction Time(hr)	10	10	10	10
Product of Polymerization		Yield (wt %)	85.0	87.5	90.0	87.0
		Iodine Value	10.5	11.2	14.3	20.8
Aero-Engine Oil Fraction		Viscosity in S.U.S. at 250°F	129.5	100.5	94.5	103.4
		Viscosity Index	105	104	96	84
	British Air Ministry Oxidation Test	Viscosity Ratio	1.58	1.60	1.81	2.00
		Conradson's Carbon (%)	1.29	2.02	2.36	3.66
		Acid Value	0.31	0.35	0.35	0.36
		Saponif. Value	14.09	15.73	18.32	17.29
		Yield for Product (wt %)	23.0	23.5	20.1	14.2

Table XIII(B)3
DISTILLATION OF ALUMINIUM CHLORIDE SLUDGE

			Distilled Oil		Gas	
Exp. No.	Distillation Temp. (°C) (in sludge)	Yield of Residue (wt %)	Yield (wt %)	Density d^{15}_{4}	Yield (wt %)	Calorific Power Cal/m³
1	375	42.8	44.0	0.815	13.2	5856
2	390	42.0	44.0	0.815	14.0	9652
3	390	41.0	43.9	0.830	15.1	17150

ENCLOSURE (B)3

Table XIV(B)3
EFFECT OF TIME AND TEMPERATURE OF COKING $AlCl_3$ SLUDGE

Coking		Yield of Cokes (wt %)		Composition of Cokes			
Temp. (°C)	Time (hr)	For Residue	For Sludge	Al (wt %)	Cl (wt %)	C (wt %)	Experimental Formula
500	1	73.1	30.7	17.10	17.52	65.39	$AlCl_{0.78}$
600	1	75.0	36.4	12.39	14.45	73.16	$AlCl_{0.89}$
600	3	74.1	32.3	12.59	14.51	79.90	$AlCl_{0.96}$
700	1	66.2	28.8	10.43	9.86	79.71	$AlCl_{0.72}$
700	3	63.0	27.4	8.94	9.34	81.72	$AlCl_{0.80}$
800	1	60.9	26.5	9.89	9.85	80.26	$AlCl_{0.76}$
800	3	62.3	27.1	9.69	9.41	80.92	$AlCl_{0.74}$

Table XV(B)3
CHLORINATION OF COKE*

Coking of Residue		Chlorination of Cokes	Yield of $AlCl_3$ Recovered for Sludge (wt %)
Temperature (°C)	Time (hr)	Temperature (°C)	
500	1	600	58.0
500	1	700	79.4
500	1	800	83.0
500	3	600	71.8
500	3	700	79.4
500	3	800	90.3
600	3	600	76.6
600	3	700	70.6
600	3	800	77.3

*In each chlorination, time was 3 hours, and the passing rate of chlorine was 5 lit/hr/20gm of coke.

ENCLOSURE (B)3

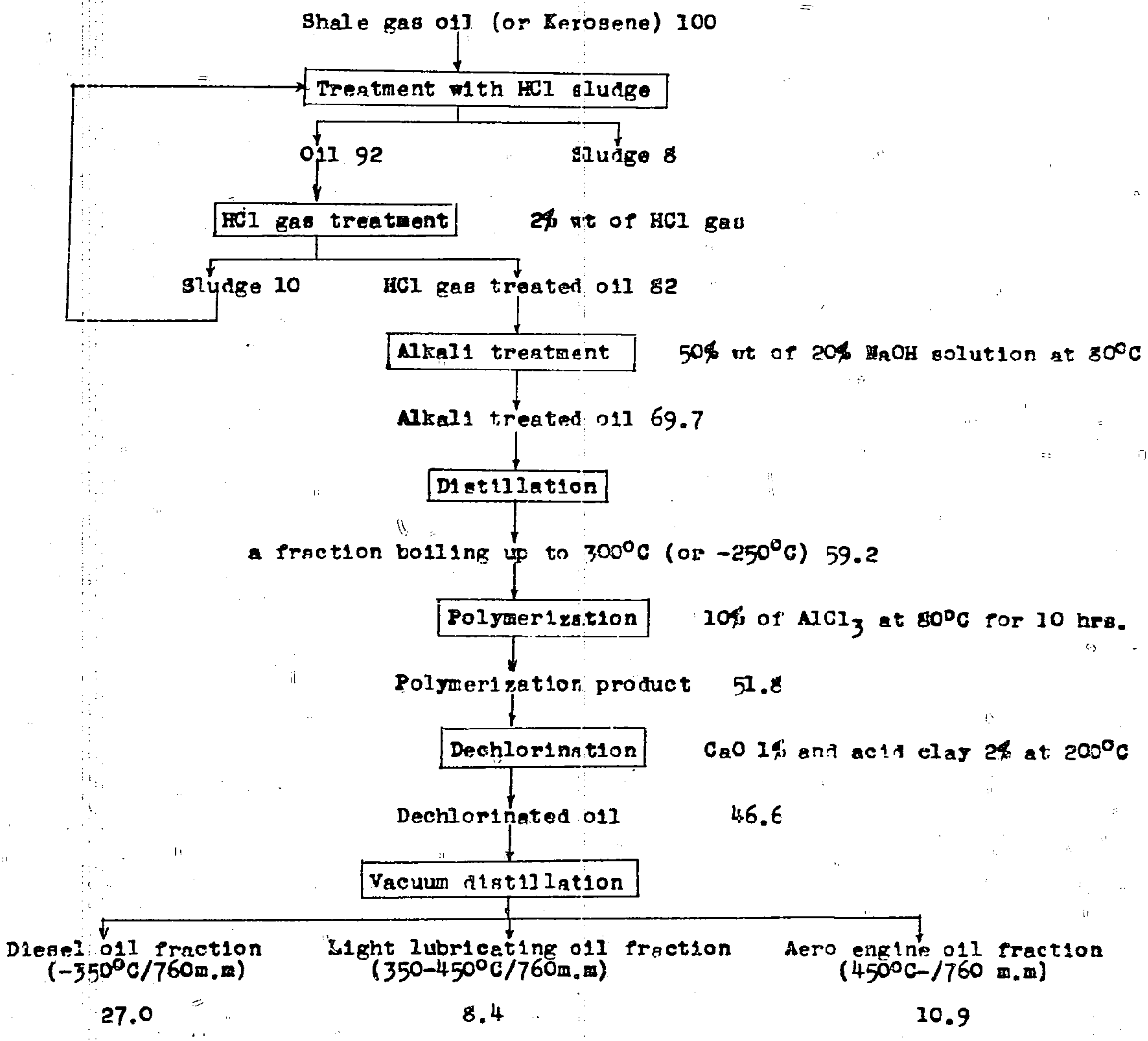

Figure 1(B)3

SCHEME FOR THE PREPARATION OF AN AEROENGINE OIL FROM SHALE GAS OIL OR KEROSENE

ENCLOSURE (B)3

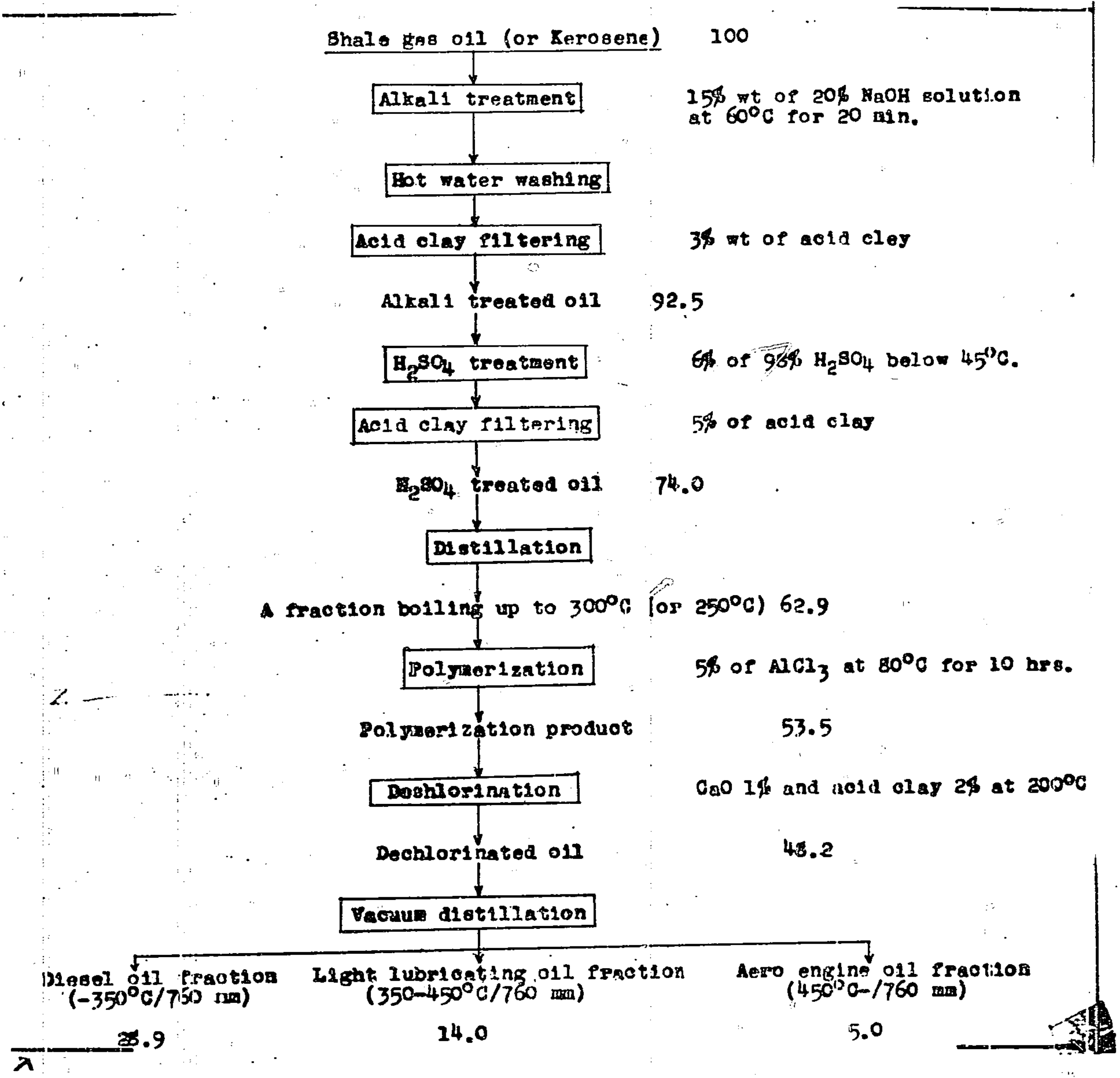

Figure 2(B)3

SCHEME FOR THE PREPARATION OF A MOBILE OIL FROM SHALE GAS OIL OR KEROSENE

ENCLOSURE (B)3

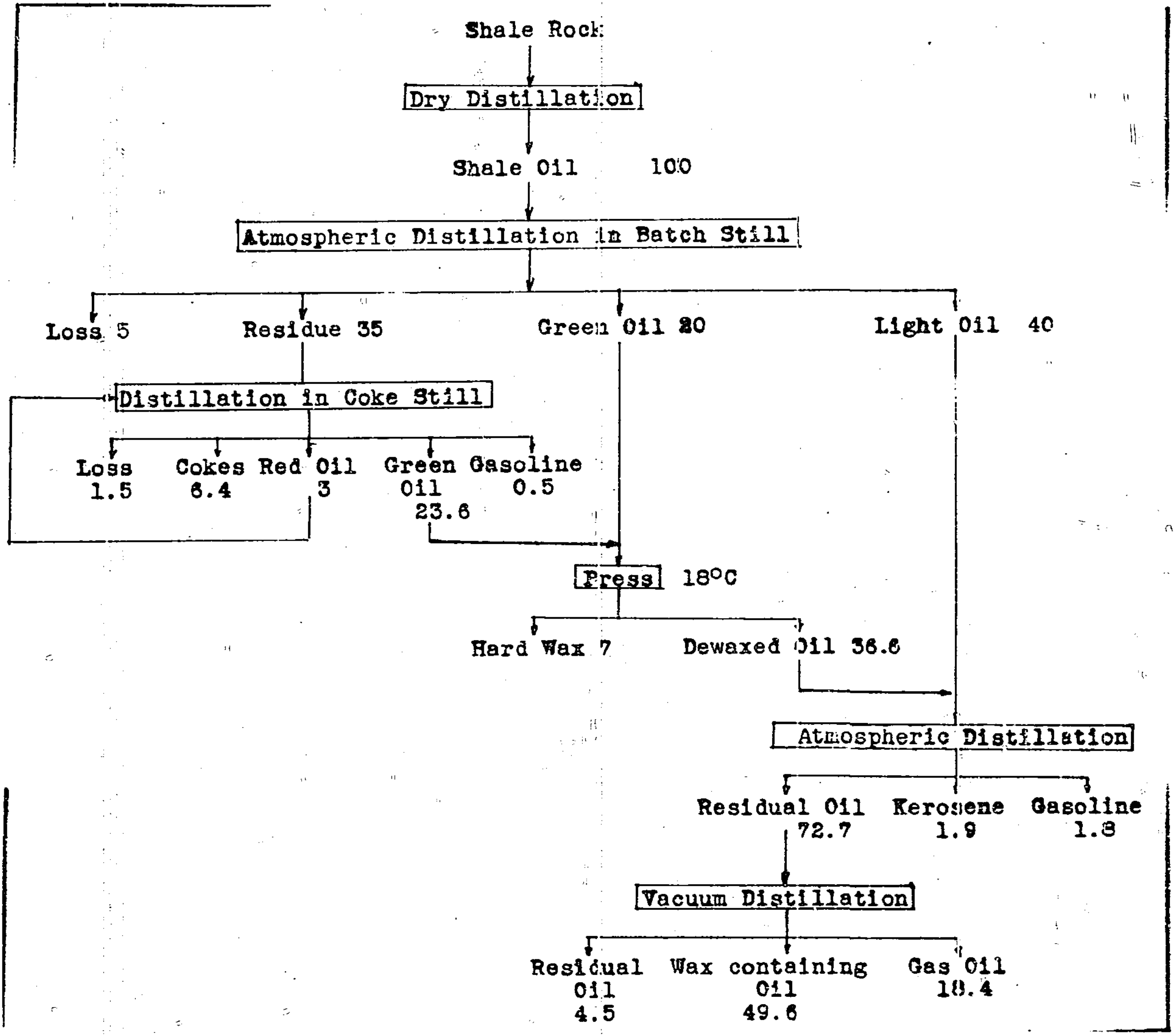

Figure 3(B)3

SCHEME OF PRODUCTION OF GAS OIL AND KEROSENE FROM SHALE

ENCLOSURE (B)3

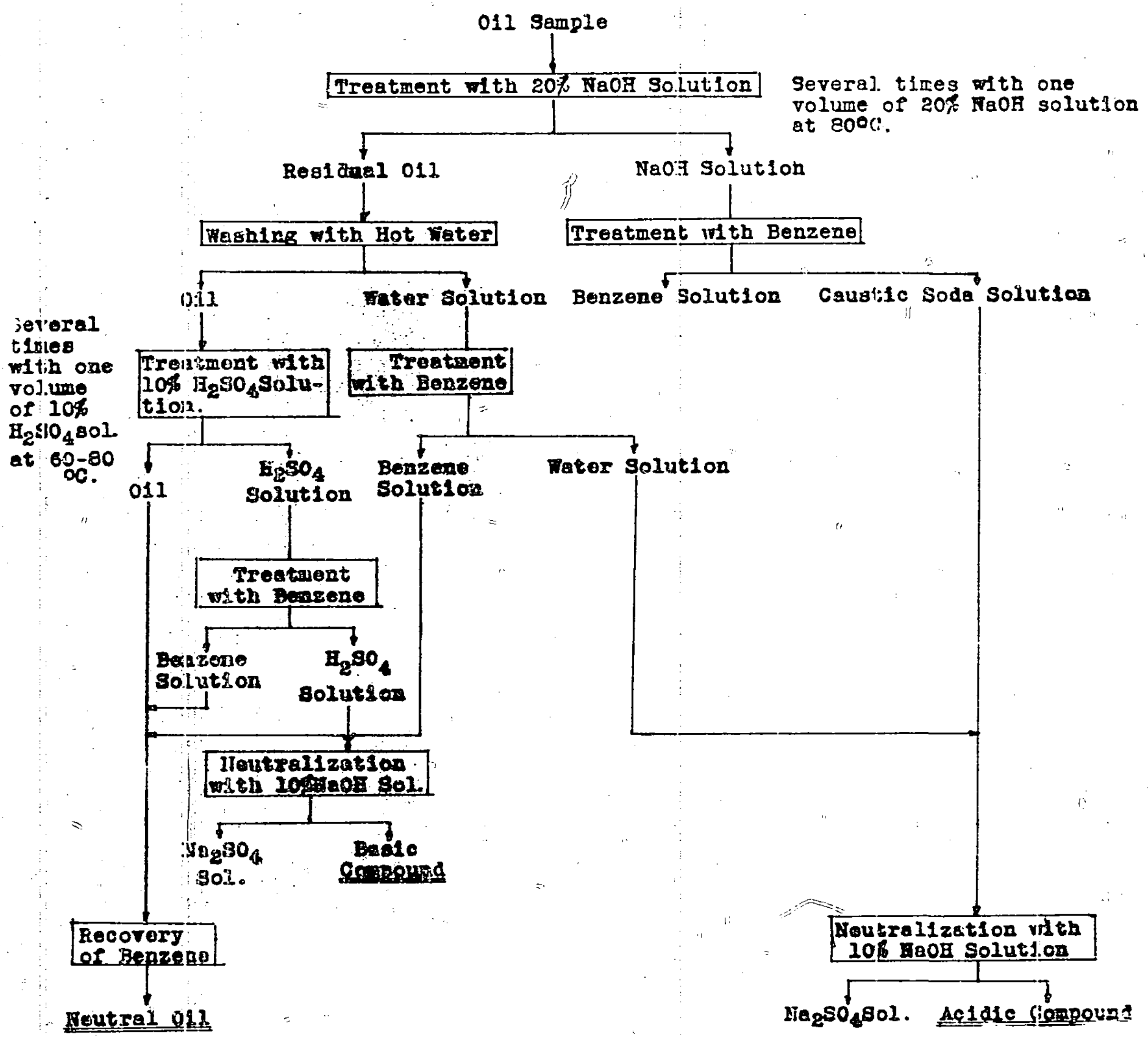

Figure 4(B)3

METHOD FOR DETERMINING ACIDIC AND BASIC COMPOUNDS IN SHALE OIL

ENCLOSURE (B) 4

STUDIES ON THE MANUFACTURE OF AERO-ENGINE OILS FROM RESIDUAL OILS BY SOLVENT EXTRACTION

by
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Research Period: 1937-1943

Prepared for and Reviewed with Authors by
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December 1945

ENCLOSURE (B)4

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)4

SUMMARY

A. As the operation of the propane dewaxing process is greatly influenced by cooling temp., cooling rate and filter-aids, these factors were investigated for deasphalted Osage residual oil in 3 volumes of propane. The results obtained were as follows:

1. At -40°C cooling temperature, and a cooling rate of 1°C per min., the pour point of the dewaxed oil was -18°C~-22°C, and at a cooling rate of 5°C per min., the pour point was the same.

2. At -35°C cooling temperature and a cooling rate of 1°C per min., the pour point of the dewaxed oil was -15°C~-19°C , and at a cooling rate of 5°C per min., the pour point was -12°C~-15°C.

3. As a filter-aid, Japanese acid clay was not suitable. Addition of 3% of diatomaceous earth was effective in increasing the filtering capacity by 5%. Acetone was more effective and promoted the filtering capacity by 10%. Phenol, when 1% by weight was added had no effect on the filtering capacity, but 5% by weight decreased the filtering capacity by 20%.

4. Aero-engine oils were prepared in the laboratory from the natural residual oil boiling over 250°C at 5mm Hg by successive propane deasphalting, phenol extraction, acetone-benzol dewaxing, and topping of the raffinate in vacuo. Yield of aero-engine oils are tabulated below.

Yields of Aero-Engine Oil from Crude Oils

Crude oils	Yields %(wt) of total crude
Iran	3.0
Arabia	2.0
Burma	2.0
KADO	10.0
CHOKAIZAN (Japan)	2.3
YAMORI (Japan)	2.5
OMONOGAWA (Japan)	0.9
RIRIKU (Sumatra)	2.2

Note: Viscosity of these products was 115~125 S.U.S. at 210°F and viscosity-index was 90~95.

B. The solvent extraction process, which uses amyl alcohol and furfural as solvents, for the production of aero-engine oil was studied and the following results were obtained:

1. Deasphalting and dewaxing were accomplished by treating the residual oils with 3 volumes of amyl alcohol at -20°C. (optimum condition of operation)

2. In the furfural extraction of the deasphalted and dewaxed oil, it was found best to treat with 4 volumes of furfural at 60°C~120°C.

3. Yields of aero-engine oils from residual oils, when treated by above method, are tabulated below.

Yields of Aero-Engine Oil by Amyl Alcohol-Furfural Process

Crude	Yields of Aero-Engine Oil
OMONOGAWA (Japan)	2.1 (wt)% of total crude
OHA (Sakhalin)	4.8 (wt)% of total crude
Rhodessa (U.S.A.)	7.2 (wt)% of total crude
Posalika (Mexico)	3.8 (wt)% of total crude

Note: Viscosity of these products was 115~125 S.U.S. at 210°F and viscosity-index was 90~95.

I. THE PROPANE - PHENOL PROCESS

A. Introduction

1. The Term of Study was from April 1937 to March 1943. In this solvent process, especially in the propane dewaxing, there were various factors controlling the dewaxing effect which were not known in Japan. The author studied this problem with a view to developing its industrial application in Japan. The investigation of the preparation of aero-engine oils by the propane-phenol process was carried on, intermittently, when crude oil was available from 1937 - 1943.

2. Key Research Personnel Working on Project.

Eng. Capt. Dr. I. KAGEHIRA

B. Detailed Description of the Propane-Phenol Process

1. Propane Dewaxing. Osage deasphalted oil was used for this experiment. The properties of this oil are as follows:

Properties of Osage Residual Oil

Density (25/4)	0.9205
Viscosity in S.U.S. at 100°F	2460
Viscosity in S.U.S. at 210°F	118.5
Viscosity-index	60
Conradson's carbon residue (%)	5.2
Pour point (°C)	+11

This residual oil was deasphalted with 5 volumes of liquid propane at 45°C and the yield and properties of the deasphalted oil are tabulated below:

ENCLOSURE (B)4

Properties of the Deasphalted Oil

Yield from Osange residual oil (wt%)	71.4
Density(25/4)................................	0.9087
Viscosity in S.U.S. at 100°F	1282
Viscosity in S.U.S. at 210°F	96.3
Viscosity-index	87
Conradson's carbon residue (%)	2.43
Pour point (°C)	+27

This deasphalted oil was subjected to propane dewaxing and the results shown in Table I(B)4 were obtained.

The effect of use of filter-aids on filtering capacity at -40°C with 3 volumes of liquid propane is shown below:

Effect of Filter-Aids

Filter-Aids	Increasing of Filtering Capacity (%)
Japanese acid clay alone	non effective
With 3% of diatomaceous earth	+50%
With 5% of acetone	+100%
With 5% of phenol	-20%

2. Propane-Phenol Extraction of Various Residual Oils to Produce Aero-Engine Oil. Several residual oils were subjected to the following procedures and the yields of aero-engine oil were determined.

a. Deasphalting. In deasphalting, liquid propane obtained by the hydrogenation of cracking plant gas and having the composition tabulated below was used.

Composition of Liquid Propane

C_3H_8	80%
C_3H_6	0.5%
C_4H_{10}	15%
C_4H_8	0.5%
the others	4.0%

Experiments were carried out with 5 volumes of liquid propane, stirring the mixture for 30 min. at 45°C and then allowing to stand for 1 hr. at the same temperature.

b. The apparatus for the propane deasphalting and propane dewaxing procedures was made from iron and is shown in Figure 1(B)4.

c. In the next procedure, solvent extraction by phenol was carried out. The deasphalted oils were treated three times with 5~6 volumes of dehydrated phenol. Each time the mixture was agitated for 30 min. at 45°C and settled for 1 hr. at 45°C, separating the raffinate and the extract. Apparatus for this procedure was a common separatory funnel having a capacity of 3-5 liters.

d. The raffinates were mixed with 5 volumes of acetone-benzol solution in which the volume ratio of components was 35:65, respectively. The mixtures were cooled at -15°C~-20°C and filtered to remove waxes. From these dewaxed solutions, the solvents were distilled off, and dewaxed oils were obtained. The dewaxed oils were topped to a suitable viscosity; that is, in general, up to 250°C~280°C under a vacuum of 5mm Hg. The topped residual oils were refined by treating with 5% of dried acid clay by weight.

e. The yields of aero-engine oils thus obtained from several residual oils are tabulated below:

Yields of Aero-Engine Oils From Various Crudes

Crudes	Yield of Oil Wt% to Total Crude
Iran	3.0
Arabia	2.0
Burma	2.0
KADO	10.0
CHOKAIZAN (Japan)	2.3
YAMORI (Japan)	2.5
OMONOGAWA (Japan)	0.9
RIRIKU (Sumatra)	2.2

Note: Viscosity of these products was 115~125 S.U.S. at 210°F and viscosity-index was 90~95.

II. THE AMYL ALCOHOL~FURFURAL PROCESS

A. History

The term of study was from April 1937 to November 1940. From many deasphalting methods, the author chose the amyl alcohol method, since in Japan, amyl alcohol is available as a by-product of alcohol fermentation and is easier to obtain than other solvents. It was recognized that amyl alcohol has not only a deasphalting action, but also a dewaxing action.

For solvent extraction, the furfural process was chosen, since it is suitable for naphthenic oils, as indicated by the author's studies on Japanese crude oils, and K. P. Likhuskin's conclusions relative to Balanchamy's crude oil. Consequently, the process utilizing these two methods was called the amyl alcohol~furfural process.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. Comdr. S. IIMURE

C. Experimental Results

1. Properties of Japanese crudes and their distillates are tabulated in Table II(B)4. The determination of wax content was carried out by filtering at -30°C with 4~6 volumes of acetone-benzol solution.

2. It was recognized from Table II(B)4 that the lubricating oil fraction had, in general, high densities and low viscosity-indexes.

ENCLOSURE (B)4

a. Ultimately, Japanese crude oils are of naphthenic or mixed-base character.

b. Experiments were carried out to choose a suitable solvent for Japanese crude oils. Oha deasphalted and dewaxed oil was used for this purpose. Three volumes of each solvent was added and the consolute temperatures were measured. After standing for 30 min. at 20°C below the consolute temperature, the raffinates and extracts were separated. The raffinates were treated with 1-2% of dried acid clay by weight. The effects of 4 solvents are tabulated in Table III(B)4. According to Table III(B)4, comparatively higher yield of raffinate, based on viscosity of product, was obtained in the furfural extraction.

3. Deasphalting and Dewaxing with Amyl Alcohol. Omonogawa residual oil was used as the raw material and its properties are tabulated below.

Properties of Omonogawa Residual Oil

Yield to total crude, (Vol%)	27.0
Density(15/4)	0.9461
Viscosity in S.U.S. at 210°F	122.5
Flash point (°C)	238.5
Pour point (°C)	+29.0
Conradson's carbon (%)	6.45

The solvent analysis of the components of Omonogawa crude was carried out by Engler's method. (See Figure 2(B)4 The results are tabulated below.

Results of Solvent Analysis by Engler's Method

Resins	24.0% (wt)
Asphaltenes hard	5.5% (wt)
Asphaltenes soft	29.5% (wt)
Waxes hard	12.4% (wt)
Waxes soft	4.0% (wt)
Oily parts	24.2% (wt)
Total	99.6% (wt)

4. Mechanism of Cooling Treatment by Amyl Alcohol. The Omonogawa residual oil was dissolved in 2~3 volumes of amyl alcohol (Boiling point, 130°C~132°C). The solution was gradually cooled to 0°C, -5°C, -10°C, -15°C and -20°C respectively and filtered at the same temperatures.

Analytical data by Engler's method of each soluble and insoluble part are tabulated in Table IV(B)4 (See also Figure 3(B)4)

The deasphalted and dewaxed oils were refined by treatment with furfural at suitable temperatures.

The results obtained are tabulated in Table V(B)4

The best results were obtained using a solvent ratio of 3:1 at -20°C for deasphalting.

D. Source of Amyl Alcohol

Commercial amyl alcohol was used in the experiments. The properties of this amyl alcohol are tabulated below.

Properties of Amyl Alcohol

Density(20/4)	0.838
Refractive index(n_D^{25})	1.398
Acid value	3.1
Ester value	30.4

E. Results Obtained Using the Amyl Alcohol-Furfural Process on Various Crude Oils.

1. **Description of Experimental Apparatus.** The oil and amyl alcohol were mixed in a 5 liter beaker and cooled by ice and salt. The oil layer and asphalt layer were separated by decantation. The deasphalted and dewaxed oil was then agitated with furfural in a 5 liter beaker and the mixture was poured into a separatory funnel.

2. **Results of Omonogawa Oil.** Omonogawa residual oil was used as the raw material and its properties are tabulated below.

Properties of Omonogawa Residual Oil

Yield for total crude, (Vol%)	27.0
Density(25/4)	0.9461
Viscosity in S.U.S. at 210°F	122.5
Flash point (°C)	238.5
Pour point (°C)	+29.0
Conradson's carbon (%)	6.45

The properties of Omonogawa deasphalted and dewaxed oil by treatment with 3 volumes of amyl alcohol at -20°C are tabulated below.

Properties of Omonogawa Deasphalted and Dewaxed Oil

Yield to total crude (Vol%)	14.9
Density(25/4)	0.9649
Viscosity in S.U.S. at 100°F	4041.2
Viscosity in S.U.S. at 210°F	121.3
Viscosity-index	-52.8
Flash point (°C)	177.0
Pour point (°C)	-5.0
Conradson's carbon (%)	4.70

The deasphalted and dewaxed oil was subjected to the furfural extraction as follows:

To secure as complete a selective extraction as possible, the extraction was carried out first by high solvent ratios at lower temperatures and then by low solvent ratios at higher temperatures. Results of this procedure are tabulated in Table V(B)4.

The No.3 raffinate was then treated with 3% (Vol) of Conc. H_2SO_4 to remove residual resins. The properties of the refined raffinate are tabulated below.

Properties of the Refined Raffinate

Yield for Omonogawa residual oil (Vol%)	7.5
Density (25/4)	0.8758
Viscosity in S.U.S. at 100°F	594.1
Viscosity in S.U.S. at 210°F	69.5
Viscosity-index	99.3
Pour point (°C)	-14.0
Conradson's carbon (%)	0.101

Fifty percent of this refined raffinate was distilled off so as to obtain an oil of suitable viscosity for aero-engine oil. Properties of the product are tabulated below.

Properties of Refined Product

Yield from the original residual oil (Vol%)	2.05
Density (25/4)	0.8881
Viscosity in S.U.S. at 100°F	1811.8
Viscosity in S.U.S. at 210°F	121.4
Viscosity index	93.0
Pour point	
Conradson's carbon (%)	0.27
Acid value	0.04
Saponification value	0.06
Viscosity ratio after British Air Ministry Oxidation Test	1.22

The extracts were refined with 5%(wt) of conc. H_2SO_4. The properties of the refined extracts are tabulated in Table VI(B)2. These oils were useful as a mobile oil for a car.

3. Oha Crude Oil. Properties of the Oha crude oil and its distillates are tabulated in Table VIII(B)4.

Oha 45% topped residual oil was treated with 3 volumes of amyl alcohol at -23°C ~ -25°C. The properties of the Oha 45% residual oil and and the raffinate are tabulated in Table IX(B)4. As reference, the properties of the various fractions of Oha crude are given in Table VIII(B)4.

The raffinate was extracted with furfural under various conditions and refined by treating with dried acid clay. The results obtained are tabulated in Table VI(B)4.

4. Kettleman Hills Crude. The procedure and results are tabulated in Table XI(B)4, and it was observed that an aero-engine oil having a viscosity-index of 85 could be prepared from Kettleman Hills crude.

5. Rhodessa Crude Oil. The results and the conditions of the treatment are tabulated in Table XII(B)4. Good results were obtained.

6. Posalika Crude (Mexico). Posalika crude in Mexico was of paraffinic character, but rich in sulphur. The properties of the crude and the topped residue are tabulated in Table XIII(B)4.

This residual oil was treated by the amyl alcohol-furfural process. The conditions, procedures, and properties of the product are tabulated in Table XIV(B)4.

The distribution of sulphur in each stage of the procedure for Posalika crude is indicated in Figure 4(B)4.

III. CONCLUSIONS

Investigations were carried out on the propane-phenol extraction method, especially on the propane dewaxing process, and it was concluded that this process could be successfully operated with 3 volumes of liquid propane and a cooling rate of 1~5°C/min. at -40°C, especially when 5% of acetone or 3% of diatomaceous earth by weight was added.

As another solvent extraction process, the amyl alcohol-furfural process was examined and the best operating conditions for various residual oils were determined.

It was concluded that the optimum conditions were to treat with 3 volumes of amyl alcohol at -20°C for deasphalting and dewaxing of the residual oil and with 4 volumes of furfural at 60°C~120°C, for the extraction of deasphalted and dewaxed oil.

Comparing the above two processes, the propane-phenol process is better, since the deasphalting by liquid propane is completely accomplished and the heat stability of phenol is better than that of furfural.

Two propane-phenol plants are installed in Japan, one at the Second Naval Fuel Depot, and the other at the Third Naval Fuel Depot.

No large application of the amyl alcohol-furfural process has been made.

Table I(B)4
RESULTS OF PROPANE DEWAXING

Cooling Temp.*	Cooling Rate	Pour Point Dewaxed Oil
-40°C	1°C/min 5°C/min	-18 to -22°C -18 to -22°C
-35°C	1°C/min 5°C/min	-15 to -19°C -12 to -15°C

*In three volumes of liquid propane.

ENCLOSURE (B)4

Table II(B)4
PROPERTIES OF JAPANESE CRUDES AND THEIR DISTILLATES

Oil Field	Oil Cell	Crudes Density (15/4)	Yield (Vol%)					Properties of a fraction boiling 220-330°C/7mm Hg			
			I.D.-200°C/760mm	200°C-280°C/760mm	280°C/760mm-230°C/7mm	220°C-330°C/7mm	Residue	Density(15/4)	Viscosity Index	Viscosity Gravity Constant	Wax Content (wt%)
HOKKAIDO	No description	0.837	53	22	13.8	6.1	5.1	0.9642	- -	- -	34.47
	MASUHORO	0.855	7.2	29.4	33.6	27.0	2.8	0.9095	59.7	0.8535	11.32
	KARUMAI	0.851	44.5	19.3	13.6	16.8	5.7	- -	4.9	- -	7.92
AKITA	KUROKAWA	0.943	6.7	27.5	15.0	22.4	28.4	0.9467	-30.4	0.8965	- -
	YABASE	0.838	33.2	26.6	17.6	15.9	6.7	0.9253	10.4	0.800	6.45
NIIZU	ASAHI	0.939	- -	15.0	33.7	22.7	28.6	0.947	-25.8	0.8951	- -
	TAKIDANI	0.930	1.2	27.1	37.9	28.4	5.4	0.9571	-67.8	0.9100	- -
	OGUNI	0.942	1.8	28.0	29.3	26.4	14.5	0.9511	-26.1	0.8997	- -
	EHIGI	- -	7.0	33.7	30.4	21.9	6.0	0.9364	12.3	0.8851	3.76
NIIGATA	TAIMEN B-4	0.883	26.0	36.2	11.5	10.2	16.1	- -	- -	- -	5.72
HIGASHIYAMA	KATSURAZAWA	0.897	25.1	22.4	17.8	19.2	15.5	0.9523	-39.1	0.9004	6.20
	KATSUBO	- -	33.5	21.3	19.7	13.6	11.9	0.9535	-36.3	0.9010	5.02
NISHIYAMA	TAKAMACHI	0.837	43.9	18.0	19.7	13.1	5.3	0.9273	31.1	0.8158	10.1
	YUIRI	0.839	50.2	20.7	17.5	9.6	2.0	0.9490	-19.7	0.8977	1.36
	NAGANINE	0.780	45.0	24.0	15.2	12.0	3.8	0.9300	62.4	0.8364	5.65
	CHANOKI	- -	49.0	20.0	20.6	7.1	3.3	- -	- -	- -	4.83

ENCLOSURE (B)4

Table III(B)4
EFFECTS OF FOUR SOLVENTS ON OHA TREATED OIL

Solvent	Consolute Temp. (°C)	Yield (Vol%)	Density 60°F/60°F	Viscosity in S.U.S. at 100°F	Viscosity in S.U.S. at 210°F	Viscosity Index	Conradson's Carbon (%)
Oha deasphalted and dewaxed oil		100.0	- -	942.2	68.6	33.6	- -
Nitro benzene	20	18.0	0.8776	675.6	67.8	78.6	0.13
Phenol	70	13.3	0.8885	807.9	77.2	90.8	0.49
Chlorex	25	30.0	0.9077	1034.3	80.3	91.9	0.81
Furfural	140	25.0	0.8993	1093.5	85.2	79.5	0.95

Table IV(B)4
ANALYSIS OF FRACTIONS SEPARATED FROM OMONOGAWA RESIDUAL OIL BY AMYL ALCOHOL AT VARIOUS TEMPERATURES

		Asphaltenes (%)		Resins	Wax (%)		Oily Parts
		Hard	Soft	(%)	Hard	Soft	(%)
Amyl alcohol	at 0°C	8.37	38.13	21.78	11.50	2.10	15.85
(Boils at 130-132°C)	at -5°C	2.48	5.71	76.21	1.95	1.00	10.71
	at -10°C	0.97	2.91	74.59	3.74	1.40	14.53
Solv.Ratio 2:1	at -15°C	2.75	17.10	31.54	5.90	0.58	37.90
	at -20°C	0.26	4.90	43.53	0.53	2.85	41.60
Amyl alcohol	at 0°C	10.12	24.05	43.73	11.10	0.16	7.04
	at -5°C	1.73	31.40	58.98	1.06	0.56	4.76
(Boils at 130-132°C)	at -10°C	0.35	41.17	45.00	1.65	0.72	10.39
Solv.Ratio 3:1	at -15°C	1.79	12.96	32.48	12.27	1.42	32.75
	at -20°C	0.73	8.10	34.78	2.00	4.10	46.60

Table V(B)4
PROPERTIES OF PRODUCTS OF FURFURAL TREATMENT OF AMYL ALCOHOL TREATED OIL

			Yield (Vol%)	Density (15/4)	Pour Point (°C)	Viscosity in S.U.S.		Viscosity-Index	Conradson's Carbon (%)
						at 100°F	at 210°F		
Exp. No.1	1st stage	Amyl alcohol treatment at -20°C (solv. ratio 2:1)	6.75	0.9675	+8.0	- -	200.2	- -	5.21
	2nd stage	Furfural extraction solv. ratio 6:1 at 60°C	2.95	0.9100	-16.0	1452.2	92.4	65.3	1.01
		Furfural extraction 1) solv. ratio 6:1 at 60°C 2) solv. ratio 3:1 at 80°C	2.03	0.8745	-13.5	1010.2	82.7	81.7	0.62
		Furfural extraction 1) solv. ratio 6:1 at 60°C 2) solv. ratio 3:1 at 80°C 3) solv. ratio 1:1 at 100°C	1.81	0.8887	-15.0	940.1	80.4	87.6	0.52
Exp. No.2	1st stage	Amyl alcohol treatment at -20°C (solv. ratio 3:1)	5.19	0.9699	+4.5	- -	189.2	- -	5.15
	2nd stage	Furfural extraction solv. ratio 6:1 at 60°C	2.24	0.9069	-16.5	1198.4	84.3	66.1	0.96
		Furfural extraction 1) solv. ratio 6:1 at 60°C 2) solv. ratio 3:1 at 80°C	1.47	0.8918	-15.0	838.7	76.8	85.6	0.41
		Furfural extraction 1) solv. ratio 6:1 at 60°C 2) solv. ratio 3:1 at 80°C 3) solv. ratio 1:1 at 100°F	1.07	0.8844	-13.5	742.2	74.2	91.2	0.31

ENCLOSURE (B)4

Table VI(B)4
RESULTS OF FURFURAL EXTRACTION RAFFINATES

Conditions of Procedure	Density (15/4)	Pour Point (°C)	Viscosity in S.U.S.		Viscosity Index	Conradson's Carbon (%)
			at 100°F	at 210°F		
6:1 solvent ratio at 60°C	0.9059	-17	871.6	73.7	71.7	1.49
6:1 solvent ratio at 60°C followed by 3:1 solvent ratio at 80°C	0.8996	-15.5	69.2	71.2	89.2	0.79
6:1 solvent ratio at 60°C followed by 3:1 solvent ratio at 80°C followed by 1:1 solvent ratio at 100°C	0.8820	-14	803.8	78.3	95.3	0.62
EXTRACTED OILS						
Corresponds to raffinate No.1	1.017	25	- -	311.4	- -	11.0
Corresponds to raffinate No.2	0.9410	-14	1705.8	91.4	41.0	3.6
Corresponds to raffinate No.3	0.9156	-16.5	800.7	71.1	70.9	2.36

ENCLOSURE (B)4

Table VII(B)4
PROPERTIES OF THE REFINED EXTRACTED OILS

	Density 15/4	Viscosity in S.U.S.		Viscosity Index	Conradson's Carbon (%)	Pour Point (°C)	Acid Value	Saponification Value
		at 100°F	at 210°F					
Extracted oil No.1	1.017	5404.2	119.1	-74.5	12.78	2.5	0.51	1.56
Extracted oil No.2	0.9201	777.3	67.1	56.3	1.24	-17.5	0.03	0.6
Extracted oil No.3	0.9000	539.4	60.9	73.8	0.35	-12.5	0.56	0.40

Table VIII(B)4
PROPERTIES OF DISTILLATES OF OHA CRUDE

	Boiling Point (1mm Hg)	Density (15/4)	Viscosity in S.U.S.		Viscosity-Index	Mean Molecular Weight
			at 100°F	at 210°F		
1	I.D.~182	0.9258	141.8	38.3	-646	354
2	182~190	0.9340	391.5	48.1	-26.55	- -
3	190~200	0.9341	559.3	53.5	-71.03	363
4	200~210	0.9356	821.9	59.6	-16.17	- -
5	210~220	0.9364	1106	68.6	- 3.16	420
6	220~230	0.9365	1625	80.7	4.08	- -
7	230~240	0.9358	1904	89.0	14.57	423
8	240~250	0.9360	2421	101.8	21.38	- -
9	250~260	0.9385	3257	126.7	40.70	501
10	260~270	- -	3770	131.4	30.38	- -
11	270~280	0.9442	5789	172.1	30.02	509
12	280~290	0.9471	7656	198.5	29.83	- -
13	290~300	0.9496	10290	236.7	32.57	517
14	300~310	0.9536	14380	289.3	34.56	- -
15	310 320	- -	20090	344.6	-39.45	607
16	320 330	0.9533	8409	155.8	-51.08	- -

ENCLOSURE (B)4

Table IX(B)4
PROPERTIES OF OHA 45% RESIDUAL OIL AND THE RAFFINATE

		45% Residual Oil	The Raffinate
Density (15/4)		0.9733	0.9884
Viscosity	at 100°F	- -	4,652.5
in S.U.S.	at 210°F	305.4	134.5
Viscosity index		- -	5.5
Pour point (°C)		- -	+9.5
Conradson's carbon (%)		7.82	5.16

See page 95 for Table X(B)4.

Table XIII(B)4
PROPERTIES OF POSALIKA CRUDE AND ITS TOPPED RESIDUE

	Posalika Crude	Residue (350°C—)
Density	0.867/24.5°C	0.9516/20°C
Viscosity in S.U.S. at 210°F	- -	158.7
Pour point (°C)	+1.5	+14.0
Sulphur (°C)	1.43	2.43

Table X(B)4
PROPERTIES OF RAFFINATES OF OHA RESIDUAL OIL EXTRACTED WITH FURFURAL

	Deasphalted and Dewaxed Oil with 3 Vols of Amyl Alcohol at -20°C	Raffinate with 6:1 Solv. ratio at 60°C	Raffinate with 8:1 Solv. ratio at 80°C	Raffinate with 6:1 Solv. ratio at 100°C	Raffinate with 9:1 Solv. ratio at 60°C	Raffinate with 9:1 Solv. ratio at 80°C	Raffinate with 12:1 Solv. ratio at 60°C	Raffinate with 6:1 solv. ratio at 60°C followed by 3:1 solv. ratio at 80°C
Density(15/4)	0.9887	0.9204	0.9142	0.9149	0.9149	0.9053	0.9019	0.9018
Viscosity in S.U.S. at 100°F	- -	1713.6	1467.5	1545.2	1508.2	1613.0	1227.3	1113.6
Viscosity in S.U.S. at 210°F	238.5	96.8	92.2	100.1	94.4	91.2	92.7	85.2
Viscosity index	- -	56.2	65.1	75.6	65.8	73.8	84.6	77.4
Conradson's carbon (%)	5.66	2.03	2.06	3.27	1.99	2.11	2.16	1.62
Pour point (°C)	+ 9.5	-13	-14	-13.5	-12	-15.5	-16	-15
Yield (Vol%)	100	39.4	20.0	6.7	27.9	17.3	8.7	20.0
RAFFINATES TREATED WITH DRIED ACID CLAY								
Density(15/4)		0.9122	0.9101	0.9054	0.9138	0.9051	0.9085	0.8968
Viscosity in S.U.S. at 100°F		1565	1380.2	1421.6	1486.0	1280.2	1317.8	993.8
Viscosity in S.U.S. at 210°F		91.4	89.1	94.9	92.2	89.6	88.4	79.5
Viscosity index		53	62.6	73.8	61.9	72.9	66.4	74.2
Conradson's carbon (%)		1.33	1.08	1.22	1.52	1.15	1.33	0.64
Pour point (°C)		-14	-15	-12	-14.5	-15	-16	-15.5

ENCLOSURE (B)4

Table XI(B)4
PROPERTIES OF PRODUCTS OBTAINED FROM KETTLEMAN HILLS CRUDE BY AMYL ALCOHOL--FURFURAL PROCESS

	Residual Oil (Raw Material)	Deasphalted and Dewaxed Oil with 3:1 solv. ratio at -20°C	Furfural Extraction Raffinate with 1) 6:1 solv. ratio at 60°C 2) 3:1 solv. ratio at 60°C 3) 1.5:1 solv. ratio at 80°C	Refined Oil by 5% Acid Clay
Yield (Vol%)	100	53.7	14.1	8.9
Density(15/4)		0.9651	0.8970	0.8858
Viscosity in S.U.S. at 100°F	- -	- -	1331.4	766.9
Viscosity in S.U.S. at 210°F	180.4	194.2	97.0	74.3
Viscosity index	- -	- -	85.0	85.9
Pour point (°C)	+ 32.5	+4.5	-15.0	-14.5
Conradson's carbon (%)	7.97	5.75	1.15	0.26

Table XII(B)4
PROPERTIES OF PRODUCTS OBTAINED FROM RHODESSA CRUDE BY AMYL ALCOHOL--FURFURAL PROCESS

	Rhodessa Crude	Deasphalted and Dewaxed Oil with 3 Vols of Amyl Alcohol at -20°C	Raffinate from Furfural Extraction with 3:1 solv. ratio 3:1 at 80°C	77% topped Residual Oil of Raffinate
Yield (Vol%)	100	54.3	27.6	7.2
Density 15/4	0.8818/50°C	0.9078	0.8763	0.9118
Viscosity in S.U.S. at 100°F	- -	606.4	352.1	1961.5
Viscosity in S.U.S. at 210°F	81.5	64.9	57.6	125.8
Viscosity index	- -	84.2	110.5	91.5
Pour point (°C)	+35	-23	-13	-20
Conradson's carbon (%)	3.98	1.90	0.24	0.84
Oxidation test				
Viscosity ratio				1.3
Carbon (%)				1.79

ENCLOSURE (B)4

Table XIV(B)4
CONDITIONS, PROCEDURES, AND PROPERTIES OF PRODUCTS FROM POSALIKA RESIDUAL OIL

	Posalika Crude	Deasphalted and Dewaxed Oil With 3 Vols. of amyl alcohol at -20°C	Raffinate from furfural-extraction 1st with 2:1 solv. ratio at 50°C 2nd with 4:1 solv. ratio at 80°C 3rd with 2:1 solv. ratio at 90°C	60% Residual Oil (Product)
Yield (%)	100	51.8	7.8	3.8
Density($\frac{15}{4}$)	0.9516	0.9430	0.8807	0.8980
Viscosity in S.U.S. at 100°F	- -	1300.3	487.9	1528.2
Viscosity in S.U.S. at 210°F	158.7	85.5	64.2	112.3
Viscosity index	- -	59.4	102.5	96.3
Pour point (°C)	+14	-5.5	-9.0	-19.5
Conradson's carbon (%)	5.5	3.5	0.31	0.59
Sulphur (%)	2.43	2.21	0.53	0.81

ENCLOSURE (B)4

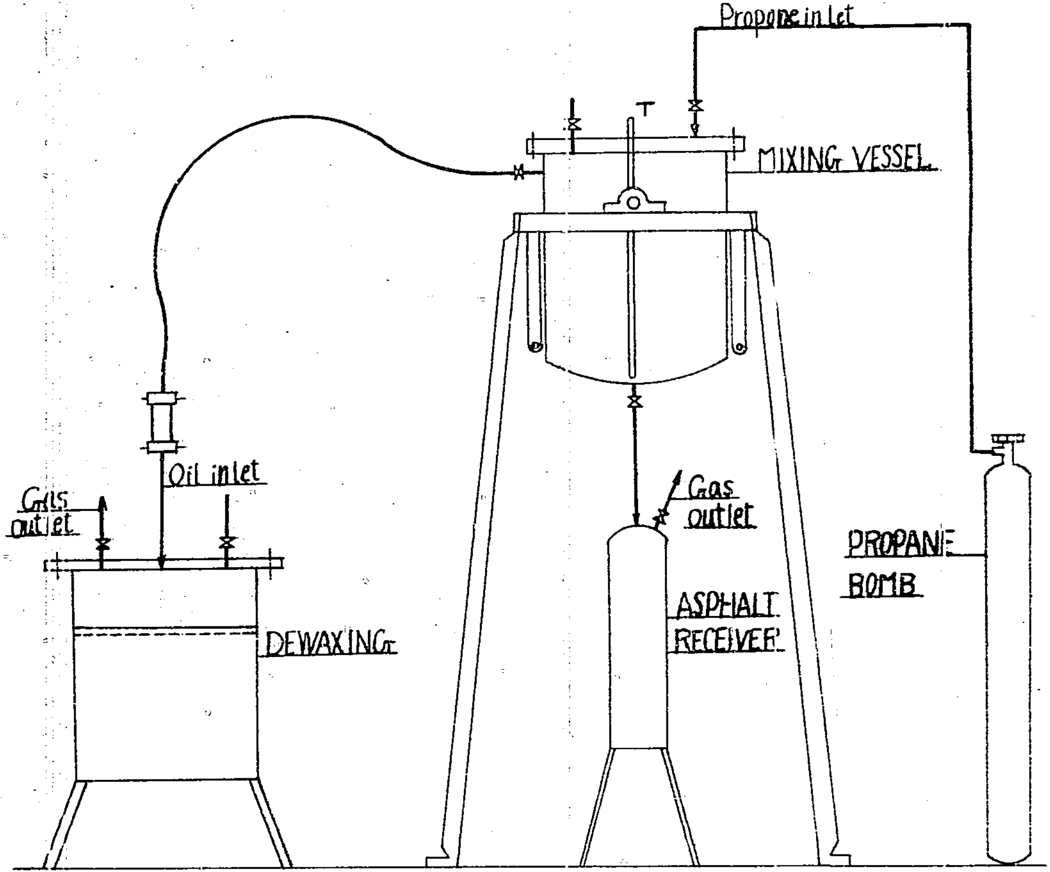

Figure 1(B)4
APPARATUS OF PROPANE DEASPHALTING AND DEWAXING

ENCLOSURE (B)4

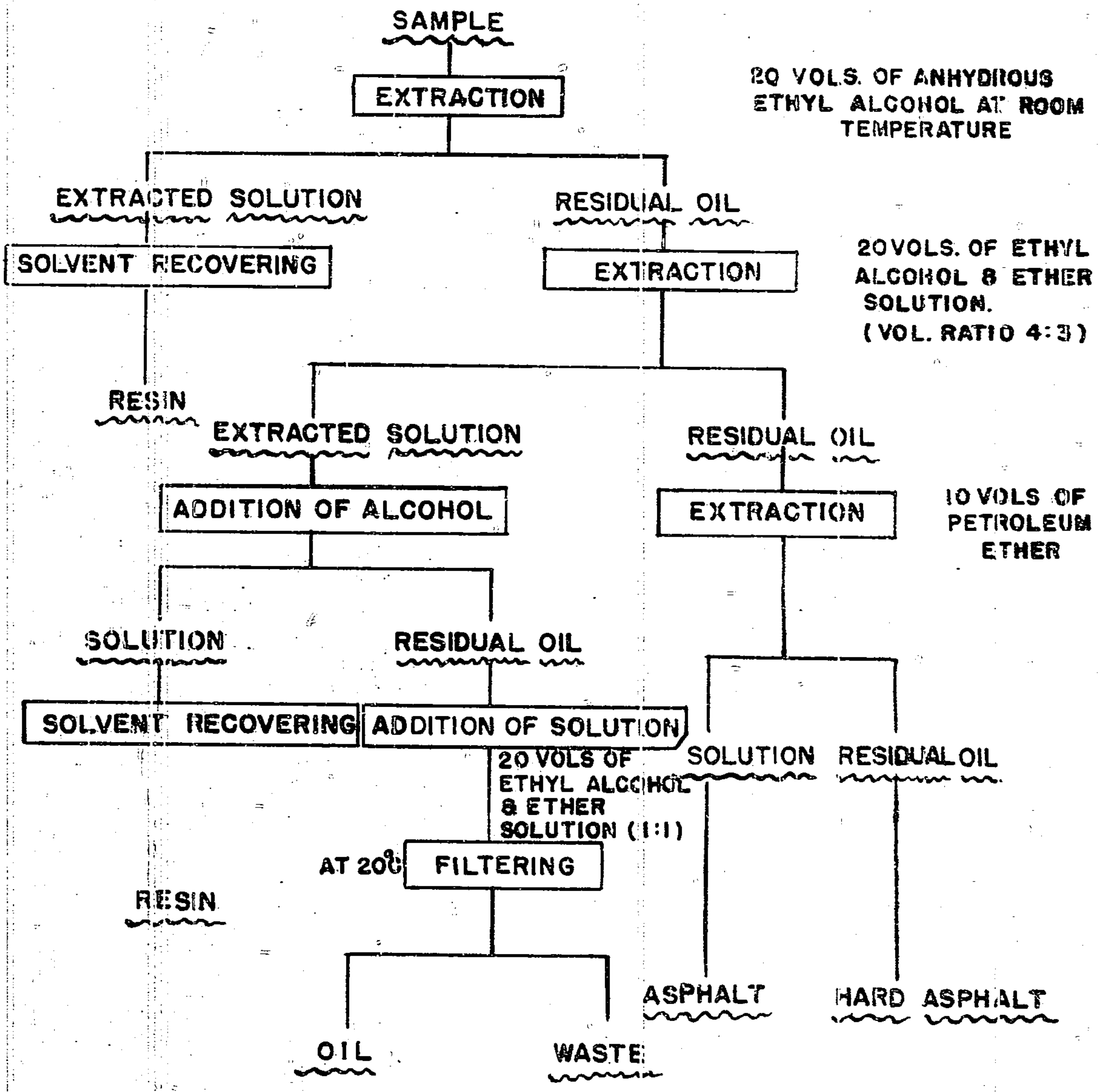

Figure 2(B)4

SOLVENT ANALYSIS BY ENGLER

ENCLOSURE (B)4

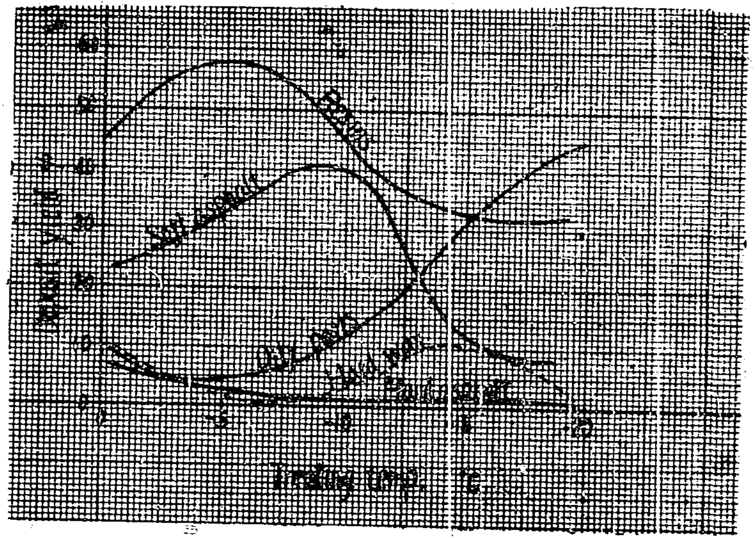

Figure 3(E)4
MECHANISM OF COOLING BY AMYL-ALCOHOL

ENCLOSURE (B)4

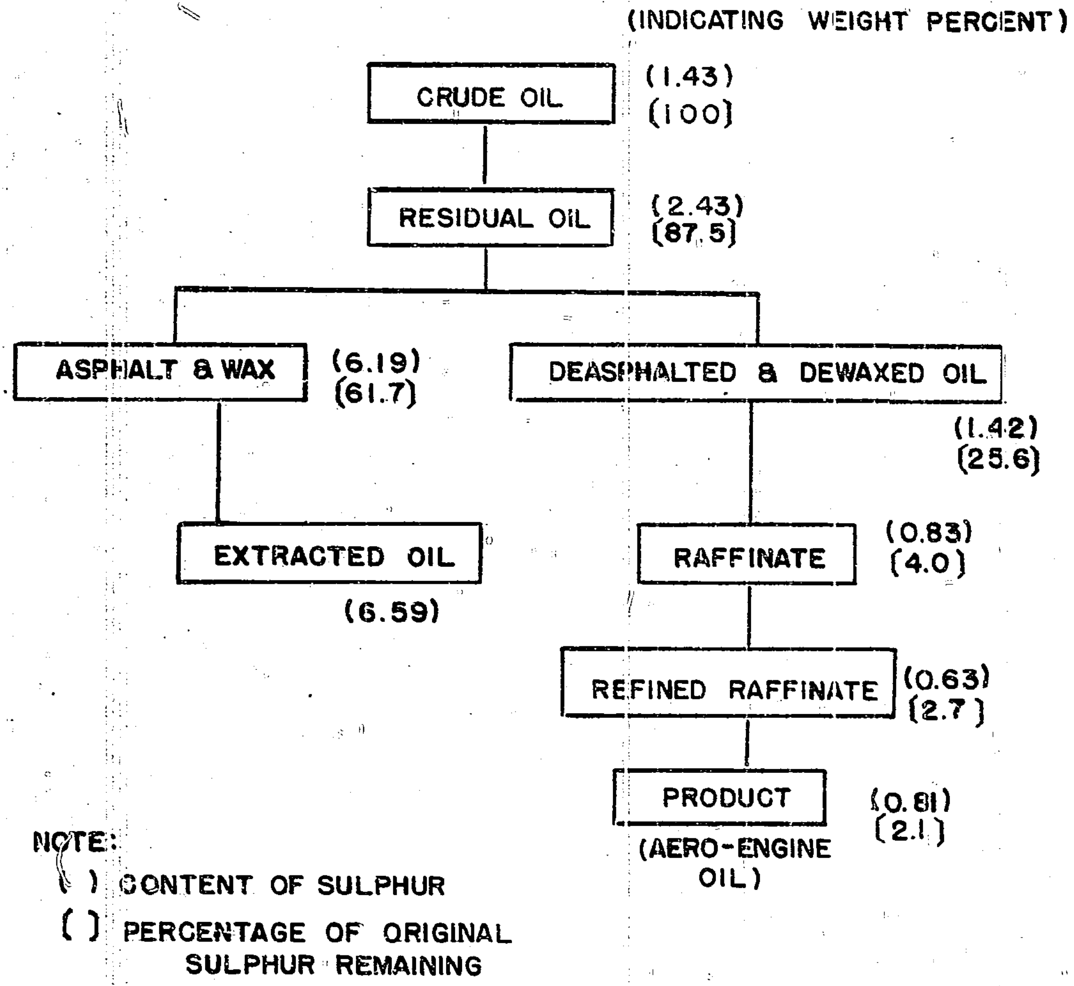

Figure 4(B)4
DISTRIBUTION OF SULPHUR IN EACH
STAGE OF PROCEDURE FOR POSALIKA CRUDE

ENCLOSURE (B) 5

PILOT PLANT FOR PROPANE-PHENOL SOLVENT EXTRACTION (PROPANE DEASPHALTING AND DEWAXING)

by

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Prepared for and Reviewed with Authors
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December 1945

ENCLOSURE (B)5

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)5

I. HISTORY

This plant was designed by Naval Technician R. MACHIDA and built at TOKUYAMA in 1937, and transfered to the First Naval Fuel Depot in 1939.

II. CAPACITY

About 10 liters per hour. (for raw material)

III. OPERATING METHOD

The raw material in 500 liter Feed Stock Tank is transported into the Mixing Tower (Volume, 50 liters) by Feed Pump. At the same time from the Liquid Propane Reservoir (Volume, 80 liters; Pressure 25 kg/ cm^2) the liquid propane is added to the raw material in the Mixing Tower through the Propane Preheater at 40°C-50°C. The mixing is carried out in the solvent ratio 5:1 at 40°C-45°C and 20-25 kg/ cm^2. This mixture enters into the Asphalt Separating Tower (Volume, 150 liters) by its own pressure. After 1 hour of letting stand at 40°C-45°C, the oil layer and the asphalt layer are separated and the asphalt is removed into the Asphalt Receiver. (Volume, 30 liters.) The oil layer enters into the Deasphalted Oil Receiver (Volume, 100 liters) at 40°C-45°C and 20 kg /cm^2 pressure and transported into the Cooling Tower (Volume, 150 liters), through the Heat Exchanger at 30°C.

In the Cooling Tower the oil layer is cooled at -25°C and then filtered by Filter (Volume 20 liters) at -45°C and 1-3 kg cm^2 pressure.

By filtering, the oil and wax are separated, they are transported by feed pump into the Dewaxed Oil Receiver (Volume, 50 liters) at -20°C and the Wax Receiver (Volume, 30 liters) at 30°C respectively.

Dewaxed oil is transported from the Dewaxed Oil Receiver to the Dewaxed Oil Tank at 20°C (Volume, 500 liters).

At last, the deasphalted and dewaxed oil, the asphalt, and the wax are taken out from the corresponding receivers or tanks.

ENCLOSURE (B)5

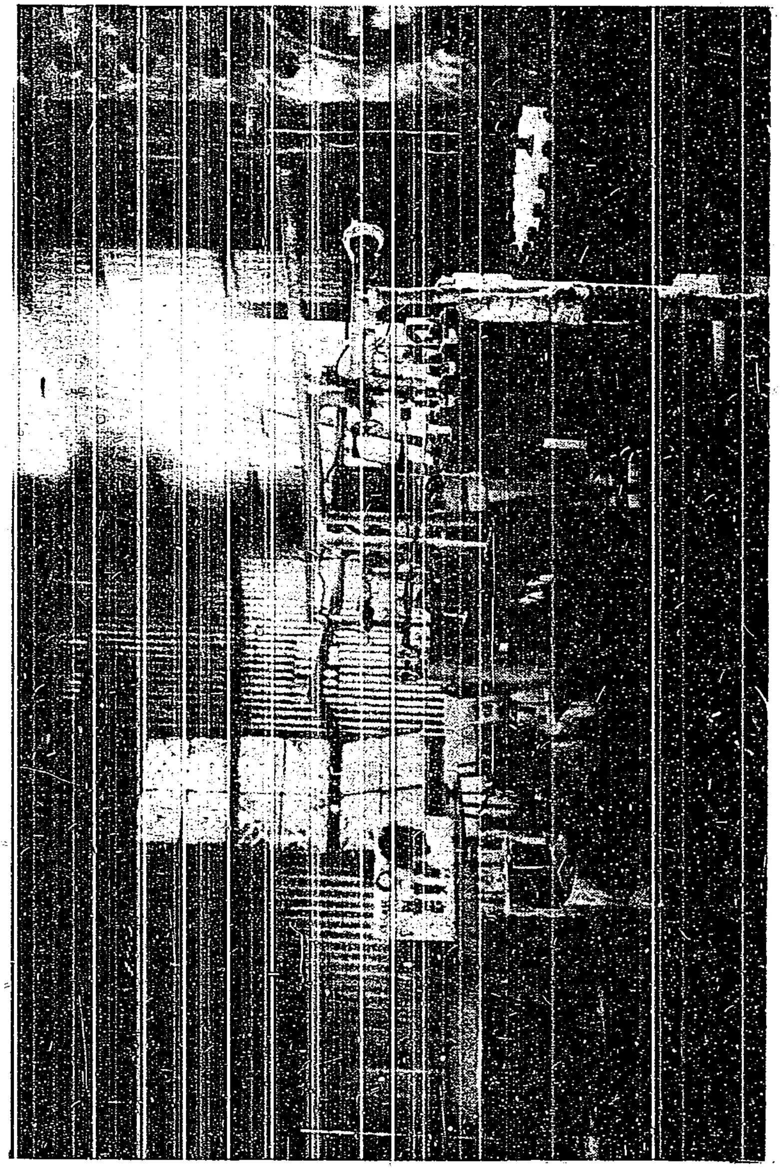

Figure 1(B)5

PROPANE PHENOL EXTRACTION PILOT PLANT

Propane Deasphalting and Dewaxing Section

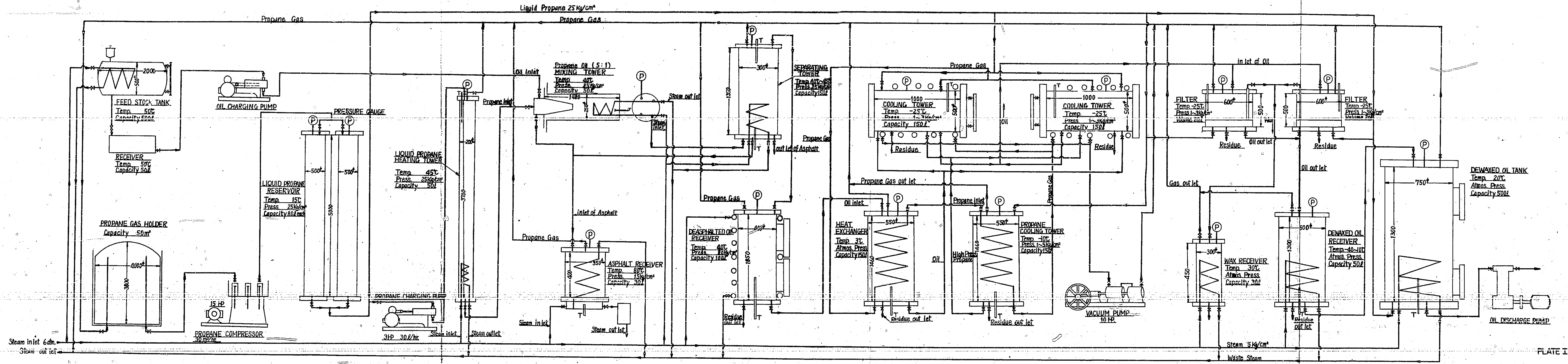

PLATE I (B)5

PILOT PLANT FOR PROPANE PHENOL SOLVENT EXTRACTION

(PROPANE DEASPHALTING AND DEWAXING)

ENCLOSURE (B) 6

PILOT PLANT FOR PROPANE PHENOL EXTRACTION (PHENOL EXTRACTION IN PROPANE SOLUTION)

by

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December 1945

ENCLOSURE (B)6

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)6

I. HISTORY

The history is the same as the propane deasphalting and dewaxing plant.

II. CAPACITY

This plant was designed the same capacity as the propane deasphalting and dewaxing plant.

III. OPERATING METHOD

This plant is one step extraction plant and the mixture of phenol and cresol is used as solvent. (Phenol 65% and cresol 35% (Volume)). See Figure 1(B)6 and Figure 2(B)6.

The raw material is the deasphalted and dewaxed oil from the propane deasphalting and dewaxing plant. The raw material is injected into the Extracting Tower (Volume 500 liters) from the bottom by charging pump.

The solvent is also injected into the Extracting Tower from the top by charging pump. The mixing and separating temperatures are about 40°C - 45°C. Raffinate is removed into the Raffinate Receiver (Volume 100 liters at 30°C and 20 kg/cm² pressure) from the top of the Extracting Tower and extract also into the Extract Receiver (Volume 100 liters at 30°C and 20 kg/cm²) from the bottom. Raffinate and extract enter into the two Stripping Towers (Volume 150 liters at 80°C, 1 - 3 kg/cm² pressure) and at last are taken out as the products.

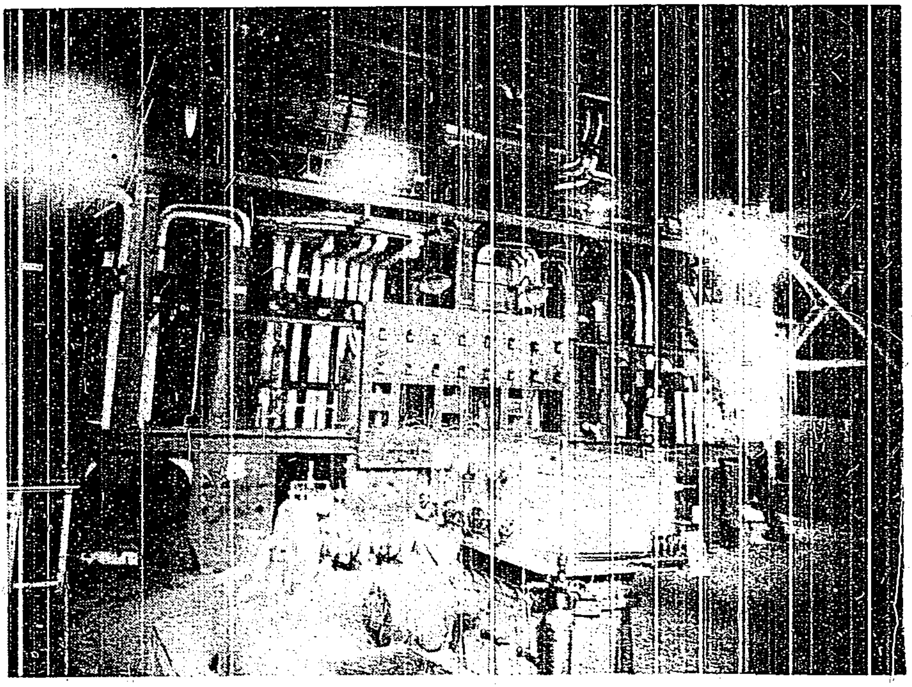

Figure 1(B)6

PROPANE-PHENOL EXTRACTION PILOT PLANT

Phenol Extraction in Propane Solution Section

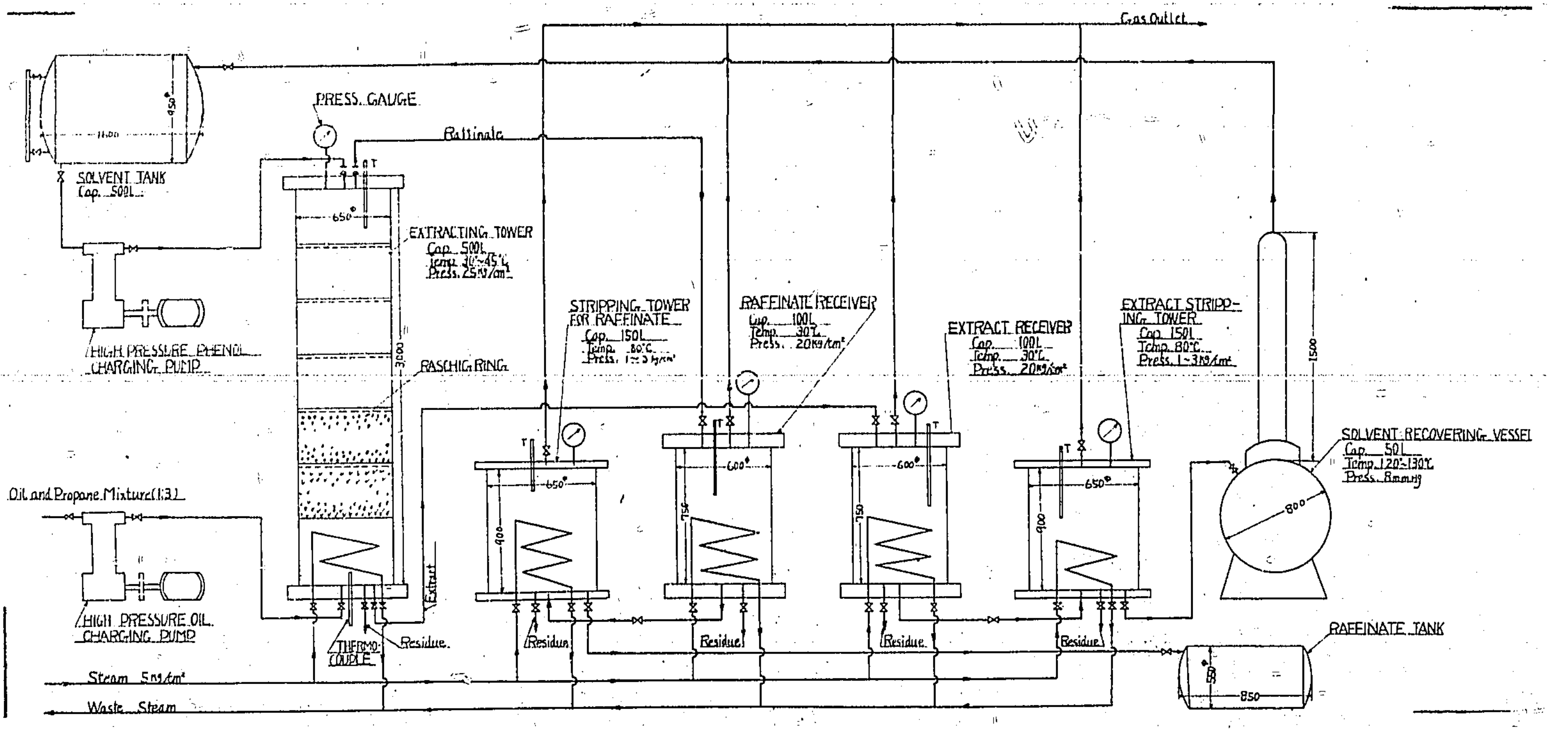

Figure 2(B) 6

PILOT PLANT FOR PROPANE PHENOL EXTRACTION

(Phenol Extraction in Propane Solution)

ENCLOSURE (B) 7

PILOT PLANT FOR HIGH PRESSURE SOLVENT EXTRACTION IN PROPANE SOLUTION WITH HIGH PRESSURE METHANE OR HYDROGEN

by

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December 1945

ENCLOSURE (B)7

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)7

I. HISTORY

This plant was designed by Eng. Lt. S. SANKA and built at the Fourth Research Laboratory in 1943. (See Figure 1(B)7.)

II. CAPACITY

About 10 liters at one time (for raw materials).

III. OPERATING METHOD

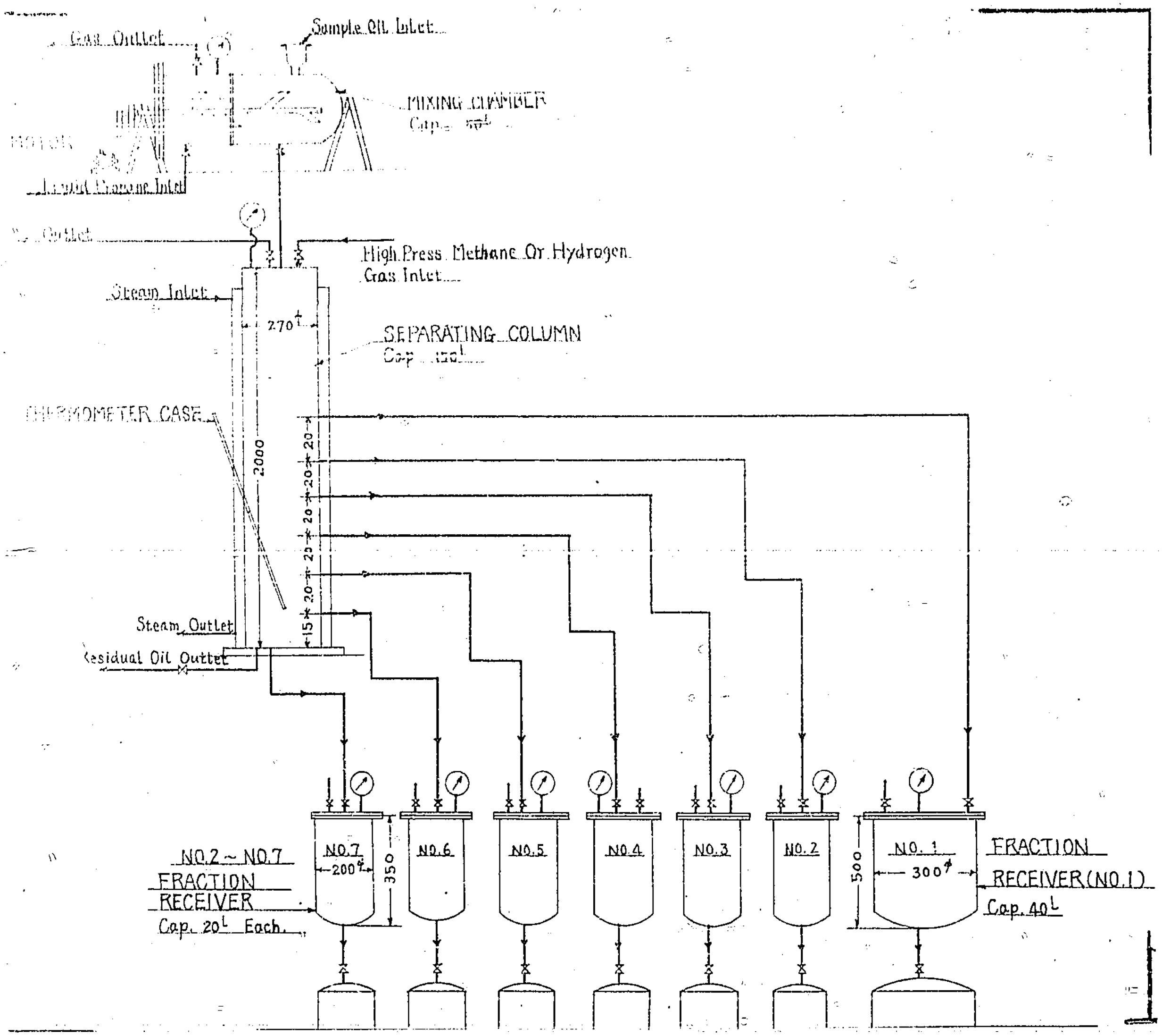
In general, components of oils are separated by distillation, but the cracking of oil by heat can hardly be avoided at higher temperatures. To avoid this cracking of oils by heat, it was intended to separate the components of oil in propane solution at a high pressure of methane or hydrogen gas.

A sample oil which contained no asphalt and liquid propane was charged in to the mixing chamber and was agitated by the motor. Then the true solution of oil and liquid propane was obtained, which was introduced into the separating column. Methane or hydrogen gas from the bomb was put into the separating column. These gases were partly dissolved in the propane solution, and then the solvent action of the liquid propane was changed and the higher molecular weight components of oil were at first separated. Increasing the pressure of methane results in amount of dissolved methane being increased, and lower molecular weight components should be separated.

For this reason many components of oil should be separated physically according to the difference of molecular weight.

However, only the experimental apparatus was erected and it was not operated because of the interference of other researches.

ENCLOSURE (B)7



PILOT PLANT FOR HIGH PRESSURE SOLVENT EXTRACTION
IN PROPANE SOLUTION WITH HIGH PRESSURE METHANE OR HYDROGEN

ENCLOSURE (E)7

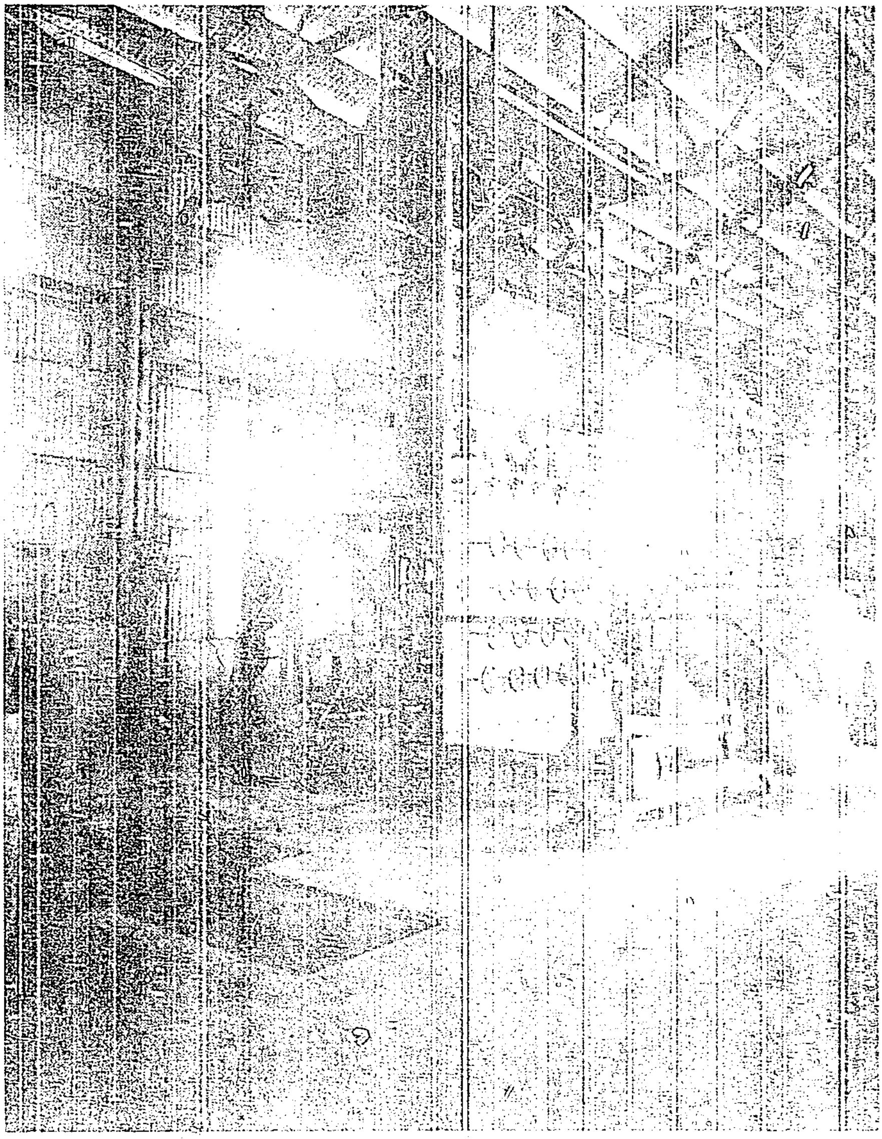


Figure 7(E)

PILOT PLANT FOR HIGH PRESSURE SOLVENT EXTRACTION
IN PROPANE SOLUTION WITH [illegible]

ENCLOSURE (B) 8

PILOT PLANT
FOR ACETONE-BENZENE DEWAXING

by

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December 1945

ENCLOSURE (B)8

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)8

I. HISTORY

This plant was designed and built by Sendagi Seisakusho at the First Naval Fuel Depot in 1944. (See Figure 1(B)8 and 2(B)8).

II. CAPACITY

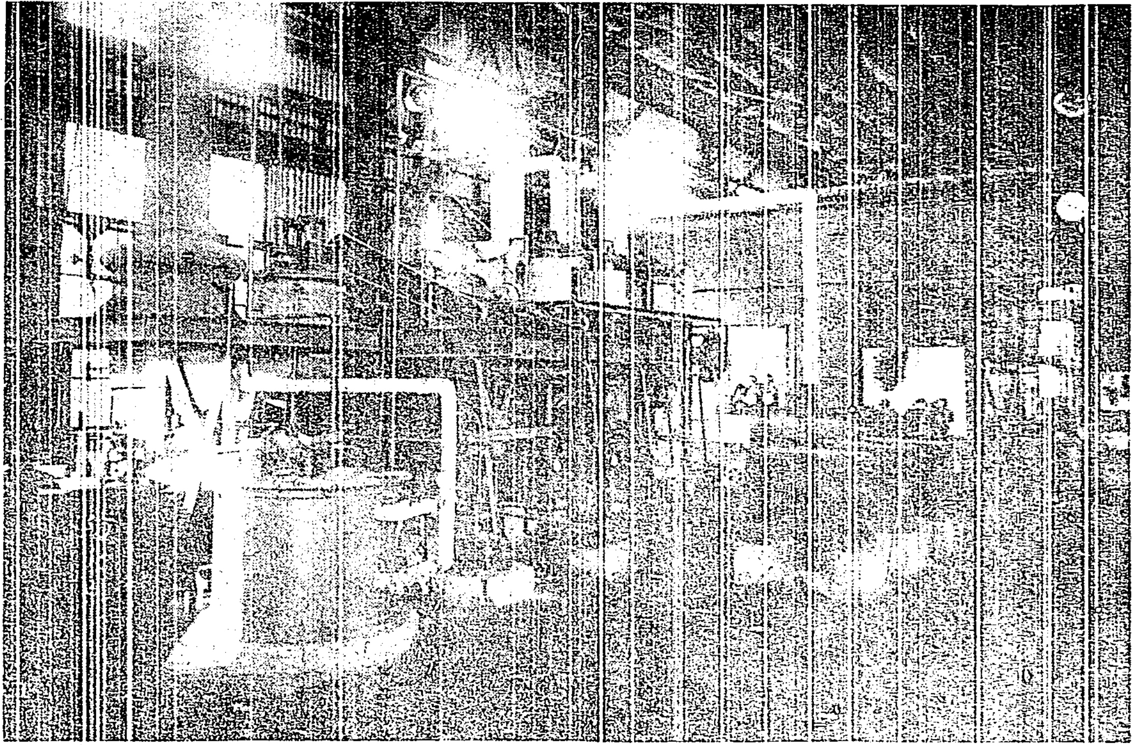
20 liters of raw material per one operation.

III. OPERATING METHOD

This plant is the three step cooling and filtering one. The mixture of acetone and benzene (acetone 60% benzene 40%) is used as solvent. Cooling is carried out by liquid ammonia. (Cooling machine has 1 cooling ton capacity)

The raw material and the solvent are mixed in the mixing vessel at 40°C to 50°C (vol 50 lit) with the solvent ratio 5:1 or 4:1. And then the mixture is transported into the filter of solution to refine (vol 200 lit at 30°C)

The mixture enters into the 1st cooler and the cooled mixture at 0°C to 10°C is transported into the 1st crystallizing vessel and then filtered by the 1st filter press through the gear pump. The 1st filtrate is transported into the 2nd cooler and cooled at -10°C to -0°C and filtered by the 2nd filter press. The 2nd filtrate is transported into the 3rd cooler and cooled at -30°C to -10°C and filtered by the 3rd filter press. At last the dewaxed oil is transported into the solvent stripping tower to separate the oil and the solvent.



PILOT PLANT FOR ACETONE-BENZENE DEWAXING

ENCLOSURE (B)8

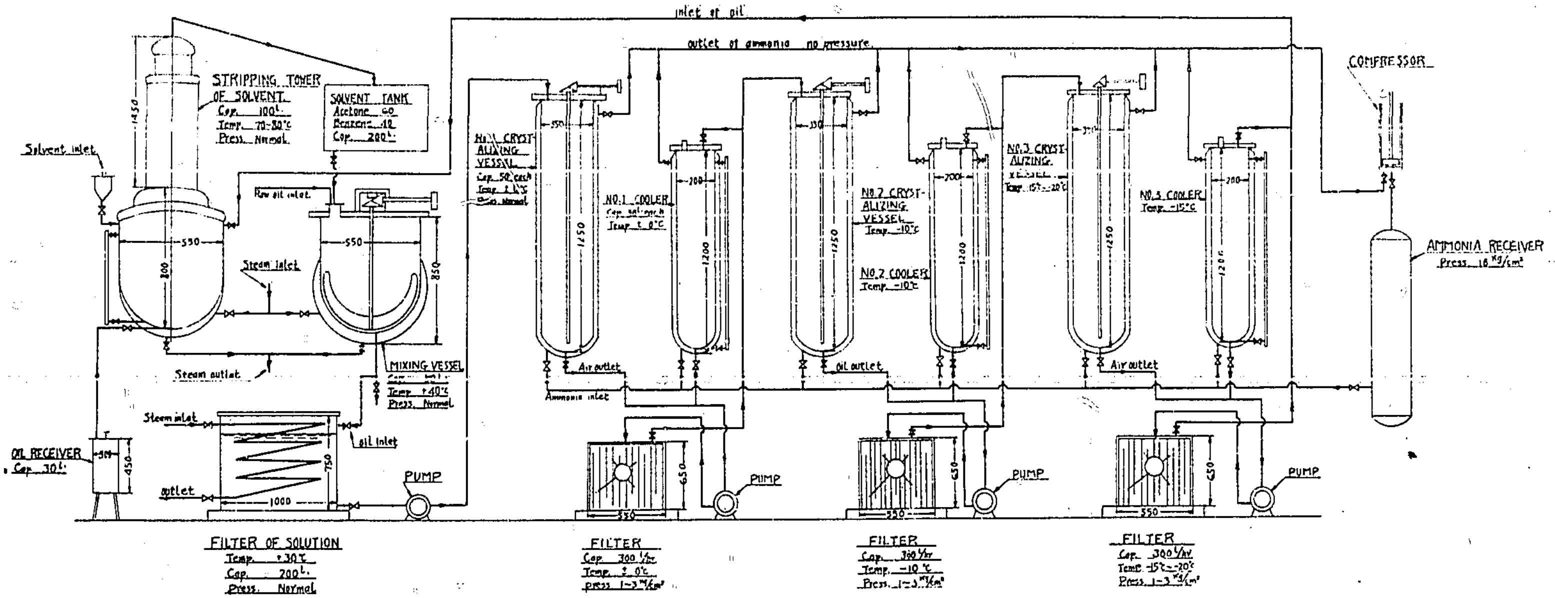


Figure 2(B)8

PILOT PLANT FOR ACETONE-BENZENE DEWAXING

ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)9

I CAPACITY

Capacity is 10 kl/day for raw material.

II OPERATING METHOD

The raw material is transported into the pipe-still through the heat exchanger from the three feed tanks (volume 50 ton for each one) by the feed pump.

The quantity of charge is controlled at 700 liters per hour at the pressure of one kg/cm^2 by the controlling valve of the feed pump.

This pipe-still is heated by the injection of the heavy oil and the superheated vapour of 5 atmospheres pressure and 600°C is used for flashing of the raw material into the fractionator.

The flashing temperature is about 340°C (calculated temperature) and the vacuum at the top of the fractionator reaches 15mm Hg by the three-step steam jet.

300 kg/hr of vapour at 10 atmospheres, and 17 kl/hr of water are needed for this three-step steam jet.

In this fractionator, four fractions, i.e., cut first drop -250°C, cut 250°C-280°C, cut 280°C- 320°C- are separated. (Calculated temperature).

Scale of the Fractionator

Diameter............ 480Φ
Height.......... 14,000Φ
Bubble plates......... 36

The first fraction is taken out from the top of the fractionator and transported into the first fraction tank (capacity 50 tons) through the condenser and the first cooler (volume 400 liters) by the feed pump of one kl/hr capacity.

The second and third fraction are taken out into the first and second stripping tower (each volume 200 liters) and transported into the second and third fraction tank (each volume 50 tons) through the second and third cooler (each volume 500 liters) by the feed pumps of one kl/hr capacity.

The residual oil is entered into the bottom tank (capacity 50 tons) through the bottom receiver (volume 500 liters) and the heat exchanger by the feed pump of 1.5 kl/hr capacity.

Table I(B)9
SCALE OF THE PIPE-STILL

		Preheating Part	Heating Part
Coil	Diameter	3/4'	3/4'
	Length	64 m	85 m
Temperature		150°C	350°C
Pressure		1 kg/cm^2	1 kg/cm^2

ENCLOSURE (B)9

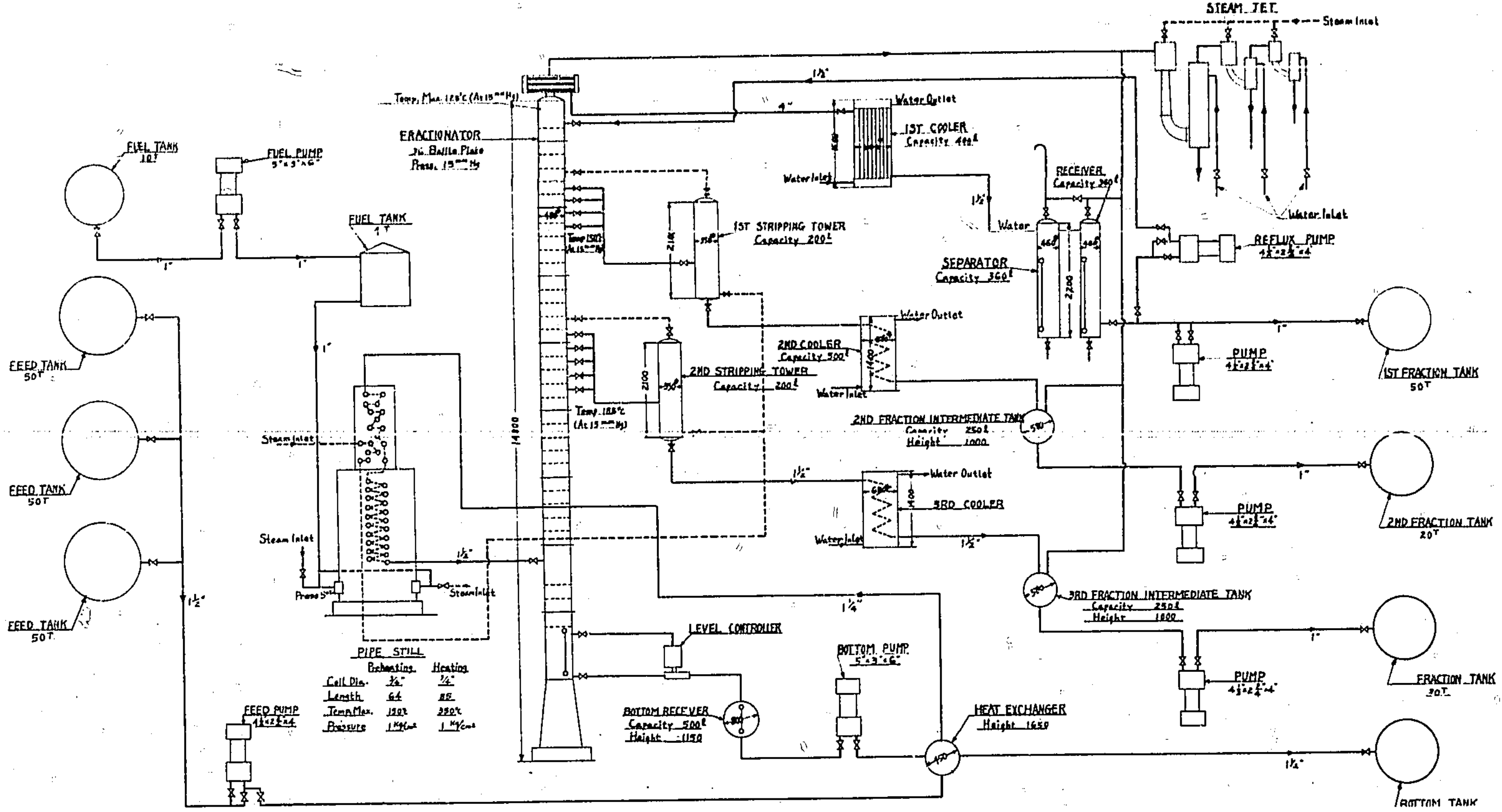


Figure 1(B)9

FLOW SHEET OF PILOT PLANT CONTINUOUS VACUUM DISTILLATION

ENCLOSURE (B) 10

STUDIES ON THE SYNTHESIS OF AERO-ENGINE OILS FROM PARAFFIN WAX

by

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Research Period: 1940-1945

Prepared for and Reviewed with Authors by
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December 1945

ENCLOSURE (B)10

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)10

SUMMARY

The object of this project was to obtain a good aero-engine oil from the cracked distillate of paraffin wax, and its results may be summarized as follows:

1. Studying the optimum conditions for polymerizing the cracked distillate of wax to obtain a good oil, i.e. the amount of $AlCl_3$, the temperature of dechlorination of crude polymer, and the available fraction of cracked distillate. The amount of $AlCl_3$ was decreased from 5% to 1% using the waste catalyst for the first stage of the polymerization of the cracked distillate of waxes. The temperature of dechlorination of the crude polymer was kept at 100-150°C to produce a low pour point oil, and the available fraction of the cracked distillate was from the first drop to 300°C.

2. To improve the stability of the polymerization product of the cracked wax, the product was extracted with 1.5 vols. of phenol-cresol mixture and the viscosity ratio in the British Air Ministry Oxidation Test was decreased from 2.07 for the original oil to 1.43.

3. By the addition of aromatic compounds, a minute amount of elementary sulphur, or both, to the cracked distillate during the polymerization, the stability of the product was considerably improved, that is, the viscosity ratio of the products was 1.2-1.5 and no undesirable effect was observed in the engine test.

4. The blended product of synthetic aero-engine oil with 10-20% of natural oil such as Texaco Airplane oil #120 or the acid treated distillate of Selia, Milli or Niizu crude oil, had good oxidation stability, the viscosity ratio being of the order of 1.3-1.6.

5. The cracked distillate of paraffin wax was polymerized with the residual oil of NIIZU or Miri crude oil or its refined oil, and the product had good oxidation stability, with a viscosity ratio of 1.5-1.6.

6. Studies were conducted on the cracking of the crude Barisol-wax obtained from the Barisol-dewaxing plant, but insufficient results were obtained before the termination of the war.

I. INTRODUCTION

The industrial manufacture of aero-engine oil from paraffin wax has been in operation since 1942 at the Fuel Depot at Balikpapan in South Borneo. The synthetic oil obtained was inferior in regard to oxidation stability and it was necessary to improve this property. Studies on this problem, therefore, were conducted from 1940 to 1944. On the other hand the supply of paraffin wax in Japan was poor, and studies were made on the preparation of aero-engine oil from Barisol-wax, in order to utilize the by-product of Japanese Barisol-dewaxing plants. These investigations have been carried on since March, 1945.

II. DETAILED DESCRIPTION

A. Investigations on the Conditions of Polymerization of Cracked Wax to Prepare Aero-Engine Oils

Researches on this problem gave the following results:

1. When the waste catalyst was used during the first stage of polymerization of cracked wax, the amount of new $AlCl_3$ necessary for the polymerization was decreased from 5% to 1%, and the reaction temperature of polymerization was easily kept constant.

2. When the dechlorination temperature of the crude polymer was kept within the range from 100°C to 150°C, it was found that the pour point of the product was about 5°C lower than that of the product dechlorinated at higher temperatures (200°C or over).

3. For the production of the aero-engine oil, the entire fraction of cracked wax boiling below 300°C can be used.

B. Investigations on the Solvent Refining of the Polymerization Product of Cracked Wax

The synthetic aero-engine oil prepared by polymerizing a fraction of cracked distillate of paraffin wax boiling from 60°C to 300°C was extracted with a mixture of phenol and cresol (60 : 40, respectively, by volume) at 40°C for 1 hour, and the results shown in Table I(B)10 were obtained.

From these studies, it was recognized that the optimum amount of solvent to improve the oxidation stability was 150% and the viscosity ratio by the British Air Ministry Oxidation Test was lowered from 2.07 to 1.43.

C. Investigations on the Condensation of Cracked Wax with Aromatic Compounds or Sulphur Compounds

1. **Investigations on the Condensation of Cracked Wax with Aromatic Compounds.** A fraction boiling from 60°C to 300°C of cracked paraffin wax was condensed with several aromatic compounds, and the results are tabulated in Table II(B)10.

   From these results it can be concluded that by condensing the cracked distillate with aromatic compounds, the oxidation stability of synthetic aero-engine oils is considerably improved.

2. **Studies on the Condensation of the Cracked Wax with Elementary Sulphur.** Studying the polymerization of the cracked distillate of waxes with elementary sulphur, the results shown in Table III(B)10 were obtained. These results showed that the addition of elementary sulphur was very effective in improving the oxidation stability of the products. Based on these results, a cracked distillate fraction boiling from 150°C to 200°C was polymerized with 5% of elementary sulphur at 150°C for 25 hours in the presence of 10% $AlCl_3$ and with this polymerization product the cracked distillate boiling from 60°C to 300°C was polymerized under the same conditions shown in Table III(B)10. The results obtained are given in Table IV(B)10.

3. **Condensation of Cracked Distillate with Elementary Sulphur and Naphthalene.** To investigate the joint effect of elementary sulphur and naphthalene on the oxidation stability of the product, cracked wax boiling from 60°C to 300°C was condensed with various amounts of

elementary sulphur and naphthalene and the results shown in Table V(B)10 were obtained.

It was found that the co-polymerization of the cracked wax with elementary sulphur and naphthalene yielded an excellent aero-engine oil having a viscosity ratio of 1.14. These results suggested the method of preparing a superior lubricating oil.

4. Tests on the Polymerization Product of Cracked Wax with Elementary Sulphur.

a. Corrosion Test. The polymerized product containing 0.1% sulphur was tested in respect to its corrosion to copper plate, and no corrosion was observed.

b. The wear and carrying capacity of the polymerization product containing 0.1% sulphur (G 120 S) was compared with that of the synthetic lubricant prepared from paraffin wax at the Naval Fuel Depot at Balikpapan (G 120 B) on a Timken Machine. The results are given in Table VI(B)10, and it was found that the sulphur containing polymerized oil had the higher load carrying capacity.

c. Engine Test by Mono-cylinder Engine. Test of G 120 S for 20 hours in a mono-cylinder test engine, "Kinsei 40 Type" showed this oil stable to oxidation and no undesirable characteristics were noted.

D. Investigation of Blends of Natural Lubricating Oil with the Synthetic Polymerization Product of Cracked Wax

A synthetic lubricant produced in the Naval Fuel Depot at Balikpapan was blended with several natural refined lubricants and tested for stability. The results are given in Table VII(B)10, and it was observed that upon blending with natural lubricant, the stability of the product was sufficiently improved.

E. Investigation of the Polymerization of Cracked Wax with Topped Crude Oil

A fraction of the cracked distillate of paraffin wax boiling from 60°C to 300°C was polymerized with several topped crude oils. The results are tabulated in Table VIII(B)10 and an interesting observation is that the addition of an unrefined topped crude oil to the polymerization process produced a stable aero-engine oil.

F. Investigations on the Cracking of Barisol-Wax

Barisol-Wax, obtained from the Barisol-dewaxing plant at the Third Naval Fuel Depot, was thermally cracked under various laboratory conditions, and the properties of the cracked distillate were compared with those of the sweated paraffin wax.

1. The properties of Barisol-Wax and the sweated paraffin wax are given in Table IX(B)10.

2. These waxes were thermally cracked with a charging velocity of about 150 gm/hr through a silica tube of the following dimensions heated in an electric furnace:

Inner diameter of the silica tube: 20mm
Length of the silica tube in the furnace: 580mm

3. The results obtained are shown in Table X(B)10. It was observed that in the case of the Barisol-wax the amount of coke deposited in the cracking tube was extremely large, the color of cracked distillate quickly changed from light yellow to dark brown, and a dark brown deposit formed on standing. These phenomena may depend on the presence of diolefins in the cracked distillate and the prevention of the formation of di-olefins will be necessary in preparing aero-engine oils from the cracked distillate of Barisol-wax by any means. Such a method is now unknown.

III. CONCLUSIONS

A. In respect to the operating conditions for synthesizing an aero-engine oil from paraffin wax, studies were conducted and the following results were obtained:

1. By using the waste $AlCl_3$ at the beginning of the polymerizing step of the cracked wax, the amount of $AlCl_3$ required was reduced from 5% to 1%.

2. The optimum dechlorination temperature of the crude polymer for producing a lubricant having a lower pour point was in the range of 100°C to 150°C.

3. For the preparation of an aero-engine oil, the entire fraction of cracked wax boiling under 300°C could be used.

B. By extraction of the polymerization product of cracked wax at 40°C with 1.5 volumes of the mixed solvent consisting of 40% phenol and 60% cresol, the viscosity ratio of the raffinate could be lowered from 2.07 to 1.43.

C. By condensation of the cracked wax with aromatic compounds, i.e. benzene, naphthalene and anthracene, the viscosity ratio of the product using the British Air Ministry Oxidation Test was lowered from 2.2 to 1 .

Polymerizing the cracked wax with 0.1-0.5% of elementary sulphur, a superior aero-engine oil was obtained, having a viscosity ratio of 1.3. When both elementary sulphur and naphthalene were used in the polymerization process, the viscosity ratio of the product was further lowered to 1.14.

D. By blending a natural lubricant with the polymerization product of the cracked paraffin wax the viscosity ratio of the product was lowered to 1.3.

E. The addition of topped crude oil during the polymerization process lowered the viscosity ratio of the products to 1.5.

F. In the thermal cracking of Barisol-wax, the deposition of coke in the cracking tube was excessive, and the content of diolefins in the cracked distillate was high. Unless these two conditions are prevented, a satisfactory oil cannot be made from Barisol-wax. There is no known method for accomplishing these results.

ENCLOSURE (B)10

Table I(B)10
RESULTS OF EXTRACTION OF THE SYNTHETIC AERO-ENGINE OIL

Solvent (vol.% to crude polymer)	Yield of raffinate (%)	Vis. in S.U.S.		Vis. index	Conradson's carbon (%)	Acid Value	Saponification Value	Iodine Value	Pour pt. (°C)	Viscosity Ratio
		at 100°F	at 210°F							
0	100	1.274	115	112	0.412	0.08	0.18	20.5	-16	2.07
50	85	1.268	117	114	0.403	0.08	0.17	20.4	-16	2.06
100	82	1.322	119	113	0.354	0.08	0.10	20.2	-15	1.49
150	86	1.322	121	114	0.370	0.08	0.13	21.2	-14	1.43
200	72	1.367	123	114	0.308	0.07	0.16	21.1	-13	1.59
250	77	1.383	127	116	0.448	0.09	0.18	23.9	-13	1.57
300	24	1.357	129	118	0.32	0.06	0.10	22.2	-14	1.61

Table II(B)10
RESULTS OF CONDENSATION OF CRACKED DISTILLATE OF WAXES WITH AROMATIC COMPOUNDS

Amount of raw material polymerized (%)				Cond'n-Polymerization			Viscosity ratio of the product
Cracked distillate	Naphthalene	Benzene	Anthracene	Amount of $AlCl_3$	Temp. (°C)	Time (hr)	
100	-	-	-	5	50	10	2.08
80--90	20—10	-	-	5	80	10	1.25
70	15	15	-	5	80	10	1.26
85	5	5	5	5	80	10	1.30

Table III(B)10
POLYMERIZATION OF CRACKED DISTILLATE OF WAXES WITH ELEMENTARY SULPHUR

Amount of sulphur added (wt.%)	Condition of Polymerization			Viscosity in S.U.S.		Viscosity Index	Viscosity Ratio	Remarks
	Amount of $AlCl_3$ (%)	Temp (°C)	Time (hr)	at 100°F	at 210°F			
0.05	5	50	10	646.8	83.7	122	2.09	Sulphur content of product was 0.1%
0.2	5	50	10	638.6	83.3	123	1.72	
1.0	5	50	10	939.2	90.6	122	1.48	
2.0	5	50	10	933.2	106.0	122	1.61	
0.1	5	80	10	120.4	116.3	106.2	1.52	
0.05	5	80	18	134.5	126.2	118.8	1.77	

ENCLOSURE (B)10

Table IV(B)10
POLYMERIZATION OF A CRACKED DISTILLATE OF WAX WITH THE SULPHUR CONTAINING POLYMER

Amount of submaterial added (wt.%)	Condition of Polymerization			Viscosity in S.U.S.		Viscosity Index	Viscosity Ratio
	Amount of $AlCl_3$ (%)	Temp. (°C)	Time (hr)	at 100°F	at 210°F		
2	5	80	8	1754	145	113.7	1.33

Table V(B)10
CONDENSATION OF THE CRACKED WAX WITH ELEMENTARY SULPHUR AND NAPHTHALENE

Amount of naphthalene added (wt.%)	Amount of sulphur added (wt.%)	Condition of Condensation*		Viscosity in S.U.S.		Viscosity index	Viscosity ratio
		Temp. (°C)	Time (hr)	at 100°F	at 210°F		
10	none	50	10	1857	144.6	110	1.48
10	0.1	50	10	1442	122.1	110	1.25
10	0.5	50	10	1796	138.0	103	1.16
1	0.1	80	10	2078	163.7	113.8	1.60
2	0.1	80	10	1421	120.4	109.3	1.41
5	0.1	80	10	1398	115.9	106.5	1.29
10	0.1	80	10	1526	124.2	108	1.14

* In all cases 5% $AlCl_3$ (wt) was used.

Table VI(B)10
TIMKEN MACHINE TEST

Samples	Test temp. (°C)	Load lb/m^2	Time (min)	Width of wear test metal (mm)	Load carrying capacity (kg/cm^2)
G 120 B	85	23	3	0.89	180
G 120 S	85	30	4	0.95	220

ENCLOSURE (B)10

Table VII(B)10
BLENDING OF THE NATURAL LUBRICANT TO THE POLYMERIZATION PRODUCT OF THE CRACKED WAX

Kinds of Mixing*	Viscosity in S.U.S. at 210°F	Viscosity index	Viscosity ratio
Base oil (G 120 B)	118.6	94.6	2.26
95% G 120 B + 5% Texaco Airplane #120	119.3	94.2	1.75
90% G 120 B+10% Texaco Airplane #120	114.3	94.1	1.62
85% G 120 B+15% Texaco Airplane #120	119.3	94.1	1.48
80% G 120 B+20% Texaco Airplane #120	119.3	94.5	1.31
90% G 120 B+10% K 120 K (produced in the Third Naval Fuel Depot)	119.5	93.5	1.48
80% G 140 B+20% Texaco Airplane #80	119.7	104.8	1.38
60% G 140 B+40% Texaco Airplane #100	120.6	102.9	1.84
90% G 140 B+30% of acid treated Seria oil	127.1	95.2	1.84
90% G 140 B+10% of acid treated Mili oil	113.1	95.6	1.62
90% G 140 B+10% of acid treated Niizu oil	126.2	96.4	1.56

* All per cents are volume per cents.

Table VIII(B)10
POLYMERIZATION OF THE CRACKED WAX WITH THE TOPPED CRUDE OIL

Amount of topped crude oil added (vol.%)	Time* (hr)	Viscosity in S.U.S. at 210°F	Viscosity index	Viscosity ratio
20% residue over 200°C of Niizu crude oil	10	123	107	1.54
20% of acid treated residue over 200°C of Niizu crude oil	10	107	100	1.48
10% of residue over 200°C of Mili crude oil	8	115	107	1.62

* In all cases, temperature, 80°C, and 5% $AlCl_3$ (wt) were used.

ENCLOSURE (B)10

Table IX(B)10
PROPERTIES OF BARISOL-WAX AND THE SWEATED PARAFFIN WAX

Samples	Crude Barisol-wax	Pure Paraffin Wax
Density (d^{60}_{4})	0.847	0.778
Flash point (°C)	207.7	-
Ash (%)	0.013	-
Melting point (°C)	47.5	52.5
Conradson's carbon (%)	0.66	0.09
Wax content by Holde's method (%)	30	88

Table X(B)10
CRACKING OF BARISOL-WAX

No. of Exp.	1	2	3
Samples	Barisol-wax	Barisol-wax	Sweated Paraffin
Cracking temperature (°C)	550°C	500°C	550°C
Yield of cracked distillate boiling below 300°C	55	50	30
Amount of coke deposited in the silica tube	0.2	0.05	trace
Properties of the Cracked Distillate			
Density (d^{15}_{4})	0.80	-	
Iodine value	Ca 150	-	
Color	quickly changed from light yellow to dark brown	quickly changed from light yellow to dark brown	light yellow
Deposit	deposit formed on standing	deposit formed on standing	none

ENCLOSURE (B) 11

STUDIES ON THE COMPOSITION OF PARAFFIN WAX IN CRUDE OIL

by

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Research Period: 1943

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)11

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)11

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

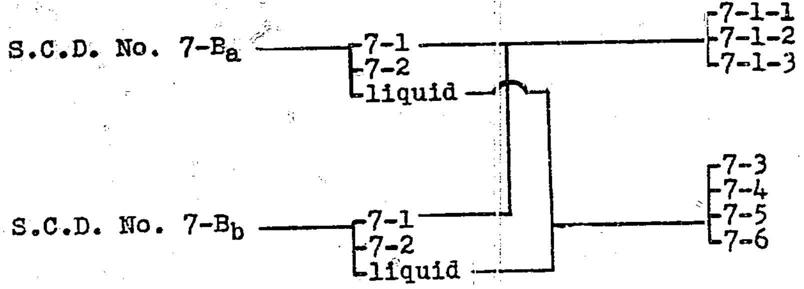
Hg, passing nitrogen into the distillation flask through a capillary tube, and measuring the pressure with a McLeod's manometer between the receiver and vacuum pump.

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.

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}.

ENCLOSURE (B)11

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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

ENCLOSURE (B)11

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

ENCLOSURE (B)11

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

ENCLOSURE (B)11

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

ENCLOSURE (B)11

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

ENCLOSURE (B)11

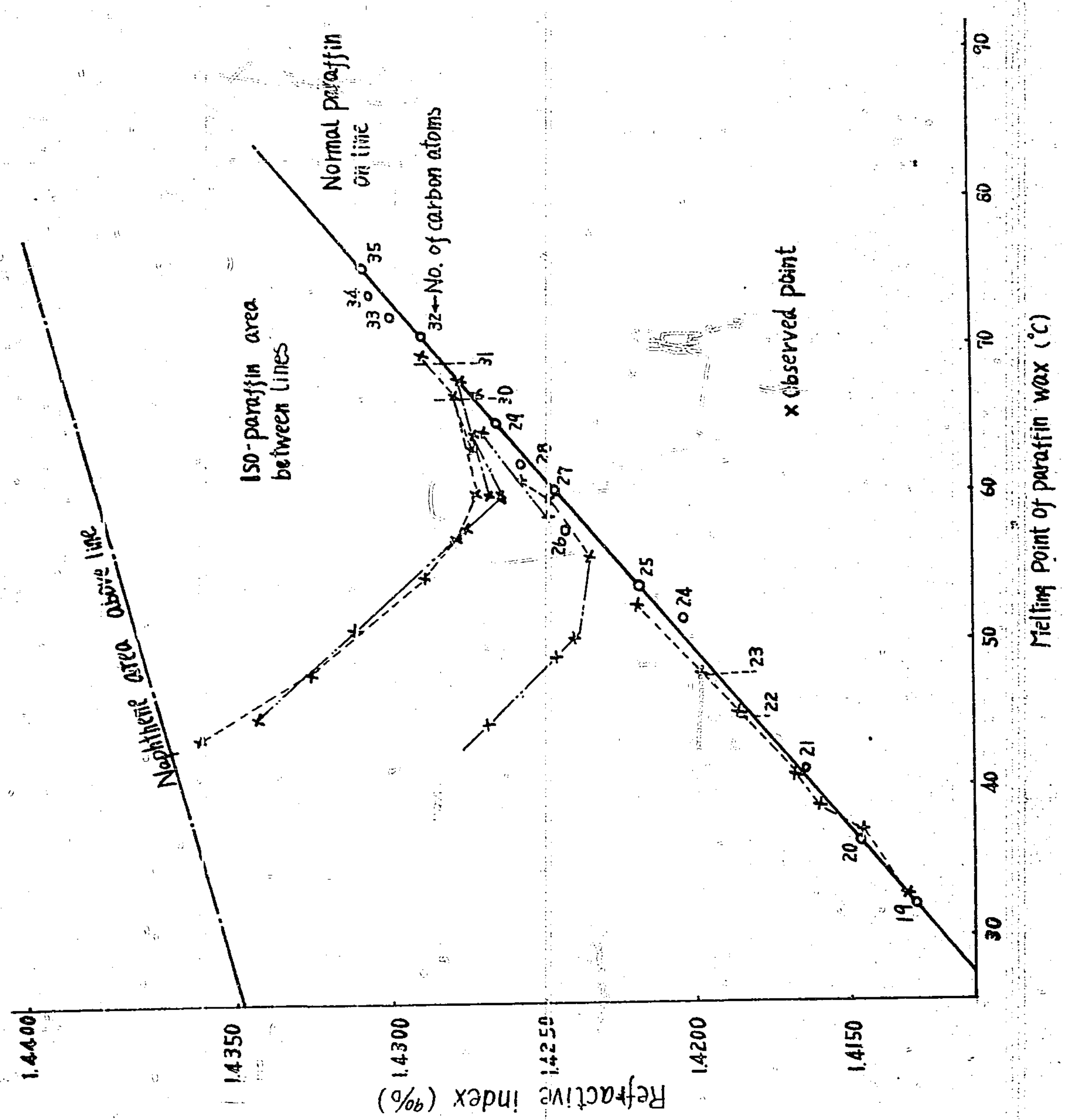

Figure 1(B)11
CHARACTERISTICS OF SANGA SANGA WAX

ENCLOSURE (B)11

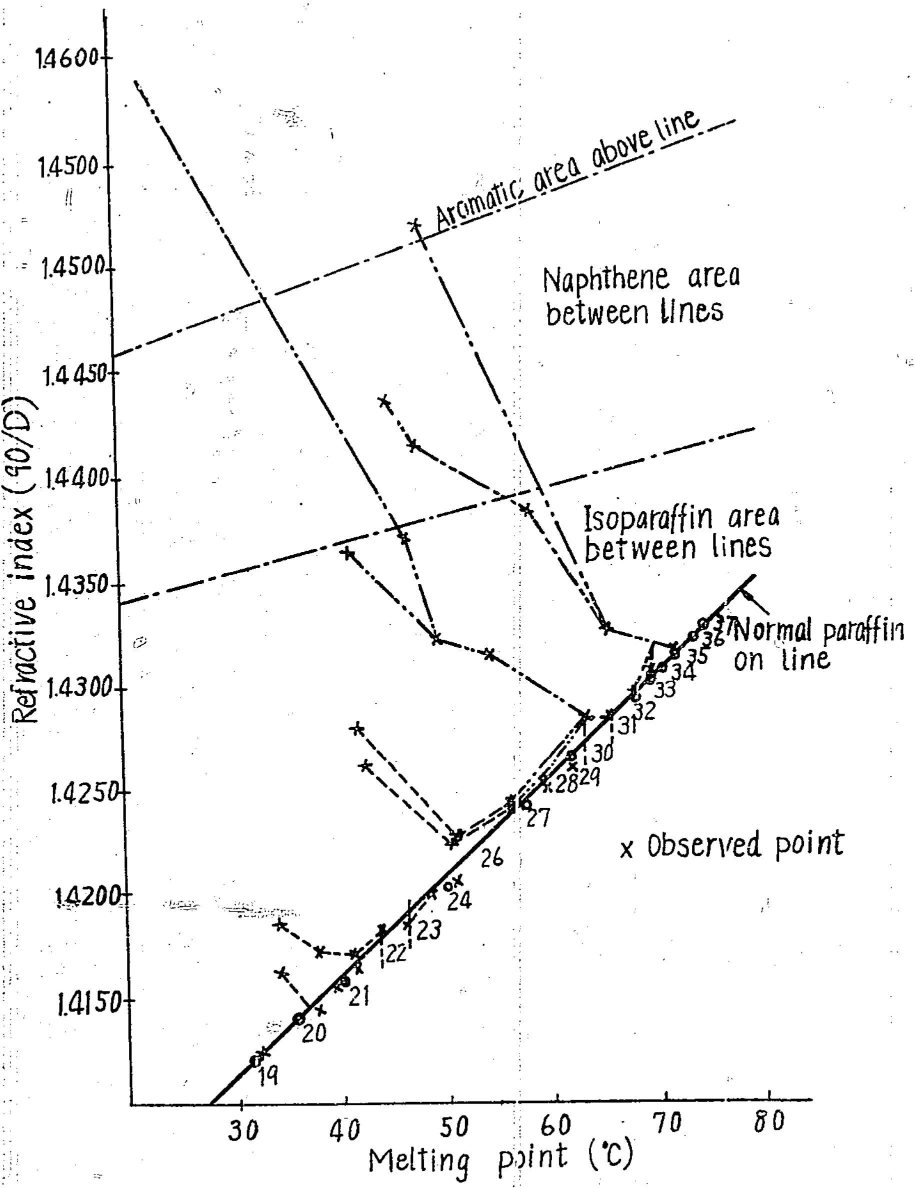

Figure 2(B)11
CHARACTERISTICS OF PENDOPO WAX

ENCLOSURE (B)11

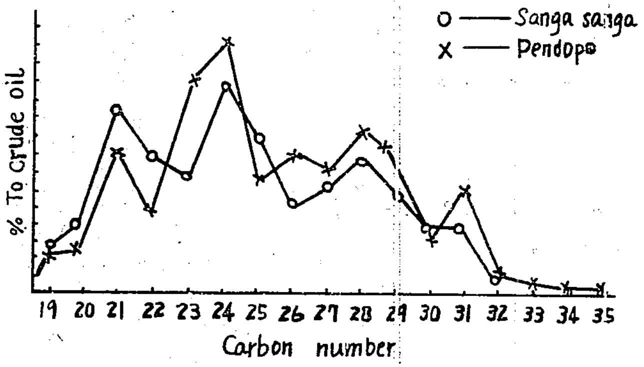

Figure 3(B)11
DISTRIBUTION OF NORMAL PARAFFIN

ENCLOSURE (B) 12

STUDIES ON THE SYNTHESIS OF AERO-ENGINE OIL FROM FATTY OILS

by

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Research Period: 1943-1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)12

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)12

SUMMARY

Subjecting a sodium soap of coconut oil to dry distillation at 500°C, olefins were obtained which were distilled with 1% of metallic sodium or 10% of solid caustic soda at temperatures below 300°C. This oil was polymerized in the presence of 10% of aluminium chloride at 80°C for 8 hours, dechlorinated, and topped to get rid of light oil. The yield of aero-engine oil #120, thus obtained from coconut oil, was 20.5%.

Fatty oils suitable as raw materials for this method were sought and it was found that fatty oils other than coconut oil and palm oil must not be used without being hydrogenated. Using the above-mentioned aero-engine oil mixed with 30% of the natural mineral oil, a full size engine test was successful.

I. INTRODUCTION

A. History of Project

It was already known that hydrocarbons mainly composed of olefins can be produced by the dry distillation of alkali soaps of fatty acids. In Japan, the dry distillation of soaps was considered as a method for obtaining hydrocarbon fuels from fatty oils. At the beginning of this research in June 1943, it was reported from the Nakabe Laboratory in TOKYO that lubricating oils could be obtained from hydrocarbons produced by the dry distillation of sodium soaps of coconut oil followed by polymerization in presence of anhydrous aluminium chloride. Although this report was short and incomplete, it presented new ideas for the synthesis of lubricating oils from fatty oils.

If a yield of aero-engine oil could be obtained greater than 15% of coconut oil and the amount of aluminium chloride could be held to less than 10% of olefins polymerized, this method could be developed to commercial scale. In dry distillation the Knowles type coke oven was used in order to save steel materials. At that time, since coconut oil could be obtained, tests were mainly centered on that soap. It was found that by this method aero-engine oil can be obtained from coconut oil, and this work was centered on finding the best method of removing the poisonous oxygen compounds in the cracked distillate of sodium soap of fatty oil.

This method was not brought to the commercial scale because the plant which was being constructed at the Sixth Naval Fuel Depot in FORMOSA was bombed.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr. A. WAKANA
Chem. Eng. Sub. Lieut. M. DEHARA

II. DETAILED DESCRIPTION

A. Test Procedures

Coconut oil was hydrolyzed by the ordinary autoclave method to glycerine and fatty acids. The fatty acids were neutralized by sodium carbonate and completely by sodium hydroxide. Sodium soap in flake was dried to less than 10% of water content and packed in paper bags each containing 20 kg.

In the following experiments, mainly the above-mentioned soap was used. At first a glass distilling flask was used in order to observe the changes during the dry distillation. Next, a copper flask was used to facilitate operation, and then a 100 liter steel batch-still heated by gas burners was used for obtaining material balance. At last, in order to save steel parts, the Knowles type coke oven, which was composed of fire-bricks and had a $1{\cdot}2m^2$ bed area, was tested. This apparatus is shown briefly in Figure 1(B)12, and the procedure was as follows.

200 kg of soap were charged through a sluice valve (S) and then heated slowly by gas burners. Some water was distilled at 100°C and most of the oil vapour came off at 350-400°C. At 500°C the distillation ceased. The dry-distilled oil was redistilled in an atmospheric batch still, and the distillate boiling from first drop to 300°C was subjected to polymerization.

It was agitated with 10% of aluminium chloride for 8 hours at 80°C and at the end of that time, the product was allowed to settle, the sludge was separated and the supernatant solution of the polymerized oil was mixed with the recovered oil obtained by hydrolysis of the aluminium chloride sludge. Then, active clay and calcium hydroxide were added to the mixture of polymerized oil for dechlorination and after heating at 250°C for 1 hour, the oil was filtered. This material was vacuum topped to produce a residue of the desired viscosity. Olefins prepared by the redistillation of dry distilled oil contained some oxygen compounds which poisoned the catalytic action of aluminium chloride, so that they required a large quantity of aluminium chloride for polymerization. Studying the preliminary refining method for the dry distilled oil, it was found best for the polymerization to redistill the oil with 1% of solid NaOH to dry the distilled oil.

Stearic acid, oleic acid and other mixed fatty acids derived from palm oil, soya bean oil and their hydrogenated oils were converted to sodium soaps and then tested in glass flasks in the same manner. Each of the above-mentioned dry distilled oils was redistilled in the presence (1%) of metallic sodium up to 300°C and then fractionated to five fractions in the presence of metallic sodium. Each fraction was polymerized with 10% of $AlCl_3$ at 80°C for 8 hours. After settling for one night, the product was separated into the supernatant polymerized oil and the aluminium chloride sludge. Each of these was treated separately, and, after dechlorination, was reduced to the desired viscosity in the same manner. The decomposed oil derived from the aluminium chloride sludge, had excellent properties and the yields were better than expected. These products had a good viscosity index and a somewhat low pour point, so that these products could be used for various purposes.

B. Experimental Results:

1. A schematic flow diagram of the processes studied, showing yields and material balance, is presented in Figure 2(B)12.

2. The physical and chemical properties of the fatty acid and distilled oils from coconut oil are shown in Table I(B)12.

3. The properties of the raw material and distilled oils are tabu-

lated in Table II(B) 12.

4. Typical compositions of the dry distilled gases and residual cokes are as follows:

Composition of Dry Distilled Gas

Gas	Volume (%)
CO_2	11.6
CO	10.3
H_2	24.2
N_2	2.7
O_2	0.1
C_nH_{2n}	22.2
C_nH_{2n+2}	28.6

Analysis of Residual Coke

Water Insoluble Carbon Matter	5%
Sodium Carbonate	89%
Undecomposed soap	#6%

5. A summary of the data showing the characteristics of polymerized oils prepared by different methods is presented in Table III (B) 12.

6. The effect of the type of sodium soap used in the dry distillation on the properties of the polymerized oil is shown in Table IV (B) 12

7. A summary of the effect of the boiling range of the fraction of dry distilled oil used on the properties of the polymerized oil is shown in Table V(B) 12

III. CONCLUSIONS

1. It was possible to operate the small Knowles type coke oven for dry distillation of soaps as a batch process but problems due to the leakage of distilled vapour through the joints of firebricks and the durability of the fire-bricks used at the bottom of the coke oven, were not solved.

2. With the Lub. oil thus produced from coconut oil mixed with 30% of mid Continent mineral oil, a full size engine test by the "Kasei-1' type aero-engine was carried out successfully. The results were comparable to those obtained with the aero-engine oil #120 in actual use.

3. It was better to use the dry distilled oil after redistillation up to 300°C, than to use the oil which had not been redistilled, the product of the former showed a large yield and low pour point.

4. When the quantity of $AlCl_3$ was 15% to the distillate, the yield of aero-engine oil was 15% for coconut oil. With 10% of $AlCl_3$, the yield of product was 10%. Thus the yield of aero-engine oil was proportional to the quantity of $AlCl_3$ used.

ENCLOSURE (B)12

5. In case the dry distilled oil was redistilled with 1% of metallic sodium, a 7.5% concentration of $AlCl_3$ was sufficient to obtain a yield of 15% of the coconut oil. However, the use of metallic sodium was difficult in practice because of limited production of metallic sodium in Japan.

6. Sodium caustic soda was tried in place of metallic sodium. The use of sodium hydroxide was successful and the quantity used was reduced from 10% to 1% with but little decrease in yield of aero-engine oil. The temperature for treating with alkali could not be lowered below 250°C. A good contact of the olefins and caustic soda was desirable.

7. In place of solid caustic soda, a 40% water solution of NaOH could be used for the preliminary refining of olefines, but to obtain the same results 6% of NaOH had to be used. The presence of water had a harmful effect on the alkali refining.

8. Sodium carbonate, calcium oxide and calcium hydroxide were not as satisfactory refining agents as sodium hydroxide.

9. In the dry distillation of soaps, the presence of excess caustic soda gave good results, but it caused the corrosion of firebricks and the products required redistillation. Therefore this method was not practised.

10. In order to improve the oxidation stability of the synthetic product, the condensation of the dry distilled oil with aromatics was tested. Solvent naphtha obtained in coal carbonization gave the best result. The synthetic lubricating oil condensed with naphthalene did not show improved oxidation stability over the synthetic oils obtained from olefins derived from wax decomposition.

11. As the starting material, stearic acid was better than oleic acid, in regard to viscosity index and yield of products. The preliminary hydrogenation of fatty oils seemed promising for the process.

12. In the dechlorination process, the best products are obtained when an inert gas atmosphere is used.

Table I(B)12
PHYSICAL AND CHEMICAL PROPERTIES OF RAW MATERIAL AND INTERMEDIATES

	Dry Distilled Oil	Alkali Redistilled Oil (I.B.P. - 300°C)
Specific Gravity d(25/4)	0.7787	0.7748
Refractive Index n(25/D)	1.4330	1.4260
Specific Refraction r(25/d)	0.3357	0.3306
Acid Value	1.20	0.28
Saponification Value	2.76	0.05
Iodine Value	115.9	131.4
Mean Molecular Weight	198	187
Elemental Analysis C(%)	82.20	83.75
H(%)	13.63	14.01
(by difference) O(%)	4.18	2.24
Mean Molecular Formula	$C_{13.5}H_{26.6}O_{0.5}$	$C_{13.0}H_{26.0}O_{0.3}$
Distillation Test I.B.P. (°C)	60	68
5%	97	102
10%	114	113
5%	127	117
20%	138	134
5%	150	142
30%	160	156
5%	170	165
40%	176	174
5%	188	180
50%	193	185
5%	204	191
60%	213	197
5%	229	205
70%	245	211
5%	263	221
80%	282	235
5%	306	251
90%		270
5%		286

<u>Fatty Acids From Coconut Oil</u>

Specific Gravity	0.8925
Iodine Value	8.5
Acid Value	249.3
Melting Point	25

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Table II(B)12
PROPERTIES OF POLYMERIZED PRODUCTS

	Specific Gravity (d_4^{25})	Viscosity (S.U.S.)		Viscosity Index	Oxidation Test Viscosity Ratio	Pour Point (°C)
		100°F	210°F			
Dechlorinated Oil	0.8507	374	63	125		
Distillate (240-285°C/2.5mm)	0.8362	69.4 (R-1, 30°C)	49.6 (R-1, 50°C)			
Residual Oil (285°C-/2.5mm)	0.8573	1250	166	114	1.8	-20

(See page 157 for Table III(B)12.)

Table IV(B)12
EFFECT OF TYPE OF SODIUM SOAPS DRY DISTILLED ON SYNTHETIC OIL

No.	Stock	Yield for Stock (wt %)	Cutting Temp. (°C)	Viscosity S.U.S. 210°F	Viscosity Index
1	Coconut oil	20.5	500-	115.8	113.6
2	Palm oil	15.0	450-	122.1	113.4
3	Hydrogenated palm oil	18.5	460-	132.8	114.1
4	Fatty acid produced from fish oil	8.3	400-	111.4	75.5
5	Fatty acid produced from Tubaki Oil	14.0	460-	100.4	81.6
6	Soya bean oil	6.6	150-	61.6	54.8
7	Hydrogenated Soya bean oil	18.4	450-	146.3	118.3
8	Rape oil	15.8	450-	133.7	77.7
9	Castor oil	difficult to dry distill owing to foaming			
10	Distilled Fatty acid produced from Whale oil	27.2	460-	123.6	90.7
11	Stearic acid	24.5	450-	133.6	112.6
12	Oleic acid	17.5	430-	117.5	79.3

Table III(B)12
EFFECT OF PRELIMINARY REFINING DRY DISTILLED OIL ON PROPERTIES OF POLYMERIZED OIL

No.	Preliminary Refining Method and Special Points	Name	Refining Agent (% Used)	$AlCl_3$ (%)	Properties of Synthetic Oils Vacuum Distilled		
					Yield for Coconut Oil (%)	Viscosity (S.U.S.) 210°F	Viscosity Index
1	Not treated			15	11.8	153.8	103.6
2	Redistilled up to 300°C		-	15	15.6	117.6	101.3
3	Redistilled up to 300°C and $AlCl_3$ decreased			10	8.9	132.4	106.3
4	Redistilled with metallic sodium, $AlCl_3$ decreased	Na	1	7.5	17.7	110.1	114.9
5	Redistilled with solid caustic soda	NaOH	10	10	20.5	115.8	113.6
6	Redistilled with solid caustic soda and then condensed with solvent naphtha*	NaOH	10	10	22.4	113.2	108.3
7	Redistilled with solid caustic soda and then condensed with naphthalene	NaOH	10	10	12.6	115.7	100.3
8	Redistilled with solid caustic soda and then condensed with benzene	NaOH	10	10	17.9	97.5	102.4
9	Redistilled with caustic soda decreased NaOH	NaOH	1'	10	16.4	115.3	107.0
10	Redistilled with 40% water solution of NaOH each 2% and repeated 3 times	NaOH water solution	6	10	18.1	130.0	115.7
11	Alkali steaming redistilled	NaOH water solution	2.5	10	10.6	134.2	108.2
12	Redistilled with solid sodium carbonate	Na_2CO_3	10	10	10.6	112.2	307.4
13	Redistilled with calcium oxide	CaO	10	10	9.3	130.8	114.7
14	Redistilled with calcium hydroxide	$Ca(OH)_2$	10	10	5.4	148.3	102.4
15	Dry distilled in presence of excess caustic soda	NaOH	20	10	16.4	142.6	108.3
16	Dry distilled in presence of excess caustic soda and NaOH quantity decreased	NaOH	15	10	15.4	104.7	107.7
17	Dry distilled in presence of excess sodium carbonate	Na_2CO_3	20	10	4.6	166.4	112.2

* Properties of Solvent Naphtha

Specific gravity (d_4^{15})	0.866
Vapour Pressure (Reid, kg/cm^2)	below 0.02
Octane Number ($0.1\%(C_2H_5)_4Pb$)	102

Composition (Vol.%)

Aromatic	99.5
Unsaturate	0.4
Sulphur	0.015

Distillation Test of Solvent Naphtha (°C)

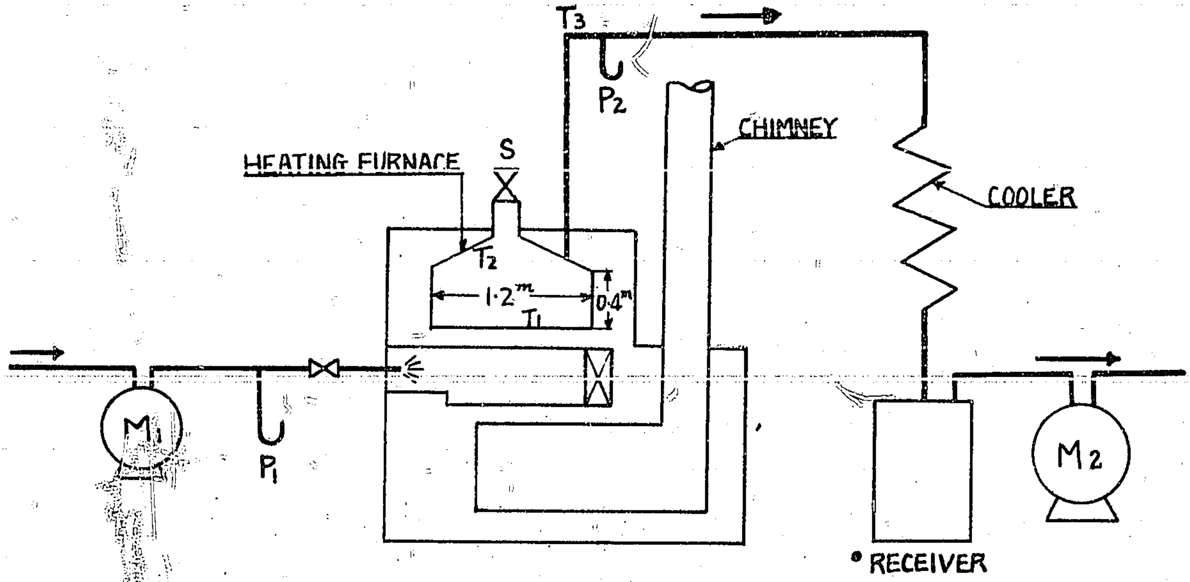
I.B.P.	132
10%	139
20%	140
30%	142
40%	143
50%	145
60%	147
70%	149
80%	152
90%	158
97%	166
Dry Point	171

Table V(B)12
EFFECT OF BOILING RANGE OF DRY DISTILLED OIL FROM SODIUM SOAP OF COCONUT OIL ON SYNTHETIC OIL

		Number					
		1	2	3	4	5	6
	Temperature (°C)	I.B.P. (56)-160	160-200	200-230	230-260	260-300	300
Distilled Fraction	Yield, wt(%)**	10.8	8.8	7.7	2.6	3.4	12.5
	Density At room temp.	0.718	0.751	0.763	0.784	0.80	
	Iodine Value	163.1	140.0	134.0	119.8	107.2	
	Pour Point (°C)	70	-50	-35	-25	-15	
Supernatant Polymerized Oil	Yield, wt(%)**	66.5	67.0	60.0	60.0	61.3	
	Yield, wt(%)*	6.7	5.9	4.6	1.5	2.0	
Dechlorinated Oil (220°C-)	Yield, wt(%)#	57.8	71.2	87.5	89.5	91.0	
	Yield, wt(%)*	3.9	4.2	4.0	1.1	1.8	
	Viscosity S.U.S. at 100°F	235.3	187.0	148	159.3	128.0	
	210°F	52.3	55.2	47.0	47.6	44.5	
	Viscosity Index	128.0	159.7	150.1	145.0	149.9	
	Pour Point (°C)	-51	-41	-31	-20	-12	
Distillate (220-530°C)	Yield, wt(%)##	61.0	48.6	51.3	50.0	62.1	
	Yield, wt(%)*	2.4	2.0	2.1	0.7	1.2	
	Viscosity Index	162.3					
	100°F	92.5	53.2	44.1	46.4	55.9	
	210°F	40.6	35.3				
Residual Oils (530°C-)	Yield, wt(%)##	37.0	50.0	48.3	49.4	37.3	
	Yield, wt(%)*	1.4	2.1	1.9	0.6	0.7	
	Yield, wt(%)**	14.1	23.8	25.4	26.4	20.8	
	Viscosity Index	110.9	118.7	120.4	118.5	111.2	
	100°F	1919.6	1391.4	1240.4	1549.2	1697.1	
	210°F	149.2	132.8	125.2	142.9	138.0	
	Pour Point (°C)	-25	-34	-30	-20	-14	
Decomposed Oil From Sludge	Yield, wt(%)**	27.5	31.0	34.0	35.0	33.7	
	Yield, wt(%)*	2.8	2.7	2.6	2.7	1.1	
Dechlorinated Oil (260°C-)	Yield, wt(%)@	72.7	53.2	88.2	87.5	96.3	
	Yield, wt(%)*	2.0	1.4	2.3	2.4	1.1	
	Viscosity Index	104.4	116.0	136.1	126.3	127.2	
	100°F	757.5	583.3	303.4	359.7	335.8	
	210°F	80.2	74.9	60.6	63.1	60.6	
Residual Oil (470°C-)	Yield, wt(%)##	75.7	76.8	72.7	70.0	66.7	
	Yield, wt(%)*	1.5	1.1	1.7	1.7	0.7	
	Yield, wt(%)**	15.1	12.7	21.8	21.5	21.7	
	Specific Gravity d_4^{25}	0.8740	0.8704	0.8632	0.8770	0.8763	
	Viscosity Index	97.7	104.4	118.6	110.7	109.5	
	100°F	2435.2	1938.5	1345.8	1724.8	1716.0	
	210°F	150.9	139.6	129.4	138.6	136.3	
	Carbon Residue (%)	0.66	0.75	0.52	1.09	1.39	

* For coconut oil
** For distilled fraction
\# For polymerized oil
\#\# For dechlorinated oil
@For decomposed oil

ENCLOSURE (B)12

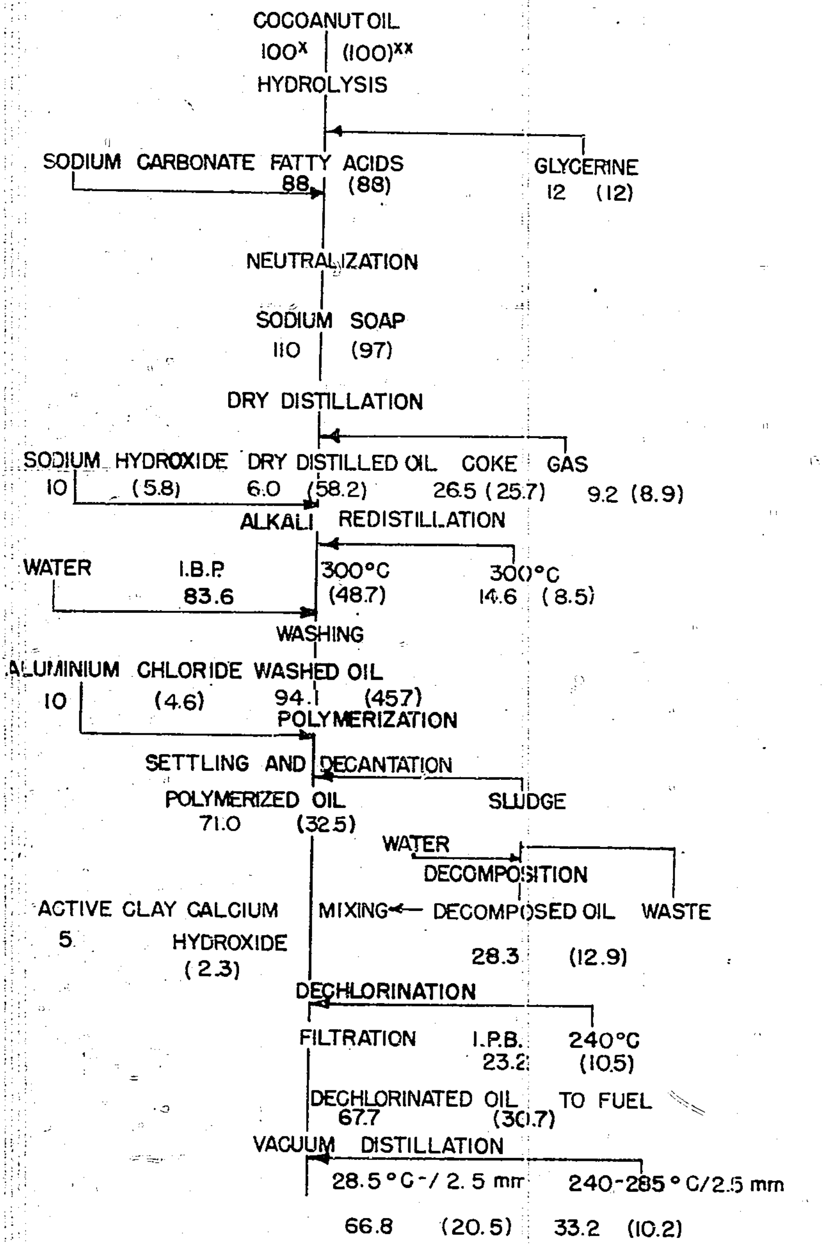


One Charge	200 Kg.
Bottom Area	1·2 m²
Temperature	500°c
Time For Dist.	8 Hrs.

M_1	Gasmeter For Fuel Gas
P_1	Manometer For Fuel Gas
T_1	Pyrometer (Bottom)
T_2	Pyrometer (Top)
T_3	Thermometer (Distilled Vapour)
P_2	Manometer For Distilled Gas
M_2	Gasmeter For Distilled Gas
S	Sluice Valve For Charge

Figure 1(B)12

DIAGRAM OF SOAP DRY DISTILLATION APPARATUS



X LEFT NOTED FIGURES INDICATE YIELD WT.% FOR TREATED MATERIAL

XX RIGHT NOTED( )FIGURES INDICATE YIELD WT.% FOR COCOANUT OIL.

Figure 2(B)12

SCHEMATIC FLOW DIAGRAM OF YIELDS AND MATERIAL BALANCE

ENCLOSURE (B) 13

STUDIES OF PRELIMINARY PURIFICATION OF DRY DISTILLATE FROM SODA SOAP

by

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Research Period: 1945

Prepared for and Reviewed with Authors by
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ENCLOSURE (B)13

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)13

SUMMARY

Subjecting the sodium soap of a fatty acid to dry distillation, an oil which is thought to be composed of olefinic hydrocarbons with some impurities was obtained. This oil was purified by alkali distillation with 10% caustic soda and could be polymerized with no less than 10% of $AlCl_3$. The necessity of using this high quantity of $AlCl_3$ offers economic disadvantages. For instance, in order to obtain a #120 aeroengine oil with a yield of 15% of cocoanut oil, the quantity of $AlCl_3$ necessary for polymerization is more than 10% of the dry-distilled oil after treatment by alkali distillation. The impurities of the dry-distilled oil were also studied to find a better method of purification than alkali distillation.

The mechanism of dry distillation of sodium soaps was studied and carbonyl compounds were found in the dry-distilled oil as impurities. Efforts were made to get rid of these carbonyl compounds by distillation after condensing with 1% of caustic soda, since the condensed products of the carbonyl compounds will remain as residual matter.

It was found that the best method is to heat the dry-distilled oil at about 150°C for 7 hours with 1% of caustic soda, attaching a water trap between the reflux condenser and the reaction vessel. It was then observed that the oil treated by the above method had a much lower carbonyl value than the oil treated by alkali distillation with 10% of caustic soda.

When carbonyl compounds are condensed in the presence of anhydrous $AlCl_3$, they split out water which diminishes the acitivity of $AlCl_3$ for the polymerization of olefinic hydrocarbons. Therefore, it is also necessary to determine the allowable maximum of the carbonyl value for the dry-distilled oil from fatty acid soda soaps in order to prepare aeroengine oil from it economically.

I. INTRODUCTION

A. History of Project

About twenty years ago efforts were made to obtain lamp oil from the sodium soaps of fatty acids by dry distillation. During the war, more efforts were made to get an aeroengine oil from these dry distilled oils of soda soaps. The amount of $AlCl_3$ required for the polymerization of dry-distilled oil was comparatively large due to impurities of the oil, and it has been reported that the best method of purification is by alkali distillation. There are two reactions in the dry distillation of soaps, namely:

1. $2R.COOM \rightarrow H.C. + M_2CO_3 + CO$ $M = Na, K.$
2. $(2R.COO)M \rightarrow R.COR + M.CO_3$ $M = Ca, Ba, Mg, etc.$

According to M. SAITO's* studies, ketones are formed in Reaction 1 during the dry-distillation of sodium soaps, and, subsequently, olefines are formed by thermal cracking of these ketones.

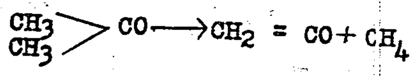
If it is assumed that this mechanism is correct, the thermocracking of ketones suggested by S. ARAKI** can be applied and accordingly asymmetric alkyl ketones would be formed in the dry-distilled oil to some extent.

By qualitative analysis it was found that this assumption was correct, since some carbonyl compounds were present in the dry-distilled oil. Thus, to exclude the carbonyl compounds from the dry-distilled oil in order to decrease the amount of $AlCl_3$ needed for polymerization, studies were conducted concerning the purification of dry-distilled oil.

Main reaction of this cracking is the thermocracking of alkyl-radicals:

$$(CH_3.CH_2)_2\ CO \longrightarrow CH_3.CO\ C_2H_5 \quad \text{etc.}$$

Side reactions are:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \longrightarrow CH_2 = CO + CH_4$$

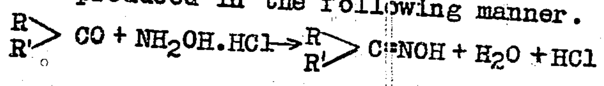
$$2CH_2 = CO \longrightarrow (CH_2)_2 + 2CO \quad \text{etc.}$$

II. DETAILED DESCRIPTION

To determine the quantity of carbonyl compounds in the oil, the method reported by HATOYAMA,*** using hydroxylamine hydrogen chloride, was used, and the carbonyl value was expressed as the mg of CO in 1 gm of sample. In this method an alcoholic solution of hydroxylamine hydrogen chloride in an excess KOH containing a drop of bromphenol blue indicator was prepared. This solution was poured into the sample and, after the reaction was complete, was titrated with 0.1 N HCl solution until excess alkali was neutralized. The carbonyl value was calculated as follows:

$$\text{CO value} = \frac{28.02 \times (\text{CO } 0.1\text{ N HCl for blank} - \text{CO } 0.1\text{ N HCl for sample})}{10 \times \text{gm of sample}}$$

In this reaction oximes are produced in the following manner.



$$\begin{matrix}R\\R'\end{matrix}\!\!>CO + NH_2OH.HCl \rightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C=NOH + H_2O + HCl$$

A. Treating with Alkali

Caustic soda was powdered and gradually added to a three-necked flask such as was used for the polymerization of oils. It was allowed to settle several hours. After filtering this precipitate, the filtrate was distilled from the first drop to 300°C, the distillate was washed with water, dehydrated by acid clay, and its carbonyl value measured. Using 1% of caustic soda, the effects of temperature and concentration of caustic soda solution and sodium metal were examined. The results are given in Table I(B)13.

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* J. Soc. Chem. Ind. Japan. 30(1927) 265
The mechanism of thermo-cracking of Stearin-soda.

** J. Chem. Soc. of Japan. (1930) 560
Thermo-cracking of ketones.

*** Report of Nippon-Yushi Research Committee. p84 March, 1944.
HATOYAMA, "Qualitative Analysis of Carbonyl Compounds in Hydrocarbons"

From these results it may be concluded as follows:

1. The influence of temperature is not appreciable.

2. The more solid caustic soda used, the further the polymerization proceeds, and the more the carbonyl value will be lowered.

3. When an aqueous caustic soda solution is used, the condensation of carbonyl compounds does not proceed to any great extent.

From these facts it was observed that water acts as a poison in the polymerization of carbonyl compounds with caustic soda and it can also be concluded that solid alkali serves to promote the polymerization of carbonyl compounds. The sixth experiment is of interest since it gives the lowest carbonyl value. This can be explained by the fact that some of the sodium metal first becomes caustic soda because of traces of water and further water produced from the reaction catalyzed by the caustic soda also reacts immediately with sodium metal and is removed. Hence, no poisonous influence of water on the polymerization occurs.

B. Alkali Distillation

Alkali distillation has been said to be the best method for the preliminary purification of dry-distilled oil and to give lower carbonyl values. This may be explained as follows:

1. In the alkali-distillation the polymerizing reaction of carbonyl compounds proceeds smoothly because the water is removed from the reaction zone as soon as produced. The presence of water in the alkali-distilled oil can easily be recognized by the turbidity.

2. Caustic soda remains undistilled and its concentration increases as the reaction proceeds.

There are some interesting relations between the alkali-distillation method and the carbonyl values of the product:

1. No great difference of effect can be observed when 1% or 10% of caustic soda is used although the latter gives a slightly lower carbonyl value.

2. Distilling the oil twice with 1% caustic soda, the same result was obtained as when 10% caustic soda was used.

From the results shown in Table II(B)13, the following two conclusions may be drawn:

1. Caustic soda acts as a catalyst, and the reaction depends more upon its catalytic condition than its quantity.

2. Polymerization of carbonyl compounds occurs during a comparatively long time, yet in the case of alkali-distillation, the time of distillation is not constant and the time is not adequate.

Therefore, with the same quantity of caustic soda the carbonyl values of the product will vary.

For these reasons it was intended to polymerize carbonyl compounds with caustic soda before alkali distillation.

ENCLOSURE (B)13

C. Alkali Distillation after Treating with Alkali

The dry-distilled oil was treated with 1% of caustic soda by the same method as for the alkali treatment and was distilled. The results are given in Table III(B)13.

Comparing the results of Table III(B)13 with Table I(B)13, the following points will be observed:

1. Method (C) is better than (A) but almost the same as (B).
2. Hardly any influence of pretreatment of alkali is observed.
3. When a dehydrating agent such as CaO is present, the results are slightly better.

These results showed that water was very injurious to the activity of caustic soda in the polymerization of carbonyl compounds. To eliminate the water from the reaction zone the following methods might be adopted.

1. To use chemical dehydrating agents in the reaction flask.
2. To use a means of removing the water formed during the reaction.

In the first method, the dehydrating agent must be stable towards heat and not react with olefinic hydrocarbons. For this purpose some alkali metals would be suitable.

In the second method a water reflux trap was used, and its behavior was studied.

D. Alkali-Distillation Using a Water Trap

Dry-distilled oil was heated with 1% caustic soda in a flask fitted with a reflux condenser and a reflux water trap. After refluxing, the oil was distilled. Detailed procedure was as follows:

A 200 gm sample was heated without caustic soda and 0.08cc of water was found in the water trap. When 1% of solid caustic soda and some pieces of boiling stones were added to the oil, and heated to 140-180°C, the water was distilled out gradually and after 5 hrs an additional 1.92cc of water was caught in the water trap. The oil was then distilled from the flask. The carbonyl value was determined as 11.6 after the distilled oil had been washed with water and dehydrated by acid clay. This carbonyl value was lower than that of any of the alkali-distilled oils with 1% of caustic soda. On this basis, this apparatus was adopted for use in further alkali-purification studies. The results are tabulated in Table IV(B)13.

E. Influence of Heating Time When Using a Water Receiver

Treating dry-distilled oil with 1% of caustic soda with the same apparatus as used in experiment (D), studies were carried out to determine the suitable treating time and the correlation between water formed and carbonyl-value. The results were as shown in Table V(B)13 and Figure 1(B)13.

1. The sample used was a fraction boiling up to 300°C of dry-distilled oil from sodium soap of cocoanut oil having the following properties:

ENCLOSURE (B)13

Density	0.7770
Saponification value	0.66
Iodine value	120.5
Acid value	0.29
Carbonyl value	33.0

Distilling Characteristics

First drop	72°C
10%	103°C
20%	137°C
30%	153°C
40%	172°C
50%	182°C
60%	200°C
70%	240°C
80%	252°C
90%	274°C
95%	284°C
Dry point	298°C

2. Influence of Time of Reaction on Carbonyl Value. A plot of the carbonyl value showed that it decreased rapidly during the first hour of refluxing and reached a sufficiently low carbonyl value after 7 or 8 hours, using 1% of caustic soda. From this experiment, it appears that alkali distillation is not suitable for the purpose of polymerizing carbonyl compounds from the standpoint of reaction time.

3. Correlation Between the Amount of Water Formed and Carbonyl Value. Even though the dehydrating polymerization of the carbonyl compounds seemed to be the same as in the aldol-condensation, it is necessary to correct the assumption that all oxygen atoms of carbonyl-radicals are converted to water. The time necessary for the purification can be estimated from the water producing curve, which approaches a maximum as the carbonyl value approaches a minimum.

This fact would be of value in commercial practice. The end point of the purifying reaction is the point where differential of the water in respect to time first becomes zero, namely =0: where V=volume of the water formed, t=time. If Q cc of oil is treated and the original carbonyl value "a" is decreased to "b" the correlation formula will be as follows:

$$\int dV = (a-b)\times\frac{16}{28}\times\frac{18}{16}\times\frac{Q}{1000} \quad\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\therefore\ b = a - \frac{14000}{9}\left(dV/Q\right) \quad\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

For instance, taking as an example a treating time of 7 hrs from Table I(B)13, "t" is 7, a is 33.0 and b is 94. Substituting these values in formula (2), a calculated value of water formed will be obtained as follows:

$$\left(dV/Q\right)\times 100 = 1.57cc$$

In this experiment, the water formed was 1.60cc. This agreement shows that formula (2) can be applied for determining carbonyl values instead of chemical analysis.

F. Influence of the Kinds of Purifying Agents

The influence of the quantity of caustic soda and the effect of using caustic-potash, sodium carbonate and a sodium carbonate-calcium oxide-water mixture were studied, and the following results were obtained:

1. Sample: A redistilled oil of the dry-distillation product from the sodium soap of cocoanut oil having the following properties was used:

   Carbonyl value = 45.6, time of treatment = 8 hr.

2. The results are tabulated in Table VI(B)13. From these results the following conclusions can be drawn:

   a. The necessary quantity of caustic soda is 1%.

   b. Caustic soda is better than caustic-potash as a purifying agent.

   c. Purification can be accomplished by using a comparatively large quantity of sodium carbonate.

G. Correlation Between Carbonyl Value and the Carbonyl Compounds in Any Fraction

To judge the degree of purification from the lowering of the carbonyl value, it is necessary to investigate the concept of carbonyl values. Real correlation between carbonyl value and a carbonyl compound in any fraction can be judged by comparing the carbonyl value with the amount of pure ketones contained. Previously, it has been considered that the fraction below 300°C is composed of olefines and the higher boiling fraction is composed of ketones.

The carbonyl value of pure ketones distilled between 250°-300°C is 50-100 and that of the fraction of dry-distilled oil from the soda soap of cocoanut-oil is 64.7. This fraction may be considered to consist mainly of ketones. After purification the carbonyl value of this fraction is 9.7, and it consists mainly of olefines.

Carbonyl values of some pure ketones can be calculated as in Table VII(B)13.

Various fractions of dry-distilled oil were treated twice with 1% of caustic soda using a reflux and water trap. They were redistilled from an Engler-flask and the same fractions were obtained. The carbonyl value of these fractions were determined and compared with the previous values. The results are recorded in Table VIII(B)13.

The difference of carbonyl value between fractions for both the crude oil and the refined oil was small, and the content of carbonyl compounds in each fraction was calculated using the M. W. of the pure carbonyl compounds boiling within the prescribed boiling range. (Table VIIII(B)13)

III. CONCLUSIONS

The necessity of preliminary purification before alkali-distillation in the manufacturing of aero-engine oil from vegetable oils was determined. This preliminary purification acts as a process to exclude the harmful effects of carbonyl compounds on the polymerization of olefines with $AlCl_3$ by condensing the carbonyl-containing compounds. The carbonyl value should always be considered, and should be kept at a minimum in the prepurification process. An apparatus suitable for the pretreatment of alkali-distillation is suggested in Figure 2(B)13.

To avoid the harmful effect of carbonyl compounds, the dry-distilled oil of fatty acid soda soaps must be treated with caustic soda in such a manner that the water formed by the condensation of carbonyl-compounds is removed from the reaction zone. (See Figure 2(B)13.)

Table I(B)13
ALKALI TREATMENT

No.	Purifying Agent	CO value of Sample	Temp. (°C)	Stirring Time (hr.)	Settling Time (hr.)	Yield of Purified Oil (%)	CO Value Purified Oil
1	NaOH 1%	40.0	24	1	20	61.2	22.3
2	NaOH 1%	40.0	65	10	24	55.3	27.6
3	NaOH 1%	40.0	150	10	24	56.0	27.2
4	NaOH 10%	40.0	65	10	24	35.2	24.1
5	NaOH 10% (aq.soln. 15%)	40.0	65	10	24	74.5	30.7
6	metal Na 0.6%	40.0	24	10	24	49.0	15.3

Table II(B)13
ALKALI-DISTILLATION

No.	Purifying Agent	CO Value of Sample	Method of Treatment	Yield of Purified Oil (%)	Purified Oil (CO value)	Note
7	NaOH 1%	40.0	Alkali-dist.	67.2	16.8	
8	NaOH 10%	40.0	Alkali-dist.	71.5	13.4	
9	NaOH 2%	40.0	Alkali-dist. twice with 1% NaOH in each case		13.4	after the 1st Alkali-dist. CO-value was 19.9

ENCLOSURE (B)13

Table III(B)13
ALKALI DISTILLATION AFTER TREATMENT WITH ALKALI

No.	Purifying Agent	CO Value of Sample	Treating Temp (°C)	Stirring Time (hr)	Settling Time (hr)	Yield of Purified Oil %	CO Value of Purified Oil
10	NaOH 1%	40.0	24	5	10	90.0	16.1
11	NaOH 1% CaO 10%	40.0	24	5	10		15.4
12	NaOH 1%	40.0	150	5	10	84.5	21.8

Note: Heat reflux condenser.

Table IV(B)13
ALKALI-DISTILLATION AFTER ALKALI-TREATMENT USING WATER TRAP

No.	Purifying Agent	CO Value of Sample	Treating Temp (°C)	Treating Time (hr)	Settling Time (hr)	Yield of Purified Oil (%)	CO Value Purified Oil	Note
13	NaOH 1%	40.0	140	5	20	77.5	11.6	
14	NaOH 3%*	27.6	150	10 in each case	0		1st 9.7 2nd 5.4 3rd 4.8	
15	Na_2CO_3 13.3% CaO 7%	40.0	150	6	0		14.6	water 0.671%
16	NaOH 1%	16.3	150	8	0	70.1	4.7	water 0.811%
17	KOH 1%	16.3	150	8	0	79.2	11.4	water 1.03%

*three times with 1% in each.

ENCLOSURE (B)13

Table V(B)13
INFLUENCE OF TIME*

No.	Treating Time	Water Formed (%)	CO Value of Purified Oil	Yield (%)	Calc. Quantity of Water Formed Using the Formula $x100 \underset{\%}{=} \frac{9}{100}(a-b)$
18	1	0.5	18.3	84.0	0.9
19	2	0.8	19.3	92.0	0.4
20	3	1.0	16.6	84.8	1.0
21	5	1.5	12.9	93.4	1.2
22	7	1.6	9.4	85.3	1.57
23	9	1.4	9.2	70.5	1.5
24	12		8.8		1.6

*Purifying agent: 1% NaOH
Treating temp: 150°C
Initial carbonyl value = 33.0

Table VI(B)13
INFLUENCE OF THE KINDS OF PURIFYING AGENTS
(Original CO value = 45.6)

No.	Purifying Agent	Conc. (%)	Water Produced (cc)	Yield (%)	CO Value of Purified Oil
25	NaOH	2.0	2.0	93.5	11.1
26	NaOH	1.0	2.0	94.0	11.8
27	NaOH	0.5	0.5	88.0	24.6
28	NaOH	0.1	0.3	92.0	41.3
29	KOH	1.4	2.0	88.5	18.0
30	KOH	1.0	1.4	98.1	20.6
31	Na_2CO_3	5.0			10.6
32	Na_2CO_3 CaO H_2O	1.3 0.7 5.0		85	17.4

ENCLOSURE (B)13

Table VII(B)13
CALCULATED CARBONYL VALUE OR PURE KETONES

Name	Experimental Formula	Boiling Pt (°C)	Melting Pt (°C)	CO Value
Acetone	$(CH_2)_2CO$	57		482.7
Methyl ethyl ketone	$C_2H_5.CO.CH_3$	80		388.8
Diethyl ketone	$(C_2H_5)_2CO$	101		345.6
Butyrone	$(C_3H_7)_2CO$	143		245.6
Valenone	$(C_4H_9)_2CO$		42	197.1
Carbronone	$(C_5H_{11})_2CO$	227	15	164.7
Exantone	$(C_6H_{13})_2CO$	264	30	141.4
Peralgone	$(C_8H_{17})_2CO$		50	110.2
Myristone	$(C_{13}H_{27})_2CO$		76	71.0
Palmitone	$(C_{15}H_{31})_2CO$		83	62.2
Stearone	$(C_{19}H_{35})_2CO$		88	55.3

Table VIII(B)13
CARBONYL VALUE OF VARIOUS FRACTIONS

Sample	0-330°C	0-150°C	150-200°C	200-250°C	250-300°C
Dry-dist. oil	45.6	33.2	34.0	46.3	64.7
Purified oil	8.2	8.1	7.0	5.9	9.7
Pure alkyl ketones*		480-240	240-160	160-140	160-150
Average of pure alkyl ketones taken for a scale		350	200	150	75

*Range of carbonyl values of ketones listed in Table VII(B)13 and boiling within each temperature range.

Table IX(B)13
CALCULATED CARBONYL CONTENT

Sample	0-150°C	150-200°C	200-250°C	250-300°C
Quantity of CO contained in dry-distilled oil	33.2/350-9.5%	34.0/200=17.0%	46.3/150=30.0%	64.7/75=86.3%
Quantity of CO contained in purified oil	8.1/350-2.3%	7.0/200-3.5%	5.9/150=3.9%	9.7/75=12.9%

ENCLOSURE (B)13

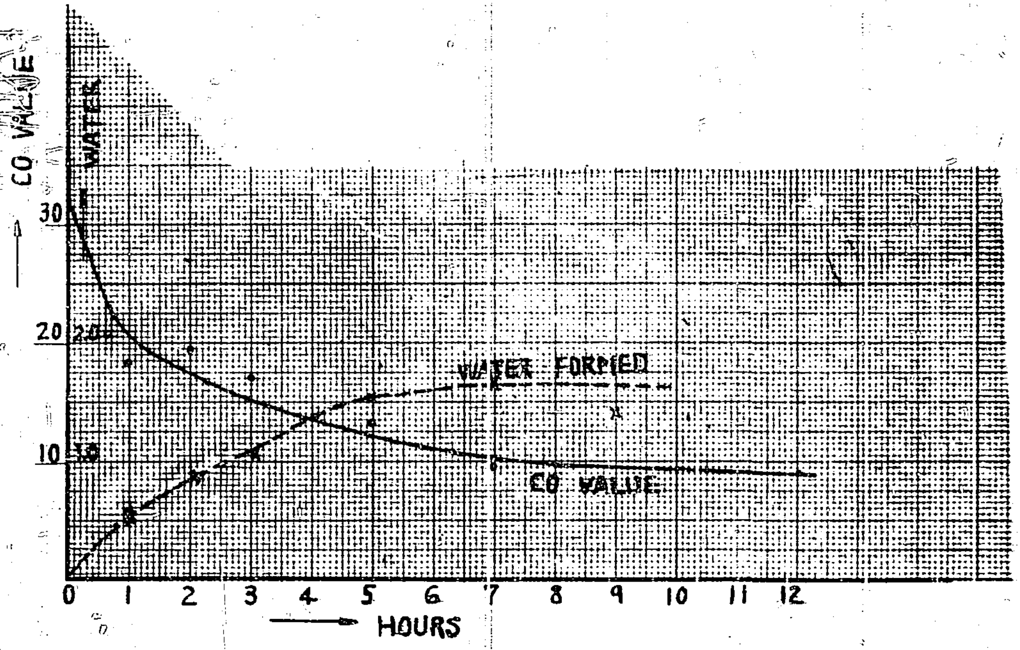

Figure 1(B)13
EFFECT OF TIME OF REACTION ON
CARBONYL VALUE AND WATER FORMED

ENCLOSURE (B)13

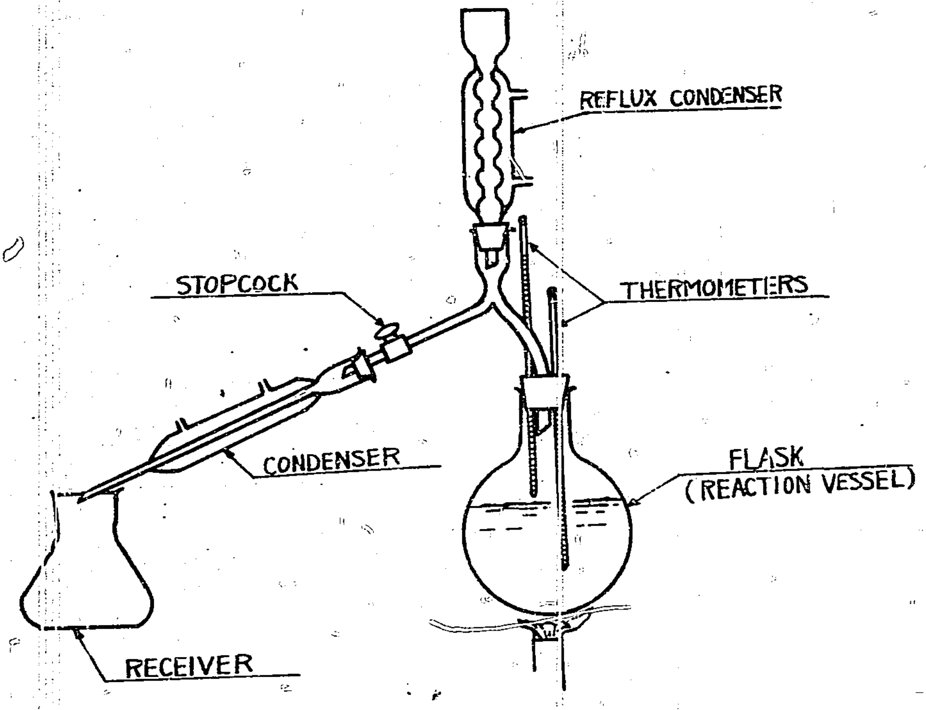

Figure 2(B)13
APPARATUS FOR PRETREATMENT
OF ALKALI-DISTILLATION

Figure 2(B)13

The dry distilled oil and caustic soda are put in the flask and heated for seven or eight hours at 150°C, while the stopcock is closed. The water produced is caught in the tube above the stopcock and the oil returns to the reaction vessel. Then heating is stopped and the stopcock is opened to take out the water. Heat is applied again and the purified oil is obtained in the receiver.

ENCLOSURE (B) 14

STUDIES ON THE SYNTHESIS OF AERO-ENGINE OIL BY CATALYTIC CRACKING AND POLYMERIZATION FROM FATTY OILS

by

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Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)14

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)14

SUMMARY

Owing to the difficulties of importing crude oil to manufacture aero-engine oil, cracking of fatty acids to olefines with alkali-carbonate catalyst has been experimented with in some of the chemical laboratories in Japan. We have studied the cracking of fatty acids of cocoanut oil with soda-carbonate, to seek the suitable conditions of temperature and space-velocity in the cracking of fatty acids to get good lubricating oil with high yield. We also wanted to know what is the best carrier of catalyst and, in conformity with the reports from other laboratories such as that of the Mitsui Chemical Company, cokes and pumice-stones were used.

This experiment has not yet been completed, but to obtain a cracked oil of good quality with high yield, it seems best to crack fatty acids at the temperature between 500°C and 525°C and space-velocity of 0.18.

I. INTRODUCTION

A. History of Project

Because of the difficulty of importing crude oil to produce aero-engine oil, its production was intended from fatty oil by cracking fatty acids to olefines and polymerizing the olefines.

Research was carried on from May, 1945.

B. Key Research Personnel Working on Project

Chem. Eng. Sub. Lt. T. SAKURA.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Through the stopcock of a separating funnel fatty acids were dropped into a quartz tube filled with catalyst. heated in an electric furnace, the temperature being measured by a thermocouple in the catalyst zone. Cracked oil was caught at the first trap jointed to the tube, the remaining oil vapor was cooled through a spiral condenser and caught at the second trap, and the gas was discarded. Diameter of the quartz tube was 3.3cm and the length 1 meter. A simplified flow diagram is shown in Figure 1(B)14.

B. Test Procedures Details of Test Procedures and Conditions

Fatty acids were melted by the heat of the electric furnace and dropped in the tube naturally through the stopcock. Upper part of the quartz tube is filled with carrier only and through this zone fatty acids were preliminarily heated. The object of preliminary heating is only to keep the temperature of catalyst zone suitable and this doesn't effect the quality and quantity of the cracked oil. To keep the condition of catalyst constant the length of catalyst zone was fixed at 50 cm. The surface of the carrier of catalyst becomes covered with carbonized oil as the reaction proceeds and fatty acids cannot flow through and so the average dia. of every piece of carrier was fixed at 1 cm. The method of covering pumice-stone and coke with soda-carbonate is as follows:

ENCLOSURE (B)14

At first pieces of carrier are put in a saturated solution of soda-carbonate at 80°C, kept at that temperature for about two hours to make the carrier absorb the solution adequately, and then cooled. After 24 hours the carrier which is covered with crystals of salt is removed and dried. Before the experiment the tube is blown down with air at 500°C to dehydrate the catalyst. It is noticed that the catalyst becomes quickly inactive after passing 200 gm of fatty acids. Hence, for the purpose of keeping the condition of catalyst constant in every experiment, 200 gm of fatty acids are passed and the experiment is stopped.

The temperature of reaction: While the temperature necessary to crack is reported to be about 525°C, experiments were made at 450°C, 500°C, 525°C and 550°C.

Volume of passing: It was noticed that the space-velocity* of 0.18 is better at 525°C and in this tube this value of S V means the passing of 60 gm of fatty acids per hour. Then we vary the volume of passing from 30 gm to 100 gm per hour to survey a good condition.

Since the diameter of the carrier is relatively large compared with the diameter of the reaction tube, we define S V as gm/hr/s where s is the total surface area of the pieces of carrier covered with catalyst expressed in cm². This value can be calculated, regarding the shape of the carrier as a tetrahedron 1cm in diameter. Correctness of the calculation can be ascertained when we measure the total surface area of several pieces of carrier.

Characteristics of cocoanut oil fatty acids: density (d_4^{50}) 0.865

Average molecular weight 190-200 (This value is derived by the experimental formula

$$\text{M.W.} = \frac{56.11}{\text{Acid value}} \times 100)$$

Acid value = 280-290

Iodine value = 2-3

Through the curve of vacuum distillation it seems that fatty acids consist mainly of Lauric acid $CH_3(CH_2)_{10}COOH$ and partially of Caprylic acid $CH_3(CH_2)_6COOH$, Capric acid $CH_3(CH_2)_8COOH$ and Myristic acid $CH_3(CH_2)_{12}COOH$ etc.

C. Experimental Result

The results shown in Table I(B)14 indicate that the yield of cracked oil boiling from room temperature to 300°C, is relatively small. This is due to the fact that the fraction of higher boiling point than 300°C is not yet cracked and contains many oxygen compounds as determined by elemental analysis. This will interfere with polymerization.

III. CONCLUSION

There appears to be no difference between cokes and pumice-stone as the catalyst carrier. When volume of fatty acid charged increases the yield becomes good, but the acid value of the cracked oil increases and the Iodine

---

*Calculation of S V: Ordinarily the meaning of S V is gm/hr/v where gm:gram put in hr:hour v:volume of the zone of a reaction tube filled with catalyst expressed in cm³.

Value decreases and the cracked oil is not suitable for polymerization. This fact may mean that fatty acids could not be cracked completely and go down without being reacted. At 450°C, yield and quantity of the cracked oil is good, but from the point of view of practical application the volume of passing is too small. At 500°C and 525°C, near the volume of passing 50-70 gm/hr (S V 0.15-0.21), a cracked oil was obtained with a high Iodine Value and low Acid Value which is estimated to be good for polymerization. At 550°C fatty acids are quickly cracked to gases.

In conclusion, at 500°C and S V 0.18 the order of cracking is desirable judging from the value of S V and I.V., but when the volume of passing is large, A.V. is comparatively large and the cracked oil contains comparatively large quantity of unreacted fatty acids.

Our experiment is not yet finished. We have to investigate how to separate oxygen compounds from cracked oil or to find a method of analysis of oxygen compounds contained in olefines. For this purpose it is proposed ot investigate ketones contained in the cracked oil by the ultra-red absorption spectrum.

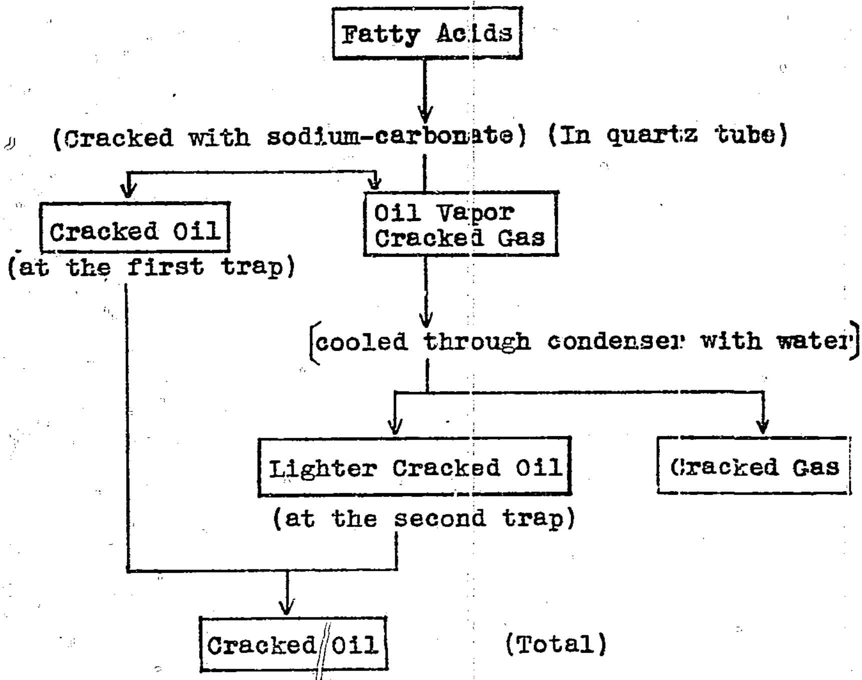

Figure 1(B)14

SIMPLIFIED FLOW DIAGRAM SHOWING FORMATION OF OIL FROM FATTY ACIDS

Table I(B)14
CONDITIONS OF CRACKING AND PROPERTIES OF THEIR PRODUCTS

	Volume of pass (gm/hr)	S.V.	Yield (-300°C)	Product (Vol x% Yield)	Acid Value (A.V.)	Iodine Value (I.V.)
450°C	20	0.06	41%	820	10	146
	30	0.09	25%	750	12	122
	40	0.12	30%	1200	21	112
	50	0.15	28%	1400	36	101
500°C	30	0.09	27%	810	16	162
	40	0.12	21%	840	22	144
	50	0.15	34%	1700	20	136
	60	0.18	40%	2400	27	140
	70	0.21	32%	2240	39	118
525°C	30	0.09	29%	870	15	162
	40	0.12	24%	960	19	154
	50	0.15	31%	1550	21	147
	60	0.18	42%	2520	25	141
	70	0.21	33%	2010	37	124
	100	0.30	31%	3100	58	107
550°C	30	0.09	23%	690	19	152
	40	0.12	22%	880	21	149
	50	0.15	24%	1200	24	147
	60	0.18	29%	1740	26	136
	70	0.21	26%	1820	39	129
	100	0.30	30%	3000	61	116

ENCLOSURE (B)14

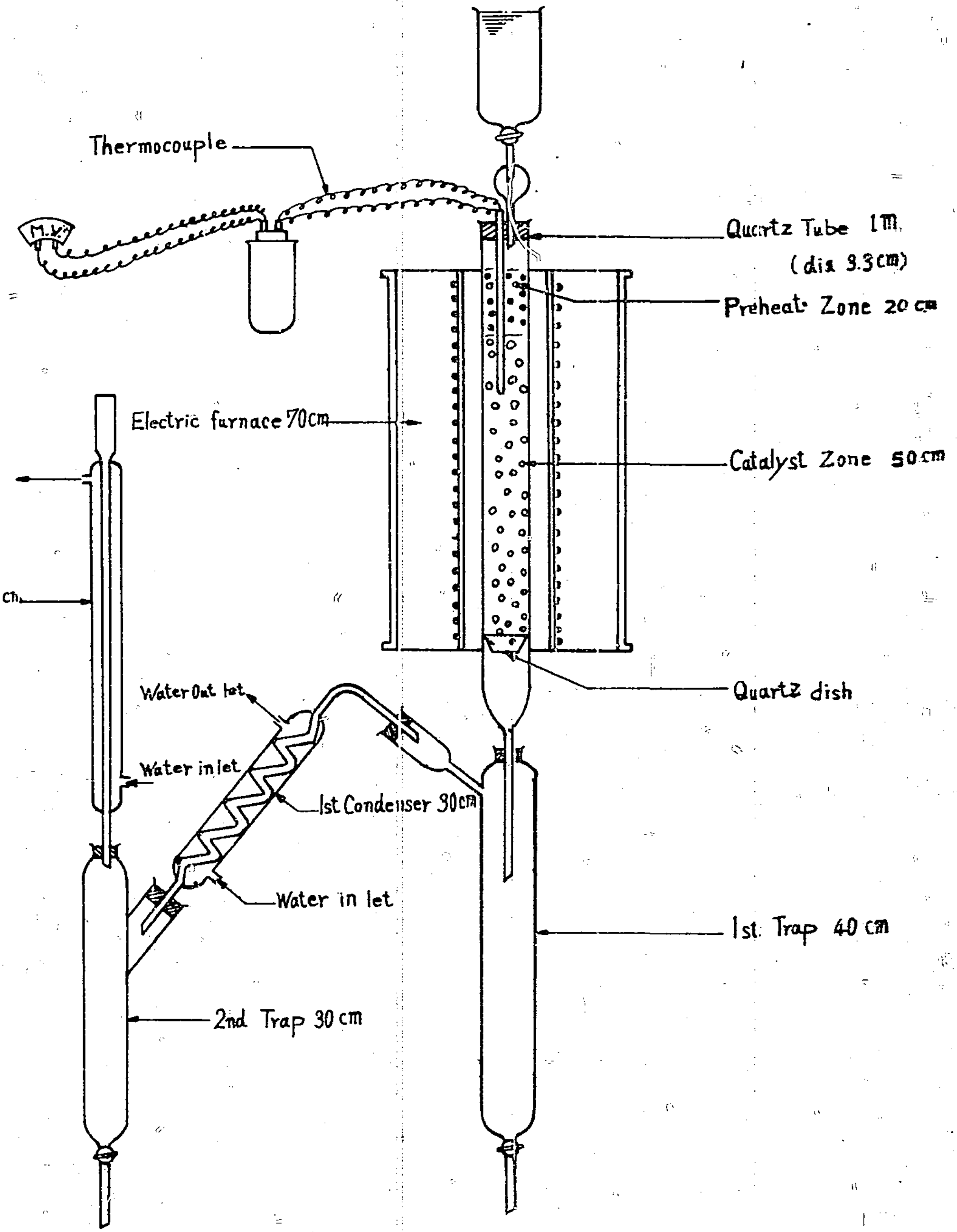

Figure 2(B)14
DRAWING OF APPARATUS

ENCLOSURE (B)14

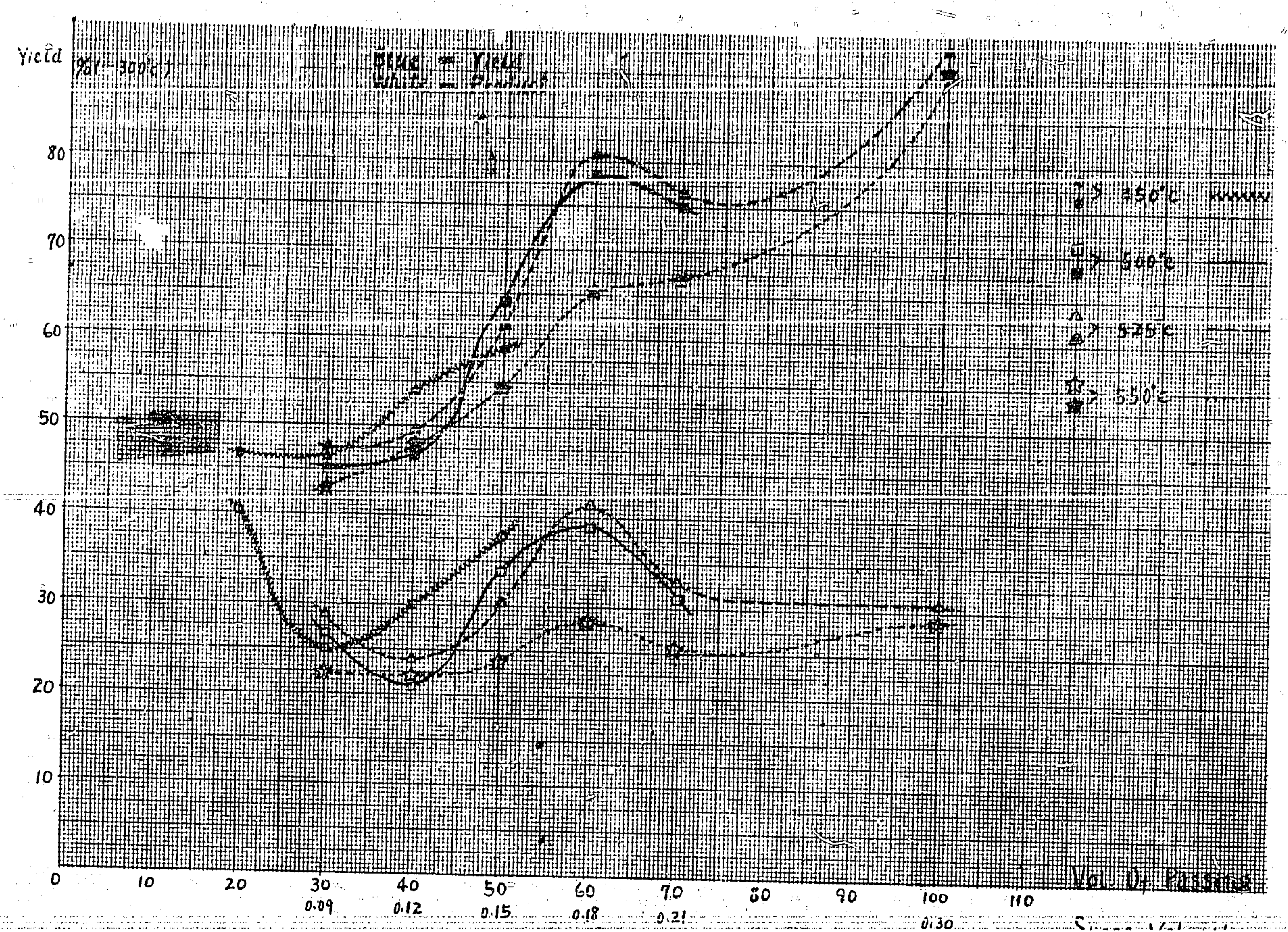

Figure 3(B)14
CORRELATION CURVE 1

ENCLOSURE (B)14

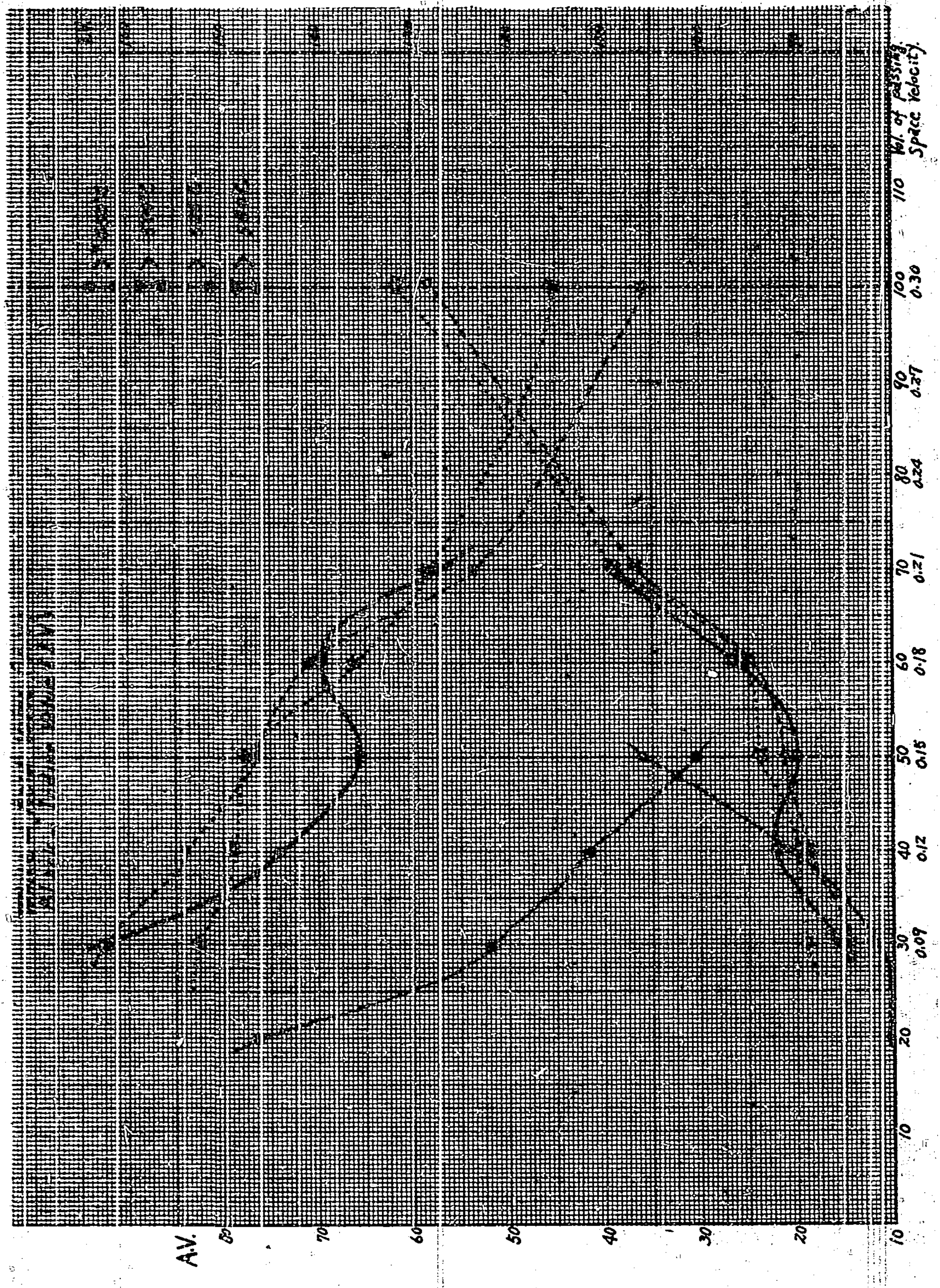

Figure 4(B)14

CORRELATION CURVE 2

ENCLOSURE (B) 15

STUDIES ON THE SYNTHESIS OF AERO-ENGINE OILS FROM RUBBER

by

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Research Period: 1943-1944

Prepared for and Reviewed with Authors by
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December 1945

ENCLOSURE (B)15

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)15

SUMMARY

The object of these studies was to investigate the method of preparing aero-engine oil from natural rubber and the results obtained were as follows:

1. Pale crepe rubber was extracted with several solvents and the molecular weight, iodine value and composition of the extracts were determined. The results showed that natural rubber consisted of isoprene polymers having different degrees of polymerization.

2. It was impossible to obtain an aero-engine oil from rubber by thermal cracking or catalytic cracking with acid clay.

3. By co-polymerization of the cracked distillate of natural rubber with 2.5 volumes or more of cracked wax in the presence of 5% $AlCl_3$ at 100°C, a desirable aero-engine oil was obtained.

4. By the high pressure hydrocracking of the pale of pale crepe rubber in paraffinic hydrocarbon solvent in the presence of nickel catalysts a desirable aero-engine oil was obtained.

I. INTRODUCTION

A. History

Natural rubber was one of the most important hydrocarbon sources available to Japan. It appeared possible to prepare an aero-engine oil if the rubber molecules could be broken into stable compounds having an average molecular weight of about 1,000. In connection with this problem studies on the composition of pale crepe rubber, the co-polymerization of the cracked rubber with cracked wax, and the high pressure hydrocracking of rubber, were conducted from April, 1943 to August, 1944.

B. Key Research Personnel Working on Project

Chem Eng. Lieut. T. ISHIWATA

II. DETAILED DESCRIPTION

A. Experiments on the composition of pale crepe rubber by solvent extraction method.

1. Experimental Method

Pale crepe rubber was cut into rectangular pieces, 2mm X 2mm X 10cm, and extracted in an atmosphere of nitrogen by a Soxhlet apparatus with acetone, alcohol, iso-octane, ethyl ether and benzene in that order.

After removing the solvent, the extracts were dissolved in pure benzene with a concentration of 1.5gm/lit and their molecular weights were determined by Staudinger's method (1).

The molecular weight was calculated by the following formulas:

$$\frac{Sc\ tc}{So\ to} - 1 = C \times Km \times P; \quad M = P \times 68(C_5H_8)$$

in these formulae:

Sc,So = density of rubber solution and pure benzene at 20°C.

tc,to = viscosity (in sec) of rubber solution and pure benzene by Ostwald's viscometer.

C = gm of rubber hydrocarbon dissolved in 1 liter of solvent.

P = degree of polymerization.

M = molecular weight.

K_m = constant

= 3.8×10^{-4}——in the case of unrefined rubber.(2)

= 3.0×10^{-4}——in the case of acetone soluble rubber(3)

= 1.1×10^{-4}——in the case of ethyl ether soluble rubber(4)

= 1.7×10^{-4}——in the case of ethyl ether insoluble and benzene soluble rubber(5)

Iodine value was measured by Wiijs' method adding 35% excess of iodine.

2. Results:

The results obtained are tabulated in Table I(B)15. The following conclusions were derived from these results:

a. The substance extracted by acetone had high oxygen content, low molecular weight, and high iodine value, and consisted of resinous matter or impurities containing oxygen compounds.(6)

b. The substance extracted by alcohol had low carbon content, high oxygen content, very small molecular weight and iodine value, and was presumed to be composed of saccharides.

c. The substances extracted by iso-octane, ethyl ether and benzene had the same elementary composition, and iodine value as isoprene.

d. Proteins were not extracted by these solvents and the greater part of them remained in the residue of extraction, based on the nitrogen content, the total content of protein in pale crepe rubber was presumed to be 2.2%.

B. Depolymerization of Natural Rubber

1. Experimental Method

Pale crepe rubber was dissolved in 4 volumes of Sanga Sanga gas oil, boiling from 150°C to 200°C, and depolymerized thermally under various conditions, and with and without the use of acid clay.

2. Results of Experiments

Results obtained are given in Tables II(B)15 and III(B)15, and the following conclusions were obtained.

a. The depolymerization of rubber molecules was affected sharply by the heating temperature and the influence of the acid clay catalyst.

b. The molecular weight decreased by depolymerization to about 1,000, but the product was very volatile and highly unsaturated and could not be used as a high class lubricating oil.

C. Polymerization of the Cracked Distillate of Pale Crepe Rubber

A fraction of cracked distillate of pale crepe rubber boiling from 100°C to 300°C was first washed 3 times with one volume of 10% caustic soda solution and then with water. The treated oil was polymerized in the presence of $AlCl_3$ or acid clay. Results obtained are given in Table IV(B)15 and it was observed that the products prepared by this method had a very low viscosity index and were unsuitable for use as high class lubricating oils.

The formation of low viscosity index oils was assumed to be due to the existence of cyclic compounds such as limonene in the raw material of the polymerization. The isoprene fraction, therefore, was distilled off and was polymerized. The results are shown in Table V(B)15.

From these experiments the following facts were recognized:

1. A good lubricant can be obtained by polymerization of the isoprene fraction of the cracked distillate of pale crepe rubber at about 0°C.

2. A higher viscosity index oil was obtained by the polymerization in the presence of $SnCl_4$.

3. Further studies are necessary for the preparation of an excellent aero-engine oil by this method.

D. Co-polymerization of the Cracked Distillate of Pale Crepe Rubber With the Cracked Distillate of Paraffin Wax

To improve the viscosity index and the viscosity ratio(British Air Ministry Oxidation Test), the cracked distillate of pale crepe rubber was co-polymerized with the cracked distillate of paraffin wax, and the results are shown in Table VI(B)15.

An excellent aero-engine oil could be obtained from the cracked distillate of pale crepe rubber by co-polymerizing with 2.5-4 volumes of the cracked distillate of paraffin wax. This method would be suitable for the synthesis of an aero-engine oil from rubber and paraffin wax.

E. Hydrocracking of Pale Crepe Rubber

ENCLOSURE (B)15

1. Hydrocracking of Pale Crepe Rubber Without Solvent.

The thermally depolymerized products of pale crepe rubber have a high iodine value. Therefore, it is necessary to hydrogenate these products to saturated compounds in order to improve their oxidation stability. Hence, the high pressure hydrocracking of pale crepe rubber in an autoclave without solvent was studied and the results tabulated in Table VII(B)15 were obtained. From these results, it may be concluded as follows:

a. The higher the temperature and the longer the time of reaction, the greater the content of the lower molecular weight components. The viscosity of the product increased sharply by topping to 150°C, but the flash point was low. However, the viscosity of the product could not be determined after making the British Air Ministry Oxidation Test, since the increase of viscosity with oxidation was too large.

b. Two-stage hydrogenation decreased the iodine value of the product, but the oxidation stability did not improve.

c. Sulphuric acid treatment of the product improved the oxidation stability but decreased the viscosity index considerably.

d. The MoS_3 catalyst was less effective for hydrocracking than the Ni-catalyst.

e. The topped residue of the product had a low flash point and a high viscosity. These results may be due to the formation of low molecular weight compounds mixed with those of high molecular weight, due to the non-uniform cracking of rubber.

2. Hydrocracking of Pale Crepe Rubber in the Presence of 2 Parts of Solvent

The hydrocracking of pale crepe rubber with 2 parts of various solvents at various temperatures was studied and the results shown in Table VIII(B)15 were observed.

From these results, the following conclusions may be made:

a. The optimum conditions for the hydrocracking of rubber with 2 parts of solvent were temperature of 300°C and reaction time of 20 hours. The shorter the time, the worse the oxidation stability.

b. It was found desirable to use a higher boiling solvent in preparing an oil of good oxidation stability.

c. The type of solvent seemed to have a marked effect on the stability of the products.

3. Hydrocracking of Pale Crepe Rubber With Various Amounts of Solvent

Hydrocracking of pale crepe rubber with various amounts of solvent was studied and the results given in Table IX(B)15 were obtained. The following conclusions may be drawn:

a. The optimum amount of solvent at the reaction temperature of 300°C was 5 parts of solvent to one part of rubber. The stability and the viscosity index of the product formed under these conditions showed the best results. It had a viscosity ratio of 2.23 in the oxidation test and a flash point of 134°C.

b. The number of aromatic nuclei in the product as determined by (1) bore a close relationship to the viscosity index, as may be seen in Table VIII(B)15 and IX(B)15. To obtain a viscosity index over 100, the number of aromatic nuclei in a molecule must be less than 4. To accomplish this, it is necessary to treat under 300°C, using a short time of reaction.

4. Hydrocracking of Pale Crepe Rubber with 5 Parts of Various Solvents

The effect of various types of solvents such as decalin as a naphthenic compound, dodecane as a pure paraffinic hydrocarbon, and the various light oils were investigated, and the results shown in Table X(B)15 were obtained (See Table X). The following conclusions may be made from these results:

a. In the case of paraffinic hydrocarbons, hydrocracking was difficult, but the reaction product had a low iodine value without decreasing the viscosity index at reaction temperatures above 350°C: that is, a highly stable lubricating oil was prepared by using this solvent.

b. In the case of the naphthenic solvent, the viscosity index of the reaction product was very low.

c. The higher the content of paraffinic components in the solvent, the higher the viscosity index and the better the oxidation stability of the product.

5. Hydrocracking of Paste of Pale Crepe Rubber

For continuous operation of hydrocracking in a pilot plant, it is necessary to dissolve the rubber in a solvent to make a rubber paste. A pale crepe rubber was dissolved in a solvent at 170°C for 5-8 hours, and the hydrocracked product was compared with that obtained by direct hydrocracking. The results obtained are given in Table XI(B)15 and it was observed that this treatment (Exp. No. 51) yielded a product of lower viscosity index and better stability than the previous treatment (Exp. No. 31).

6. Hydrocracking of Pale Crepe Rubber Paste Using Fischer Oil As A Solvent.

Pale crepe rubber and smoke sheet rubber were dissolved in Fischer oil boiling from 150°C to 250°C and the results shown in Table XII were obtained.

The following conclusions may be drawn:

a. The product of hydrocracking rubber at 300°C in the presence of Fischer oil has a high iodine value and poor oxidation stability.

b. The hydrocracking of smoke sheet rubber was more difficult than that of pale crepe rubber, but two stage hydrocracking for a period of long duration produced an oil of good stability from smoke sheet rubber.

7. Summary of Autoclave Hydrocracking Experiments

The optimum conditions for preparing a good aero-engine oil having high viscosity index and good stability from natural rubber by hydrocracking are summarized as follows:

a. Solvent: Paraffinic solvent such as Fischer oil.

b. Volume of solvent: 5 parts to 1 part of rubber.

c. Conditions for dissolving rubber in the solvent. 170°C for 5-8 hours.

d. Catalyst: Reduced nickel catalyst, consisting of 65% of NiO, 30% of diatomaceous earth, and 5% of graphite.

e. CONDITIONS OF HYDROCRACKING

1st stage: 100 atmospheres of initial pressure, 300°C reaction temperature.

2nd stage: 300°C reaction temperature.

8. Procedure for continuous hydrocracking of natural rubber paste in the pilot plant.

20 parts of pale crepe rubber were dissolved in 100 parts of Fischer oil boiling from 200°C to 250°C at 170°C for 8 hours. This paste was hydrocracked in the continuous hydrocracking pilot plant shown in Figure 1(B)15 under the following conditions:

Catalyst: Nickel catalyst, consisting of 65% of NiO, 30% of diatomaceous earth and 5% of graphite, previously reduced in the reaction cylinder.

Amount of Catalyst: 3 liter of catalyst in both the reaction and preheating cylinders.

Pressure of reaction: 200 kg/cm^2

Temperature of preheating cylinder: 300°C

The results of these experiments are summarized in Table XIII(B)15. From these results it was recognized, that the conditions of hydrocracking in experiment No. 7 were best. These conditions were as follows:

Catalyst: Nickel catalyst

Temperature of preheating cylinder: 300°C

Temperature of reaction cylinder: 400°C

Pressure of reaction: 200 kg/cm^2

Amount of charge: 1.5 lit/hr to 3 lit of catalyst in each reaction and preheating cylinder.

Amount of H_2 gas: 1.5 m^3/hr.

ENCLOSURE (B)15

A mixture of 47 parts by weight of the product of experiment No. 7 and 53 parts of aero-engine oil #80 has the following properties and conforms to the specification for Naval aero-engine oil.

Reaction	neutral
Density(25/4°C)	0.8965
Flash Point°C	199°C
Viscosity(S.U.S.) at 100°F	1323.7
at 210°F	122.0
Viscosity Index	114.8
Viscosity Ratio	1.25
Conradson's Carbon	1.10

III. CONCLUSIONS

It was observed, that natural rubber consisted of polymers of isoprene having various degrees of polymerization.

The thermally depolymerized product of natural rubber in a solvent is an oil having a molecular weight of about 1,000, high volatility, and a highly unsaturated nature, which is not suitable for use as a first class aero-engine lubricant.

A comparatively good lubricating oil was obtained by the polymerization of the isoprene fraction of the cracked distillate of natural rubber. To prepare a high quality aero-engine oil by this method, however, further investigation is necessary.

An excellent aero-engine oil was obtained by the co-polymerization of the cracked distillate of rubber with 2.5 to 4 volumes of the cracked distillate of paraffin wax.

A good aero-engine oil was obtained by the hydrocracking of natural rubber paste with paraffinic hydrocarbons in a continuous hydrocracking pilot plant.

Note: No plant using these processes was built for producing lubricating oil for practical use.

There were plants (NIPPON Oil Co. and Tea Fuel Oil Co. etc.) in Japan, however, which, during the war, thermally depolymerized natural rubber added this product in a concentration of 10% to mineral oil for use in automobiles. However, this type of product had poor oxidation stability.

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The Analysis of Rubber P.23, etc.

Table I(B)15
SOLVENT EXTRACTION OF PALE CREPE RUBBER

	Solvent		Acetone	Alcohol	Iso-octane	Ethyl Ether	Benzene	Residue of Extraction
	Yield of Extract(%)		2.78	3.24	9.32	15.66	28.38	40.62
Properties of Extract	Mol. wt		15,200	2,300	41,000	126,000	157,000	210,000
	K_m		3.8×10^{-4}	3.8×10^{-4}	1.1×10^{-4}	1.1×10^{-4}	1.7×10^{-4}	3.0×10^{-4}
	Iodine Value		525.4	11.4	296.4	370.5	368.5	318
	Elementary Analysis (%)	C	75.60	69.11	86.60	86.60	86.45	86.15
		N	none	none	0.02	0.01	0.01	0.8
		Ash	0.01	0.07	none	0.01	0.01	0.02
		H	10.80	10.08	11.88	11.98	12.06	11.86
		O	13.59	20.74	1.86	1.40	1.38	1.17

Table II(B)15
THERMAL TREATMENT OF PALE CREPE RUBBER WITHOUT CATALYST

No. of Exp.	Conditions of Reaction		Properties of Product			Remarks
	Temp. (°C)	Time (hr)	Mol. wt	Iodine Value	Km	
1	150	20	72,000	368.9	3.8×10^{-4}	used 4 volumes of solvent
2	200	20	26,700	324.6	3.8×10^{-4}	used 4 volumes of solvent
3	200	30	18,100	315.2	3.8×10^{-4}	used 4 volumes of solvent
4	300	10	3,000	310	3.8×10^{-4}	used autoclave
5	300	4	816	146.9	3.8×10^{-4}	used autoclave without solvent

Table III(B)15
THERMAL TREATMENT OF PALE CREPE RUBBER WITH ACID CLAY

No. of Exp.	Conditions of Reaction			Properties of Products			Remarks
	Temp. (°C)	Time (hr)	Amount of Acid Clay	Mol. wt	Iodine Value	Km	
1	150	20	25	9,700	240	3.6×10^{-4}	used 4 volumes of solvent
2	200	20	25	6,400	278	3.8×10^{-4}	used 4 volumes of solvent
3	200	20	5	9,800	186	0.4×10^{-4}*	used 4 volumes of solvent
4	200	10	10	9, 00	101.2	0.4×10^{-4}	used 4 volumes of solvent
5	200	10	20	7,000	70.9	0.4×10^{-4}	used 4 volumes of solvent
6	300	2	10	1,020	135.8	0.4×10^{-4}	non solvent used autoclave
7	300	4	10	578	133.7	0.4×10^{-4}	non solvent used autoclave

*The reason for using the Staudinger's value of cyclic rubber molecule, i.e. 0.4×10^{-4}, for the constant Km, was because considerable cyclization of the rubber molecule caused by the action of acid clay, made it unsuitable to use the constant of rubber hydrocarbon as it is.

Table IV(B)15
POLYMERIZATION OF SIMPLE CRACKED DISTILLATES OF PALE CREPE RUBBER

			1	2	3	4	5	6	7
	No. of Exp.		1	2	3	4	5	6	7
Conditions of Reaction	Range of Fraction(°C)		100~150	150~200	200~250	250~300	100~250	150~200	150~250
	Catalyst	Type	AlCl$_3$	AlCl$_3$	AlCl$_3$	AlCl$_3$	Acid Clay	Acid Clay	Synthetic Acid Clay
		Amount(%)	5	3	3	5	20	20	20
	Temp. (°C)		100	120	120	100	150	300	300
	Time (hr)		8	8	8	8	8	6	6
Yield of Product (%)			22	38	64	57.7	6.3	15.4	14.6
Properties of Product	Iodine Value		72.4	139.9	38.7	68.4	108.9	48.2	37.6
	Density(20/4°C)		0.9628	0.9693	0.9612	0.9542	0.9438	0.9607	0.9830
	Viscosity (S.U.S.)	at 100°F	2,269	9,303	2,745	2,884	7,123	3,095	610
		at 210°F	72.0	117.6	69.1	90.2	54.8	65.3	47.3
	Viscosity Index		-159.6	-269.2	-28.9	-66.8	-211.1	-406.6	-226.2
	Flash Point		135	102	145	171	185	176	174

Table V(B)15
POLYMERIZATION OF ISOPRENE FRACTION OF THE CRACKED DISTILLATE OF PALE CREPE RUBBER

No. of Exp.			25	26	24	20	23	29	31	32	34
Conditions of Reaction	Solvent (parts)*		1	1	1	none	none	none	none	none	none
	Temp. (°C)		80	80	60	35	35	30	30	0	-10
	Time (hr)		8	8	8	8	8	8	8	8	8
	Catalyst	Type	AlCl3	AlCl3 + Acid Clay	AlCl3	AlCl3	AlCl3	AlCl3	SnCl4	AlCl3	AlCl3
		Amount (%)	3	2+5	5	3	5	1	10	5	3
Yield of Product (%)			5.5	22.0	30.7	20.0	20.5	12.0	31.3	11.0	12.5
Mixing Ratio of Niizu Oil			77	47	42	none	20	none	none	30	80
Properties of Product	Iodine Value		30.1	28.4	32.0	40.8	41.0	42.3	56.5	58.4	58.0
	Density(20/4°C)		0.9234	0.9274	0.9218	0.9216	0.9226	0.9211	0.9316	0.9210	0.9231
	Viscosity (S.U.S.)	at 100°F	1,260	2,180	1,501	2,726	3,026	4,242	1,608	1,075	3,382
		at 210°F	60.6	77.7	70.1	92.3	106.7	178.4	70.1	88.6	117.1
	Viscosity Index		-110.8	-85.1	-54.3	-4.1	0	77.6	72.7	89.3	12.9

*Solvent is a South Borneo's light oil boiling from 150°C to 250°C.

ENCLOSURE (B)15

Table VI(B)15
CO-POLYMERIZATION OF THE CRACKED DISTILLATE OF PALE CREPE RUBBER WITH THE CRACKED DISTILLATE OF PARAFFIN WAX

	No. of Exp.		7	8	9	19
Conditions of Reaction	Cracked Distillate of Pale Crepe Rubber (150∼250°C) (%)		50	40	30	20
	Cracked Distillate of Paraffin wax (150∼250 C) (%)		50	60	70	80
	Temperature (°C)		100	100	100	100
	Time (hr)		8	8	8	8
Yield of Product (%)			30	24	30	14.1
Properties of Product	Iodine Value		19.2	16.4	15.2	14.1
	Density (20/4°C)		0.9124	0.9063	0.8726	0.8789
	Viscosity (S.U.S.)	at 100°F	888	1,971	1,072	1,206
		at 210°F	68.8	107.6	99.0	104.1
	Viscosity Index		38.4	64.1	106.7	104.3
	Viscosity Ratio		2.94	2.42	1.77	1.20

*In all cases the catalyst was 5% $AlCl_3$ (wt)

ENCLOSURE (B)15

Table VII(B)15
HYDROCRACKING OF PALE CREPE RUBBER WITHOUT SOLVENT

No. of Exp.			1	2	3	4	4'**	15	5***	5'	6#	12	14
Conditions of Reaction	Temperature (°C)		300	300	300	300		400	300 — 200		300 — 100	300	300
	Time (hr)		2	4	6	8	•	2	4 — 4		4 — 8	6	6
	Catalyst		Ni	Ni	Ni	Ni		Ni	Ni		Ni	MoS_2	MoS_2
Yield of Product (%)			94	92	86	79	60	35.3	68	52	64	83	57
Properties of Product	Mol. wt*		3,393	1,975	959	884	1,030	665	820	1,068	640	1,217	1,278
	Iodine Value		309.4	126.0	57.3	16.4	18.4	26.1	31.2	33.4	51.5	69.5	34.6
	Density (20/4°C)		0.9321	0.9214	0.8992	0.8820	0.9002	0.9083	0.8853	0.8998	0.8976	0.9085	0.8974
	Viscosity (S.U.S.)	at 100°F	6,588	1,602	585	174	2,423	1,037	172.7	3,180	228	1198	
		at 210°F	605	123.8	91.6	49.5	101.4	69.4	48.6	102.0	47.6	141.0	53.0
	Viscosity Index		124.4	104.4	131.7	193.8	21.8	21.3	142.3	-27.7	8.86	-20.8	128.7
	Viscosity Ratio							(10.4)		(6.9)		(42.0)	(14.5)
	Pour Point (°C)		-12	-24	-35	-61	-21	-2	-28	-22	-33	-21	+12
	Flash Point (°C)		84	42	35	21	42	12	31	79	38	43	118

*For the constant, or determination of molecular weight, Km of the hydrorubber's value, 1.4 x 10^{-4}, was used.
**Topped residue above 150°C of No. 4.
***2 stage hydrogenations acid treated
#2 stage hydrogenations.

Table VIII(B)15
HYDROCRACKING OF PALE CREPE RUBBER WITH 2 PARTS OF SOLVENT

No. of Exp.		16	25	21	23	22	26	17	18	19
Conditions	Temp. (°C)	300	300	300	300	300	200 300	300	350 300	300 200 200
of	Time (hr)	5	15	20	20	30	4 20	6	4 7	4 12 10
Reaction	Solvent (2 parts used.	Light oil from rubber*	Light oil from rubber	Light oil from rubber	Light oil from rubber	Light oil from rubber	Gas oil#2 (170 220°C)	Light oil from rubber	Light oil from rubber	Light oil from rubber
Yield of Product (%)		290°C T.R. 55.3	270°C T.R. 88.0	300°C T.R. 60.1	250°C T.R. 63.3	250°C T.R. 73.0	240°C T.R. 72.0	345°C T.R. 33.0	320°C T.R. 39.3	300°C T.R. 75.3
Properties	Mol. wt.	1,054	1,074	1,004	1,197	904	1,292	1,664	1,142	,988
	Viscosity at 100°F	7,046	2,680	4,009	2,081	3,256	2.744	7,312	5,921	4,000
	(S.U.S.) at 210°F	346	136.8	318	123.1	148.0	135.3	181.0	149.7	325
	Viscosity Index	83.3	77.3	92.1	83.3	72.2	73.3	22.7	25.1	
	Iodine Value	105.6	10.1	18.8	5.4	21.9	63.9	49.8	10.1	113.9
of	Viscosity Ratio	(4.5)	2.96	2.60	6.40	5.8	cannot measure	(3.1)	(2.9)	
	Density (20/4°C)	0.9057	0.8996	0.8912	0.8854	0.8989	0.9066	0.9233	0.9149	0.9381
	Flash Point (°C)	192	151	168	140	136	138	200	180	166
Product	Pour Point (°C)	-8	-14	-13	-18	-16	-12	+7.5	3.5	+5
	Refractive Index	1.4970		1.4895	1.4850	1.4920	1.4960	1.5030	1.4960	1.5147
	No. of Aromatic Nuclei**	3		5	5	5	6	11	9	7

*The light oil from rubber was a fraction of hydrogenated oil of rubber. Nickel as the catalyst and two parts of solvent were used in all cases. All light oil fractions were 150~250°C fractions.

**No aromatic nuclei were determined from the refractive index and molecular weight by H.I.Waterman's method of ring-analysis.

Table IX(B)15
HYDROCRACKING OF PALE CREPE RUBBER WITH VARIOUS AMOUNTS OF SOLVENT

No. of Exp.		27	28	29	30	31	35	32	33	34
Conditions of Reaction*	Temp. (°C)	300	300	300	300	300	300	300	300	300
	Time (hr)	15	25	15	20	15	12	20	20	20
	Solvent Parts**	3	3	4	4	5	6	8	10	14
Yield of Product (%)		(260°C T.R.) 75.0	(270°C T.R.) 90.0	(270°C T.R.) 78.5	(265°C T.R.) 91.2	(260°C T.R.) 93.3	(240°C T.R.) 55.0	(270°C T.R.) 75.0	(270°C T.R.) 67.0	(285°C T.R.) 63.3
Properties of Product	Mol. wt	1,052	1,023	1,156	1,072	952	1,632	1,530	1,462	1,549
	Iodine Value	16.1	20.9	14.7	7.1	15.5	18.0	9.9	10.2	10.4
	Density (20/4°C)	0.8788	0.8899	0.8900	0.8843	0.8779	0.9093	0.8851	0.8934	0.8949
	Viscosity (S.U.S.) at 100°F	1,159	1,745	1,283	1,808	1,414	1,584	1,478	1,553	1,547
	Viscosity (S.U.S.) at 210°F	108.1	121.5	104.3	135.2	129.2	102.2	122.9	108.5	103.4
	Viscosity Index	111.5	96.1	100.0	105.9	115.9	77.1	108.9	85.6	81.5
	Viscosity Ratio	2.65	3.58	2.46	2.33	2.23	2.89	3.05	5.90	6.40
	Flash Point (°C)	124	146	136	142	134	115	145	160	156
	Pour Point (°C)	-32	-26	-21	-25	-26	-22	-32	-24	-18
	Refractive Index	1.4828	1.4810	1.4867	1.4867	1.4819				
	No. of Aromatic Nuclei	3	5	5	4	3				

*In all cases nickel was used as the catalyst.
**Solvent used was light oil from rubber.

Table X(B)15
HYDROCRACKING OF PALE CREPE RUBBER WITH 5 PARTS OF VARIOUS SOLVENTS

No. of Exp.			46	47	47'	39	31	49
Conditions of Reactions*	Temp. (°C)		300	300	300 350	300	300	300
	Time (hr)		12	15	15 5	15	15	15
	Solvent	Type	Decalin (188°C)	Dodecane (215°C)	Dodecane (215°C)	South Sumatra's light oil (150~250°C)	Light oil from rubber (150~250°C)	Tarakan light oil (150~250°C)
		Content of paraffinic (%) H.C.	0	100	100	49.5	58.7	46.3
Yield of Product (%)			52	73	70.2	50	93.3	40
Properties of Product	Iodine Value		63.6	67.1	12.1	86.8	15.5	46.4
	Density (20/4°C)		0.9017	0.8466	0.8316	0.9167	0.8779	0.8907
	Viscosity (S.U.S.)	at 100°F	1,709	1,184	1,602	1,709	1,414	758
		at 210°F	75.4	140.5	123.8	101.2	129.2	67.0
	Viscosity Index		-41.0	129.0	104.4	67.0	115.9	59.5
	Viscosity Ratio		3.36	15.4	1.71	5.25	2.23	4.74
	Flash Point (°C)		172	95	172	135	134	172

*In all cases, nickel was used as the catalyst and 5 parts of solvent were used.

**The components of the light oils were determined by Waterman's method.

ENCLOSURE (B)15

Table XI(B)15
HYDROCRACKING OF RUBBER PASTE AND NON-PASTE RUBBER

No. of Exp.*		31	51	51'
Yield of Product (%)		93.3	57.5	
Properties of Product	Iodine Value	15.5	4.3	4.9
	Density (20/4°C)	0.8779	0.8724	0.8777
	Viscosity at 100°F	1.414	1.677	1.636
	S.U.S.) at 210°F	129.2	125.9	119.3
	Viscosity Index	115.9	103.1	98.6
	Viscosity Ratio	2.23	2.03	1.33
	Flash Point (°C)	134	124	166
	Remarks	non-paste	paste	16% of spindle oil was mixed to the product of No. 51

*Reaction conditions were: Temp., 300°C; Time, 15 hr; Solvent, 5 parts of light oil from scrubber; catalyst, nickel

Table XII(B)15
HYDROCRACKING OF RUBBER PASTE WITH FISCHER OIL AS SOLVENT

No. of Exp.		52	52'	53	54 **	55	56	57	58
Raw Material		pale crepe	pale crepe	pale crepe	smoke sheet	smoke sheet	smoke sheet	smoke sheet	smoke sheet
Conditions of Reaction	Temp. (°C)	300	300	300 350	300	300 350	300 350	300 350	300 350
	Time (hr)	15	15	15 3	15	15 4	8 7	8 7	8 10
Yield of Product (%)		84.5	76.0	80.1	63.0	70.0	75.6	81.2	80.0
Properties of Product	Iodine Value	36.0	38.4*	2.5	92.1	45.1	3.6	1.94	1.22
	Density (20/4°C)	0.8436	0.8462*	0.8437	0.8903	0.8777	0.8521	0.8421	0.8401
	Viscosity (S.U.S.) at 100°F	1,182	1,053*	1,053	1,871	1,252	1,520	1,146	1,159
	Viscosity (S.U.S.) at 210°F	131.2	111.9*	124.2	133	103.3	111.5	140.1	108.1
	Viscosity Index	125.6	120.5*	127.6	101.3	100.3	95.3	130.3	111.5
	Viscosity Ratio	34.2	2.54*	1.50	25.4	8.43	1.80	1.72	1.67
	Conradson's Carbon(%)			0.006	0.03				
	Conradson's Carbon After Oxidation Test			0.7					

*These are the characteristics of the mixture of the product from rubber (75%) and Niizu spindle oil (25%).

**In these experiments, Fischer oil solvent and nickel catalyst were used.

Table XIII(B)15
CONTINUOUS HYDROCRACKING OF NATURAL RUBBER PASTE IN THE PILOT PLANT

No. of Exp			1	2	3	4	5	6	7	8	9
Conditions of Reaction	Reaction Temp. (°C)		350	375	375	375	375	400	400	400	400
	Amount of Charge (lit/hr)		1.0	1.0	1.5	1.0	1.5	1.0	1.5	1.0	1.5
	Amount of H_2 Gas (m^3/hr)		1.0	1.0	1.5	1.5	1.5	1.0	1.5	1.5	1.5
Yield of Product from Rubber (%)			41.7	39.0	41.9	58.7	52.6	26.9	11.8	40.0	51.7
Properties of Product*	Density (25/4°)		0.8457	0.8479	0.8437	0.8624	0.8697	0.8474	0.8472	0.8519	0.9238
	Flash Point (°C)		210	211	205	224	221	213	197	218	200
	Viscosity (S.U.S.)	at 100°F	49,955	7,955		3,463	7,246	1,898	2,236	1,712	3,927
		at 210°F	2319	583	264	288	424	171.7	197.0	134.1	288
	Viscosity Index					122.5		120.5	120.9	108.1	118.4
	Pour Point (°C)		5	-9	-11	-9	-4	-15	-12	-13	-8
	Viscosity Ratio		0.69	0.94	1.29	1.30	1.35	1.47	1.20	1.25	1.23
	Conradson's Carbon (%)		0.13	0.15	0.16	0.15	0.11	0.15	0.17	0.16	0.15

*Zero iodine value.

ENCLOSURE (B)15

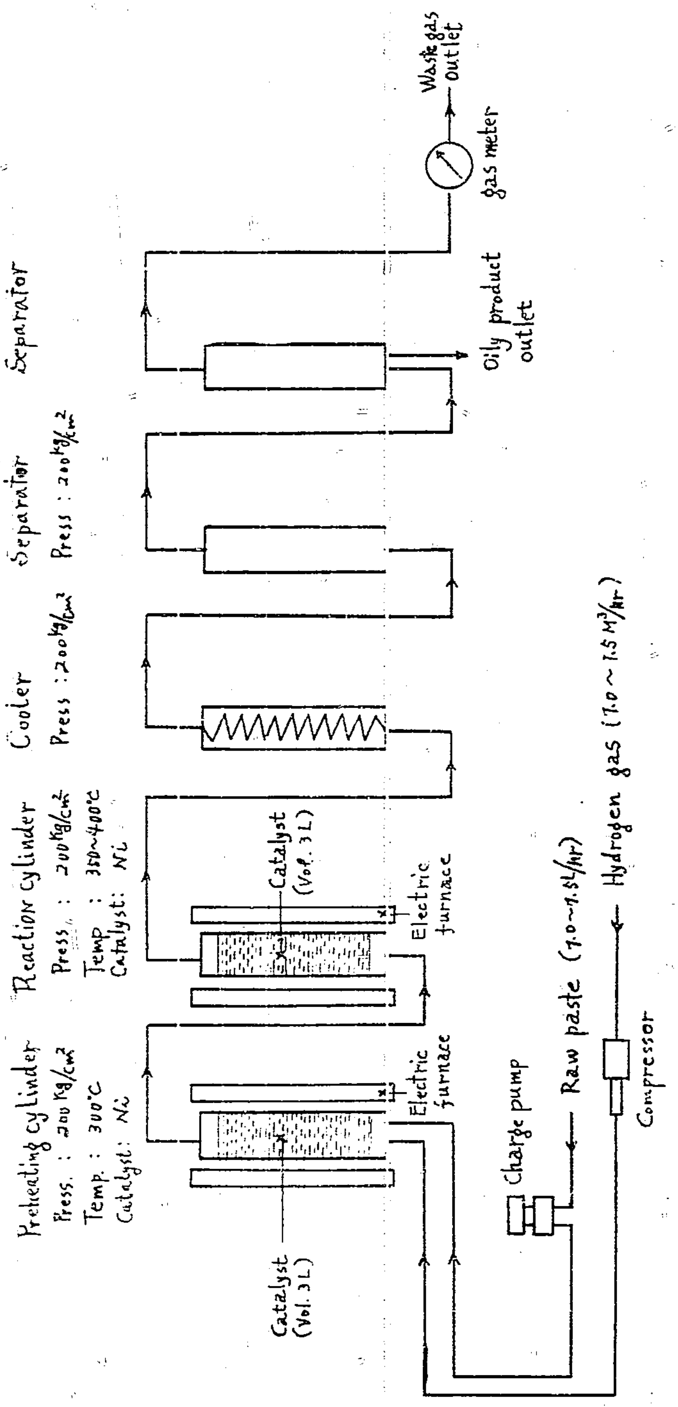

Figure 1(B)15

CONTINUOUS HYDROGENATING APPARATUS FOR NATURAL RUBBER PASTE

ENCLOSURE (B) 16

RESEARCH ON THE PREPARATION OF LUBRICATING OILS FROM BROWN-COAL TAR

by
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NAVAL ASSISTANT ENG. M. TOYAMA

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)16

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)16

SUMMARY

The object of this project was to obtain an aero-engine oil by the condensation of a distilled fraction of brown coal tar and cracked distillate of paraffine waxes in the presence of $AlCl_3$.

Only the analyses of the fractions of the tar were carried out and no significant results were obtained before the termination of the war.

I. INTRODUCTION

A. History of Project

As the stock-pile of raw material for aero-engine oil had decreased gradually since April 1945, studies were carried on to utilize brown coal tar as the raw material for the preparation of aero-engine oil.

B. Key Research Personnel Working on Project

Naval Assistant Engineer M. TOYAMA

II. DETAILED DESCRIPTION

The high boiling fractions of coal tar consist mainly of aromatic hydrocarbons, and a stable aero-engine oil can be obtained by condensing a suitable fraction of coal tar with the cracked distillate of paraffin waxes in the presence of aluminium chloride.

The first experiment was the analysis and pre-refining of the fraction of brown coal tar boiling above 250°C, (consisting mainly of aromatic hydrocarbons and a small amount of acidic and basic compounds). In general, brown coal tar was separated with the following fractions and its fractions were used as gasoline and fuel oil.

Another method of treating brown coal tar was as follows: the brown coal tar was heated to 60°C for one hour to dehydrate it, and was topped at 250°C. The residual oil was distilled into several fractions at a vacuum of 1lmm Hg.

The fraction boiling from 140 to 200°C was 17.6% by weight of the dehydrated tar.

This fraction was washed with one volume of 20% Na_2CO_3 solution and one volume of 10% NaOH solution.

The amount of oil lost by NaOH washing was 18% of the fraction by weight.

The alkali treated oil was then dewaxed with 3 volumes of acetone-benzene mixture (ratio 35:65) at -5°C.

The alkali treated and dewaxed oil was 8.6% by weight of the dehydrated tar. It was distilled into three fractions and their properties determined.

These results are shown in Table I(B)16 and II(B)16.

ENCLOSURE (B)16

Table I(B)16
PROPERTIES OF FRACTIONS OF ALKALI TREATED DEWAXED OIL

	Yield (Vol%)	Density(25/4°C)	Refractive Index(25°C)
140-160°C/11mm Hg	46.6	0.9718	1.5525
160-180°C/11mm Hg	28.3	0.9971	1.5682
180°- /11mm Hg	Residue black pitch-like substance		

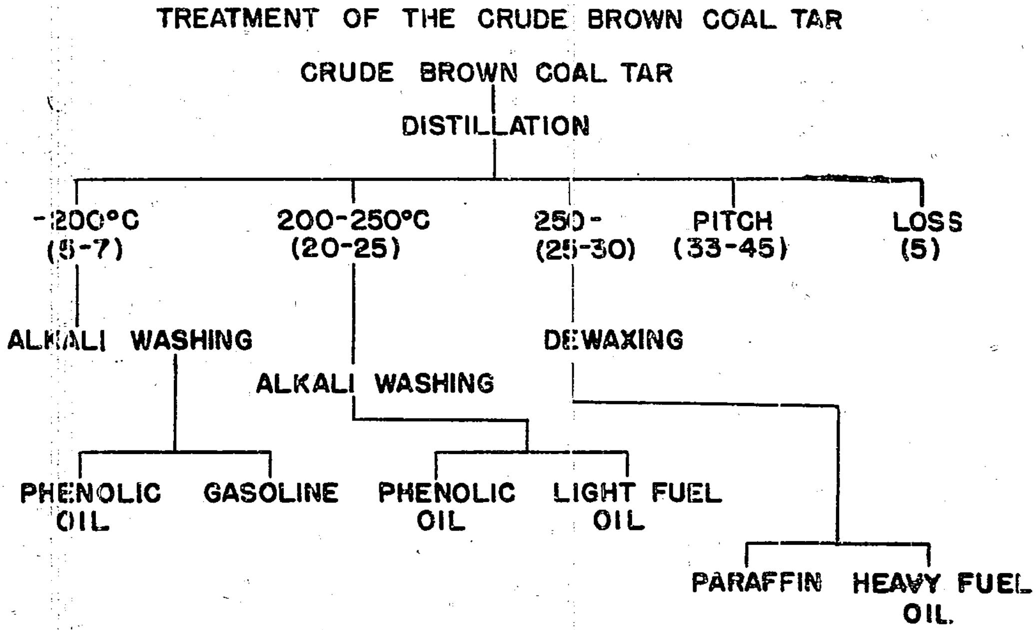

Figure 1(B)16
TREATMENT OF THE CRUDE BROWN COAL, TAR

ENCLOSURE (B)16

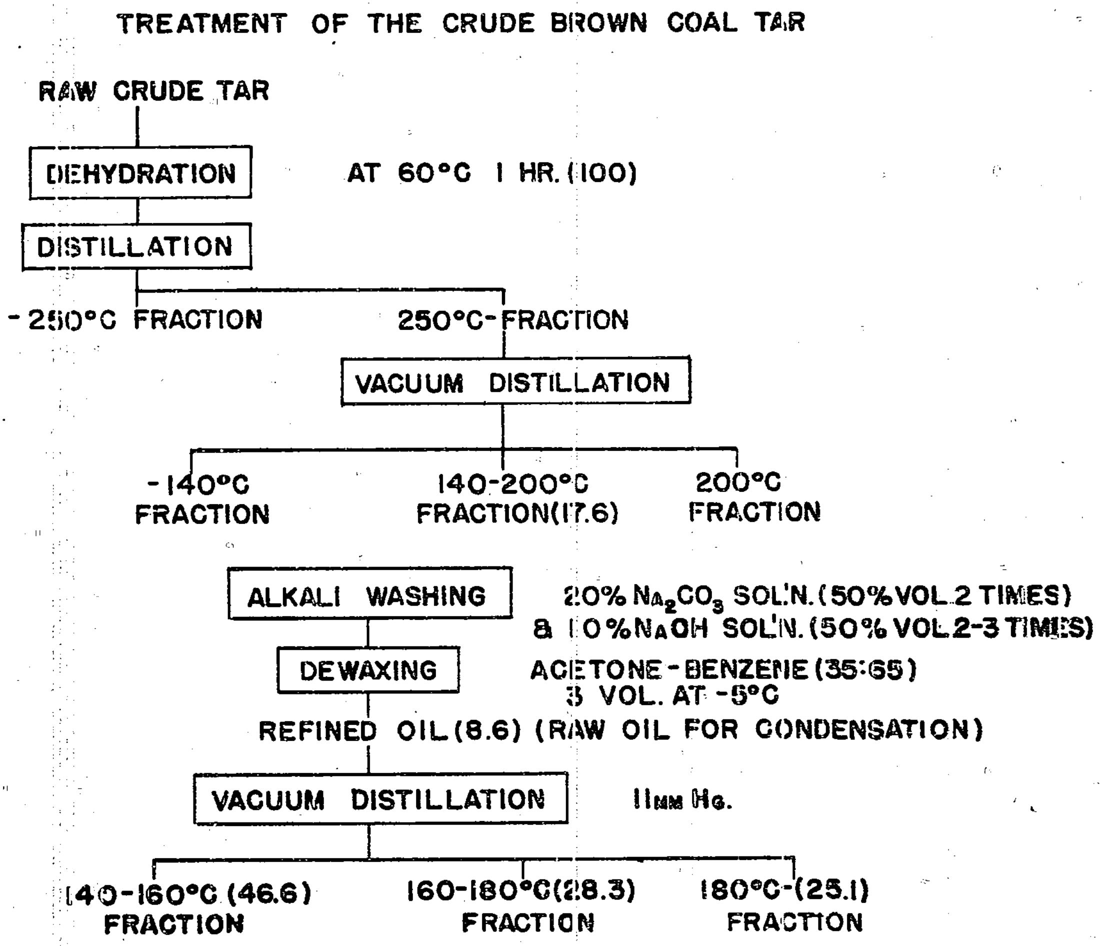

Figure 2(B)16
TREATMENT OF THE CRUDE BROWN COAL TAR

ENCLOSURE (B) 17

STUDIES ON THE MANUFACTURE OF LUBRICATING OIL FROM PINE ROOT OIL

by
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CHEM. ENGINEER N. MATSUO

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)17

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)17

SUMMARY

A precise distillation was made for the analysis of the components of pine root oil.

The tar, topped to 300°C, was distilled and cut into fractions of 10°C under vacuum of 17mm Hg. In the vicinity of 210°C/17mm about 40% was distilled which probably consisted of abietic acid.

From 230-250°C, about 20% was distilled which probably consisted of retene.

In this fraction, crystals were deposited some time afterwards. Besides the two above-mentioned fractions, various fractions were cut for every 5%-10% of distillate.

The densities of each fraction increased gradually. This was due to the fact that the components in the distillates were not remarkably different and the isomers were distilled gradually in order of the boiling point.

I. INTRODUCTION

A. History of Project

On the one hand, a large quantity of the pine root oil was available, and on the other, raw materials for lubricating oils were scarce, so it was attempted to utilize the higher boiling fractions of pine root oil or pine root tar as the raw material for lubricating oil.

We began the study in July, 1945. At first, the main substances of the higher boiling fractions or the tar of the pine root oil were studied by the component analyses.

For this purpose, the fractional vacuum distillation was begun.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut., I. SHIWATA

II. DETAILED DESCRIPTION

The experiments were carried on over too short a time to report any results other than those described in Figure 1(E)17, which shows the scheme by which the aero engine oil was to be prepared.

ENCLOSURE (B)17

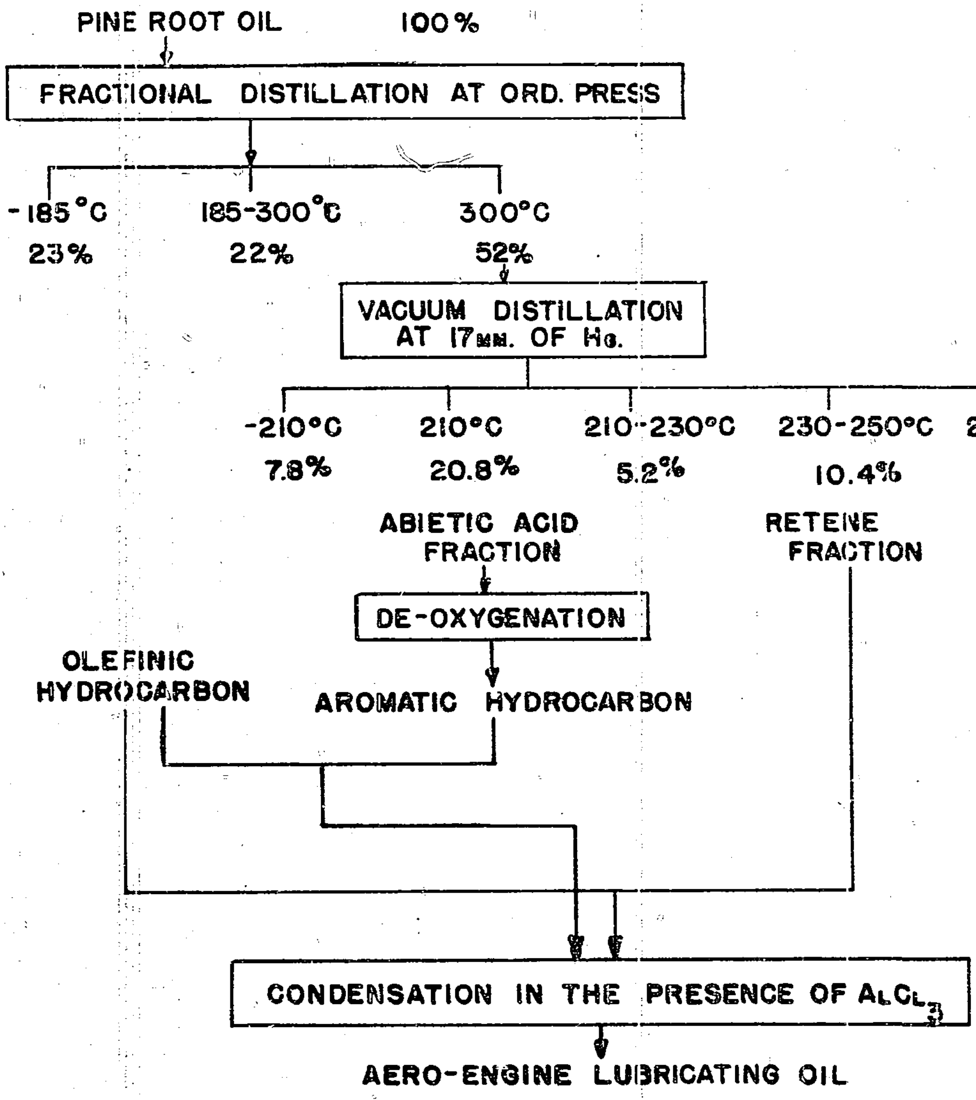

Figure 1(B)17
SCHEME FOR PREPARATION OF AERO ENGINE OIL

ENCLOSURE (B) 18

A SIMPLE FIELD METHOD
OF RECLAIMING
USED LUBRICATING OIL

by

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Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)18

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)18

SUMMARY

Because of the difficulty of transporting used lubricants from the airfield to the refineries for re-refining, there was a need for a single method of reclaiming used lubricating oil utilizing apparatus which could be fabricated at the air fields from the materials on hand.

For this purpose, the author devised a method and apparatus, and made this apparatus available for practical use.

The method is as follows: Heat the used oil to 100°C temperature and stir into the heated oil, ashes of wood, grass, roots etc. (not charcoal) using about 15% of ashes by weight, and then heat to 130°C and filter with a thin filter-paper or newspaper.

This reclaimed oil can be used in every type of engine, such as the Homare, Kasei and Atsuta.

I. INTRODUCTION

A. History of Project

At first the author tried to discover a suitable mixing agent such as aluminum silicate (aluminum silicate is not available everywhere), and then tested every minute powder, such as aluminum, silica, magnesia, CaO, active carbon,etc.

At last the author discovered that the ashes of many things such as wood, and coal, and CaO, and MgO were very effective for this purpose.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. T. FUJIMOTO

II. DETAILED DESCRIPTION

A. Description of Apparatus

This apparatus is made very easily. The materials of fabrication were available at every airfield.

This equipment is constructed in two parts, one is the filtering part and another is the vacuum part, the filtering part is in the form of an oil bath, which contains an filtering plate with drilled hole, 5mm. in diameter. The bottom of this oil bath and the water-separator are connected by pipe, including a valve and pipe union.

The vacuum part is made of a gasoline drum, and airplane boost meter, which shows the degree of vacuum, and wing hand pump which make a vacuum and draws out the reclaimed oil. The filter paper sticks to the filter net on plate, which is supported on the funnel.

wood fire is used to heat the oil bath, because an airfield has no gas or electricity.

The general view is shown in Figure 1(B)18.

ENCLOSURE (B)18

B. Experimental Results

1. Yield: 70%-85%

2. Physical and chemical properties of products are shown in Table I(B)18.

The used oil was acquired from Yokosuka Airfield. This oil had had 30 hours service in the engine of "Shiden", the name of an airplane.

3. Operating or test difficulties

a. Filter plate and filter paper: Filter paper must first be affixed on the filter net by oil-wetting the paper with new lubricant and then sticking it tightly on the net. Then, the vacuum pump (wing pump) acts from bottom of a vacuum chamber to suck the filter paper against the filter plate.

b. Heating: If the water in the used oil exceeds 0.1%, it must be heated slowly and stirred to prevent foaming.

c. Ash (mixing agent): Ash must be burned thoroughly. Before using, the ash must be dried thoroughly.

d. Vacuum system: Japanese oil drums will collapse if the vacuum exceeds 1/2 atmosphere, so a vacuum gauge (boost meter) must be utilized.

4. Advantage of this method and apparatus

a. It does not use special or high price materials.

b. It uses only firewood as fuel, which can be obtained everywhere.

c. The operating procedure is very simple, so anyone can use it.

d. This apparatus is light in weight, and can be transported easily.

III. CONCLUSIONS

1. Materials of this apparatus:

Drum	3
Wing Pump	1
Cock	3
Boost Meter	1
Thermometer	1
Glass tube	1

2. Yield of reclaimed oil: 70%-85% of used oil.

3. Capacity: Reclaimed oil can be produced at the rate of 7 to 20 liters per hour by this apparatus.

4. The reclaimed oil obtained by this method and apparatus, can be used practically at all of the naval airfields.

ENCLOSURE (B)18

Table I(B)18

PHYSICAL AND CHEMICAL PROPERTIES OF PRODUCTS

		Used Oil	Reclaimed Oil
Viscosity	100°F	1714.1	1552.4
	210°F	123.7	119.4
Viscosity Index		99.5	102.4
Ash		0.204	0.012
Acid Value		0.257	0.084

ENCLOSURE (B)18

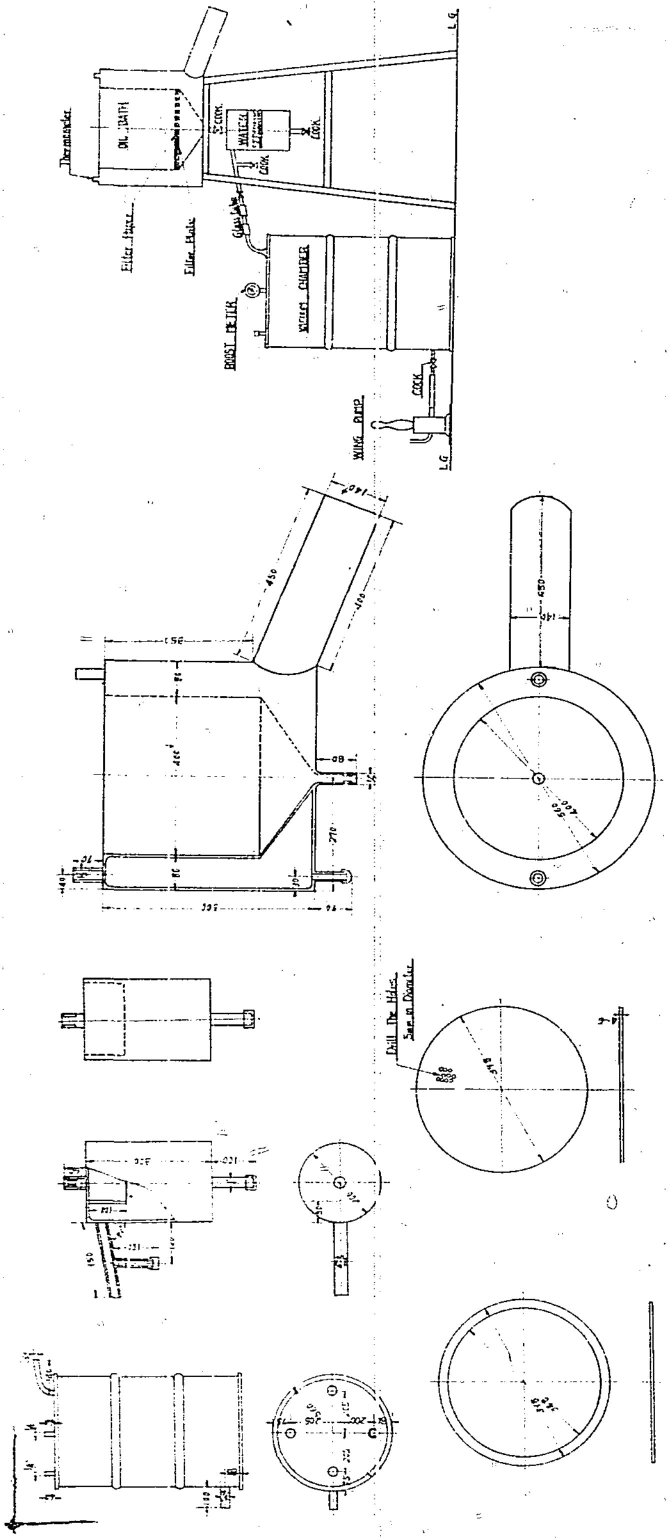

Figure 1(B)18

A SIMPLE FIELD APPARATUS OF RECLAIMING USED LUBRICATING OIL

ENCLOSURE (B) 19

STUDIES ON LUBRICATING OILS FOR THE MARINE AND AERO TORPEDO ENGINES

by
CHEM. ENG. CAPT. DR. I. KAGEHIRA
NAVAL ENG. N. MATSUO
CHEM. ENG. LT. COMDR. M. HIRATA
CHEM. ENG. LIEUT. M. MAEDA

Research Period: 1938-1943

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)19

SUMMARY

The objective of this project was to obtain an excellent lubricating oil for marine and aero topedo engines and the summary of results are shown as follows:

1. The conditions of lubrication in the marine torpedo engine resemble those in the aircraft engine and the following lubricating oil was prepared from Oha crude oil by solvent extraction and observed to be an excellent oil in practical tests:

Density (25/4)	0.8804
Flash point (°C)	222
Viscosity in S.U.S at 100°F.	1042.7
at 210°F.	92.3
Viscosity index	99
Acid value	none
Saponification	0.45
Conradson's carbon(%)	0.55
Pour point (oC)	-14

A mixture of 80% of imported aero engine oil #100 and 20% of imported aero engine oil #80 has almost the same properties as the above mentioned oil and this mixture was actually used.

2. The lubricating oil for aero torpedo engine is used at lower temperature than that for the marine torpedo engine and it is necessary to have a much lower pour point. A synthetic oil was prepared from a fraction of shale crude oil boiling from 200° to 300°C by the polymerization method and it was found satisfactory in service. Its properties are as follows:

Density (15/4)	0.8950
Flash point (°C)	225
Viscosity in S.U.S. at 210°F	93
Viscosity index	92
Saponification value	2.8
Conradson's carbon(%)	0.35
Pour point (°C)	-32
Corrosion test	OK

This oil, however, was unsuitable for use in the coldest zone and it was used mainly near the main islands of Japan or in the tropical zone.

3. For the coldest zone, a synthetic oil was prepared by polymerizing fraction boiling from 100°C to 230°C of the cracked distillate of paraffine wax and adding 1.5% of aluminium oleate to the product of polymerization.

It was found satisfactory in practical tests. This oil was observed to be suitable for use not only in the coldest zone, but also in the tropical zone. Its properties are as follows:

Density (15/4)	0.8700
Flash point (°C)	230
Viscosity in S.U.S., 210°F	96
Viscosity index	112
Saponification value	2.8
Conradson's carbon(%)	0.08
Pour point (°C)	-46

I. INTRODUCTION

A. History of Project

For the marine torpedo engine, a steam cylinder oil had been used in summer and a mixture of 75% of steam cylinder oil and 25% of rape oil in winter. The formation of sludge in the engine was comparatively large in using these oils and it was necessary to decrease it.

The conditions of lubrication in the torpedo engine resembles that in the aero engine, and an oil prepared by the same method for aero engine oil should be suitable for the torpedo engine. Thus, studies were carried on in regard to the preparation of the marine torpedo engine oil by the solvent extraction of Oha crude oil from 1938 and finished 1940 with successful results in 1943.

B. Key Research Personnel:

Chem. Eng. Capt., Dr. I. KAGEHIRA
Chem. Eng. Lt. Comdr. N. IIMUR
Chem Eng. Lt. Comdr. E. KOSUGI

II. DETAILED DESCRIPTION

A. Marine torpedo engine oil

1. **Procedure of Preparation**: Marine torpedo engine oil was prepared from 50% topped residue of the Oha crude oil by the following solvent extraction method: the residual oil was deasphalted by 5 volumes of liquid propane at 45°C, and the deasphalted oil was extracted at 45°C by 6 volumes of phenol and the raffinate was dewaxed at (-) 20°C by 5 volumes of a mixture of 35% acetone and 65% benzene. The dewaxed oil was topped to have a desirable viscosity followed by treating with 10% acid clay. These procedures are given in Figure 1(B)19.

2. **Results**: Properties of a marine torpedo engine oil prepared by the above mentioned procedure are shown below:

Density (25/4)	0.8804
Flash point (°C)	222
Viscosity in S.U.S at 100°F	1042.7
at 210°F	92.3
Viscosity index	99
Acid value	none
Saponification value	0.45
Conradson's carbon(%)	0.55
Pour point (°C)	-14

This oil was subjected to practical tests at the Kure Naval Arsenal and found to be an excellent oil for the marine torpedo engine.

But its production was not enough to supply the demand, and a mixture of an aero engine oil # 100 and an aero engine oil #80, imported from U.S.A., in a ratio of 80 to 20 by volume was actually used, since this mixture had the same properties of the former oil.

B. The Aero Torpedo Engine Oil

1. Preparation from Shale Oil

a. Procedure of Preparation. An aero torpedo engine oil was prepared from Shale oil obtained at Fushun, South Manchuria, by the following method: a gas oil fraction boiling 200° to 300°C was treated with 5 volumes of 10% caustic soda solution, 2% of 50° Be sulphuric acid, 2% of 66° Be sulphuric acid, 50% of 10% caustic soda solution and a small amount of acid clay. The refined oil obtained was fractionated by a steam distillation and a fraction boiling from 200°C to 300°C was polymerized at 80°C - 100°C in the presence of 10% of aluminium chloride. The polymer was dechlorinated at 200°C by 5% of a mixture of two parts of acid clay and one part of calcium oxide and topped off lighter fractions in a vacuum distillation. Finally 1.5% of aluminium oleate was added to the above residual oil to prevent the oil washing out by sea water in the aero torpedo engine at the end of its running on trial shots. The steps in the manufacturing procedure are shown in the Figure 2(B)19.

b. Results. The properties of an aero torpedo engine oil prepared from shale gas are as follows:

Density (15/4)	0.8950
Flash point (°C)	225
Viscosity in S.U.S. at 210°F	93
Viscosity index	92
Saponification value	2.8
Conradson's carbon(%)	0.35
Pour point (°C)	-32
Corrosion test	OK

This oil was usbjected to practical tests at the Naval Aeronautical Arsenal, YOKOSUKA, and found suitable for aero torpedo engines used near the main island of Japan or in the tropical zone, but unsatisfactory for use in the coldest zone. This oil was prepared and supplied to the Japanese Navy from FUSHUN in Manchuria.

2. Preparation from Paraffin Wax. Since aero torpedo engine oil from shale gas oil was found unsatisfactory for use in the coldest zone, its preparation from paraffin wax was studied.

a. Procedure of Preparation. (Refer to Plate 1(B)19) A fraction boiling from 100°C to 230°C of cracked distillate of paraffin wax was polymerized in the presence of 3% of $AlCl_3$ at 100°C for 10 hrs. and the polymerized product was dechlorinated at 200°C by 5% of a mixture of two parts acid clay and one part calcium oxide.

The dechlorinated oil was distilled in vacuum of 5mm Hg and its residual oil was treated with 5% of acid clay. Finally the clay treated oil was compounded with 15% of aluminium oleate. The procedure of preparation is shown in the Figure 3(B)19.

b. Results. The properties of an aero torpedo engine oil prepared from the cracked paraffin are as follows:

Density (15/4)	0.8700
Flash point (°C)	230
Viscosity in S.U.S at 210°F	96
Viscosity Index	112
Saponification value	2.8
Conradson's carbon(%)	0.08
Pour point (°C)	-46
Corrosion test	OK

(Contained 1.5% aluminium oleate.

This oil was subjected to practical tests at the Naval Aeronautical Arsenal, Yokosuka and found superior for use in the coldest zone and also for the tropical zone. Since then, 1943, this synthetic oil has been used for this service.

III. CONCLUSIONS

Marine or aero torpedo engine oils of superior properties were manufactured from Oha crude oil by the solvent extraction method and from shale gas oil or cracked distillate of paraffin wax by the polymerization method, and all of these products were used in this service. From the service performance of these products, it was concluded that marine torpedo engine oil should be a well-refined mineral oil and that the aero torpedo engine oil should be prepared from olefin-hydrocarbons in order to possess very low pour point.

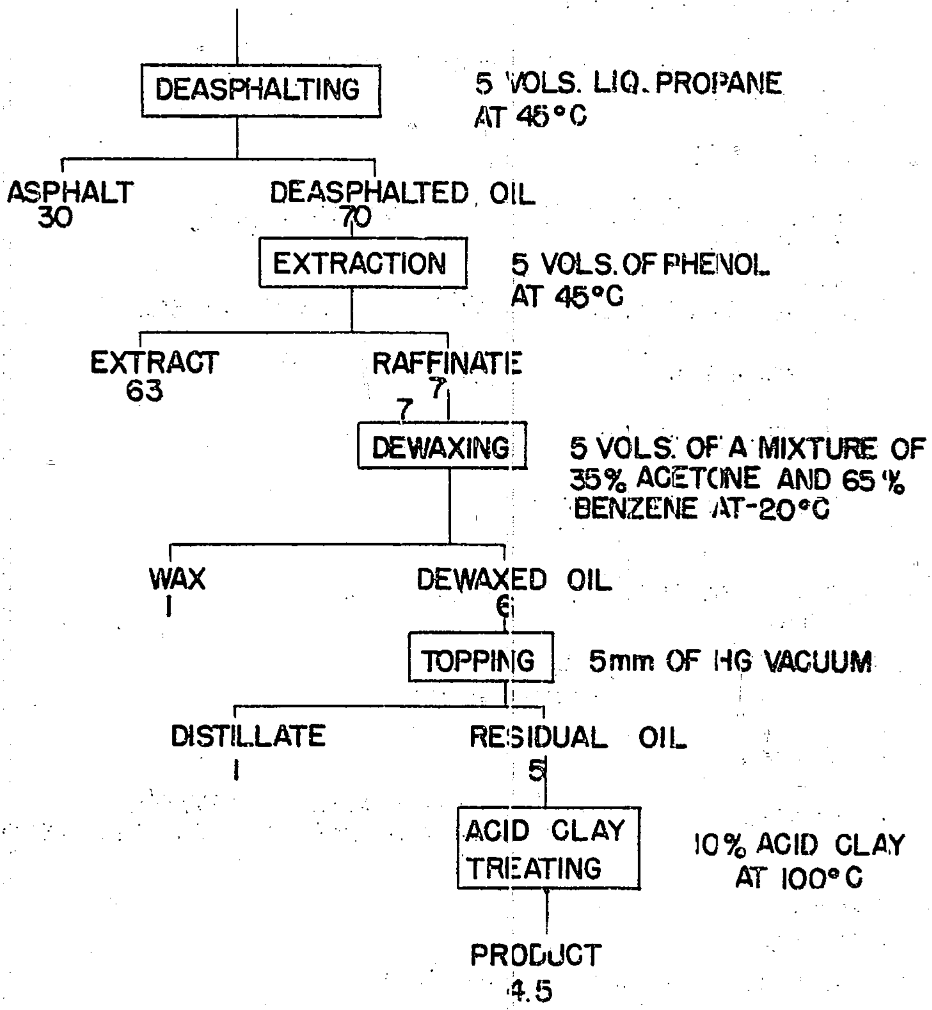

Figure 1(B)19

PREPARATION OF A MARINE TORPEDO ENGINE OIL BY SOLVENT EXTRACTION

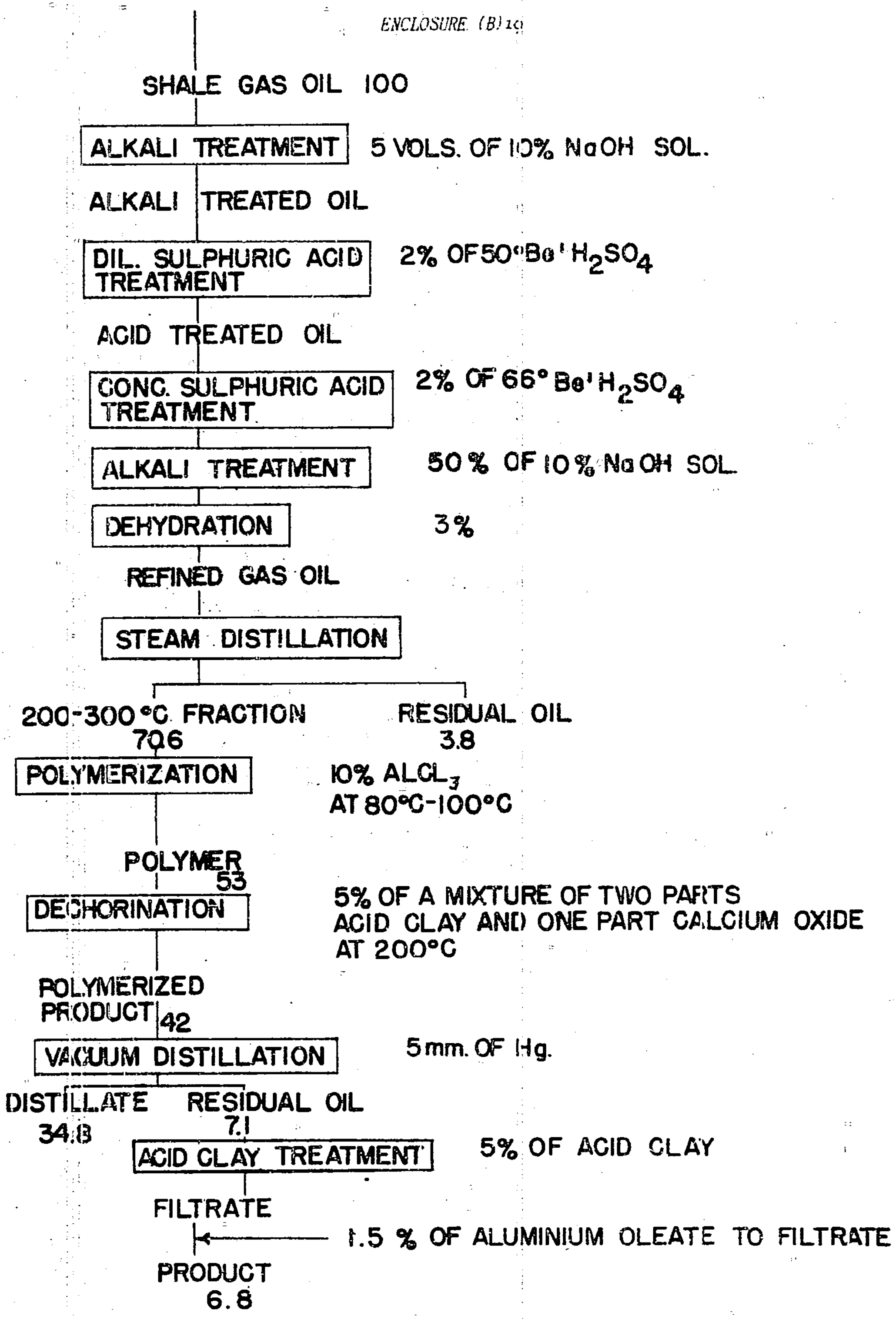

Figure 2(E)19

PREPARATION OF AN AERO TORPEDO ENGINE OIL FROM SHALE GAS OIL

ENCLOSURE (B)19

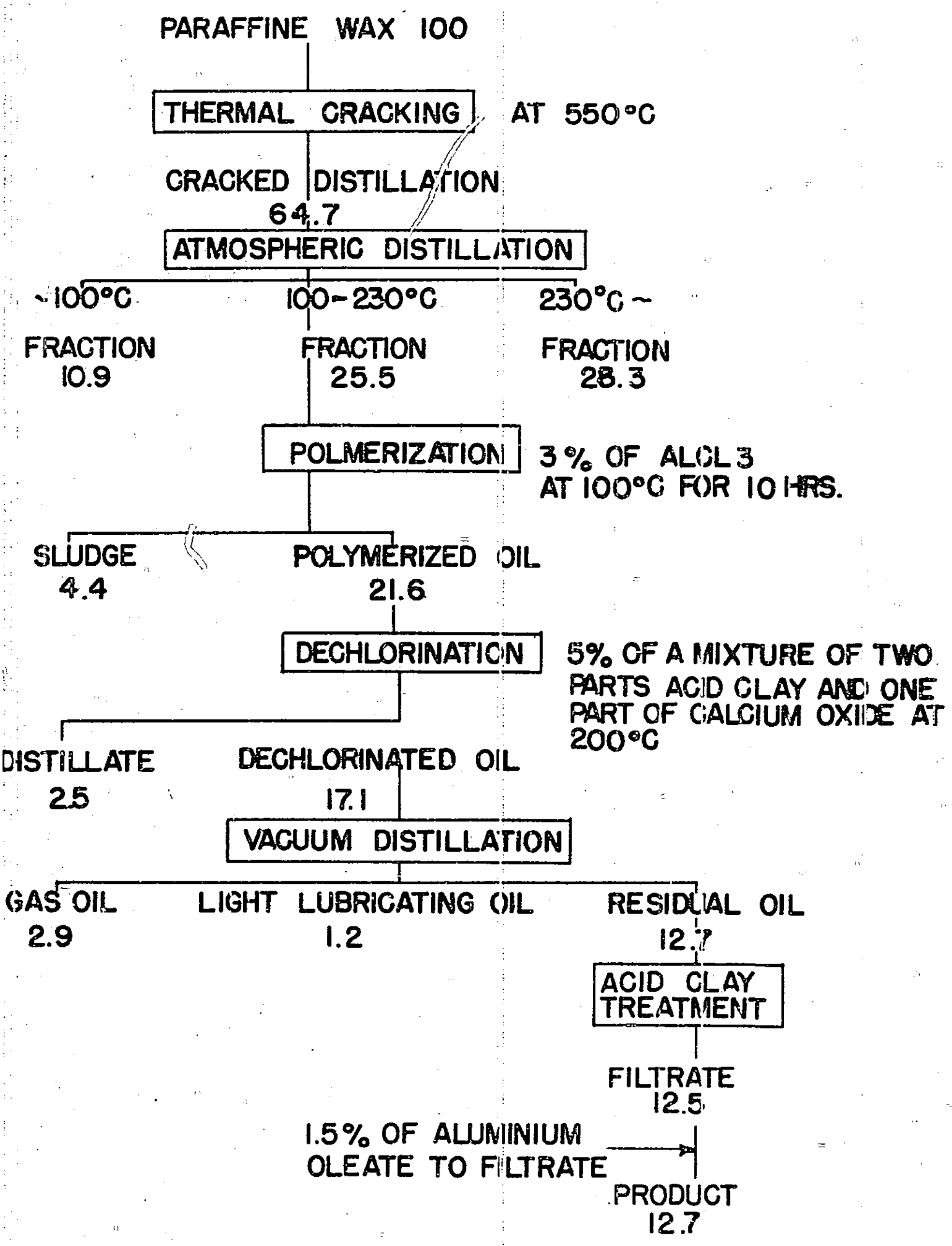

Figure 3(B)19

PROCEDURE OF PREPARING AN

AERO TORPEDO ENGINE OIL FROM PARAFFIN WAX

ENCLOSURE (B)19

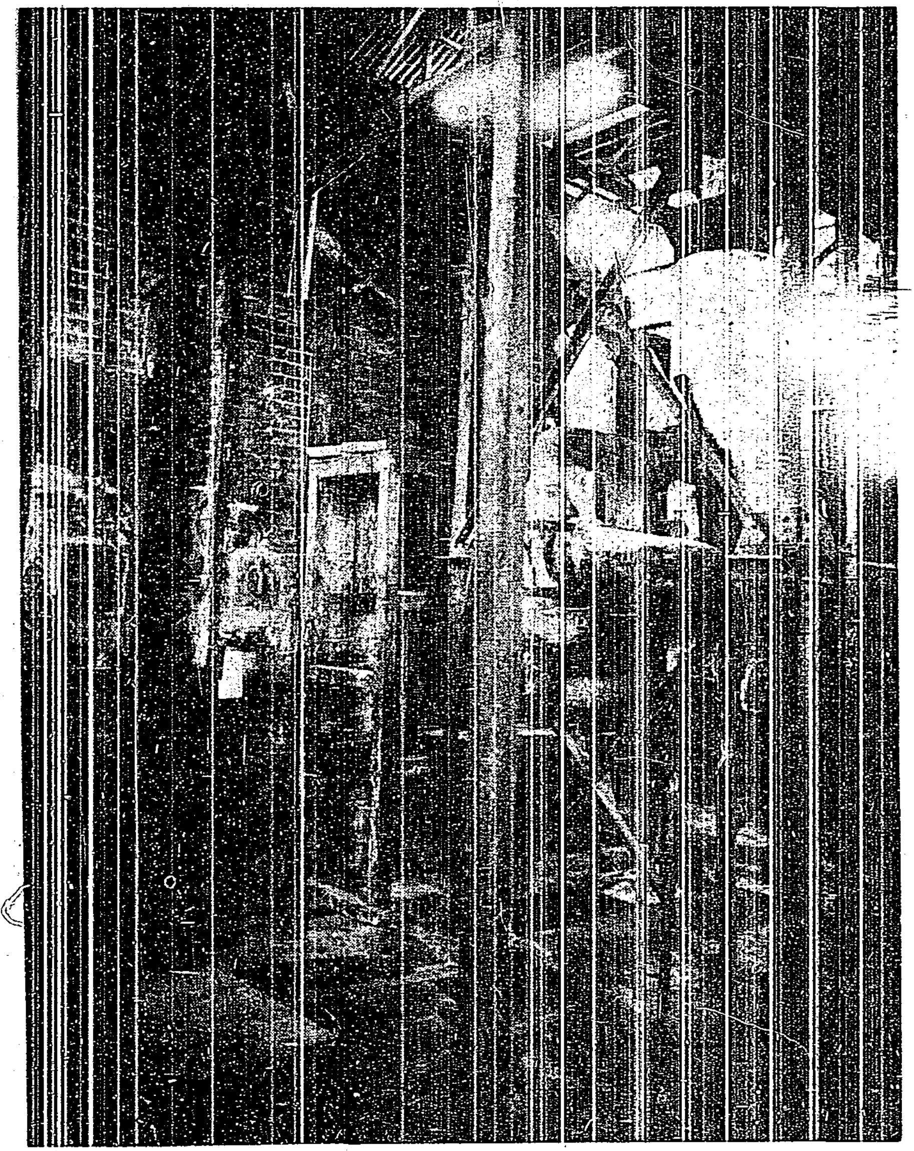

Figure 4(B)19
VAPOUR PHASE PARAFFIN WAX THERMAL CRACKING FURNACE

ENCLOSURE (B) 19

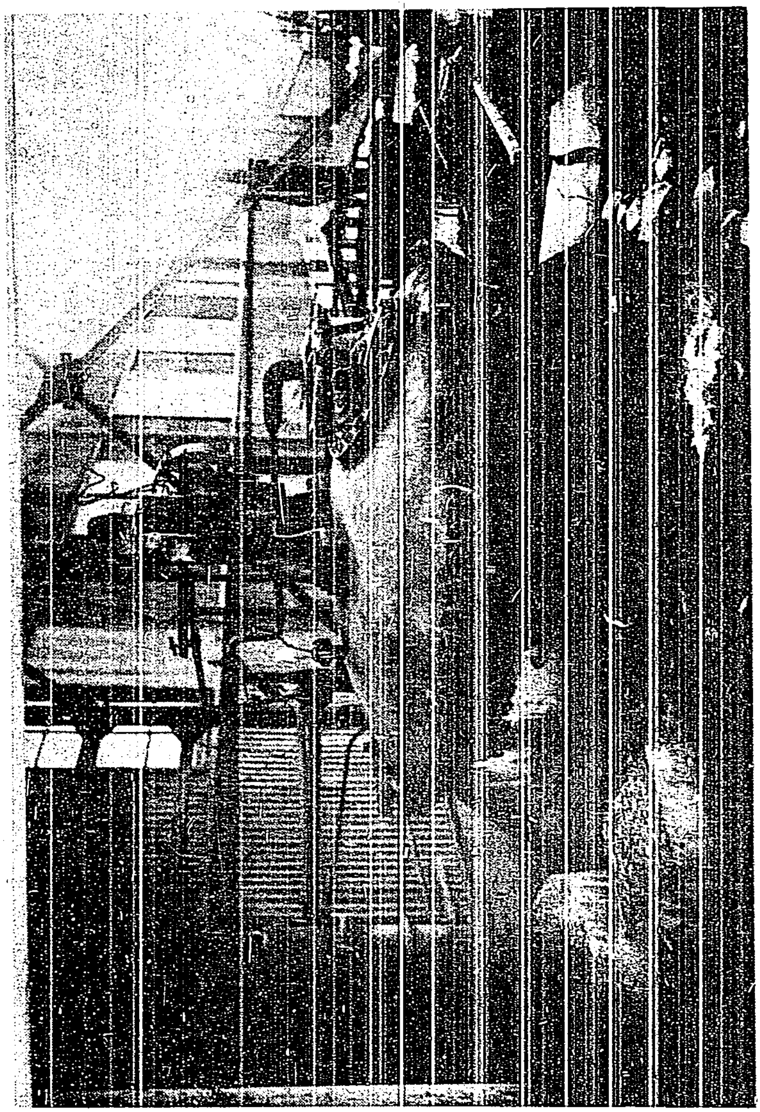

Figure 5(B)19
DECHLORINATION KETTLE

ENCLOSURE (B)19

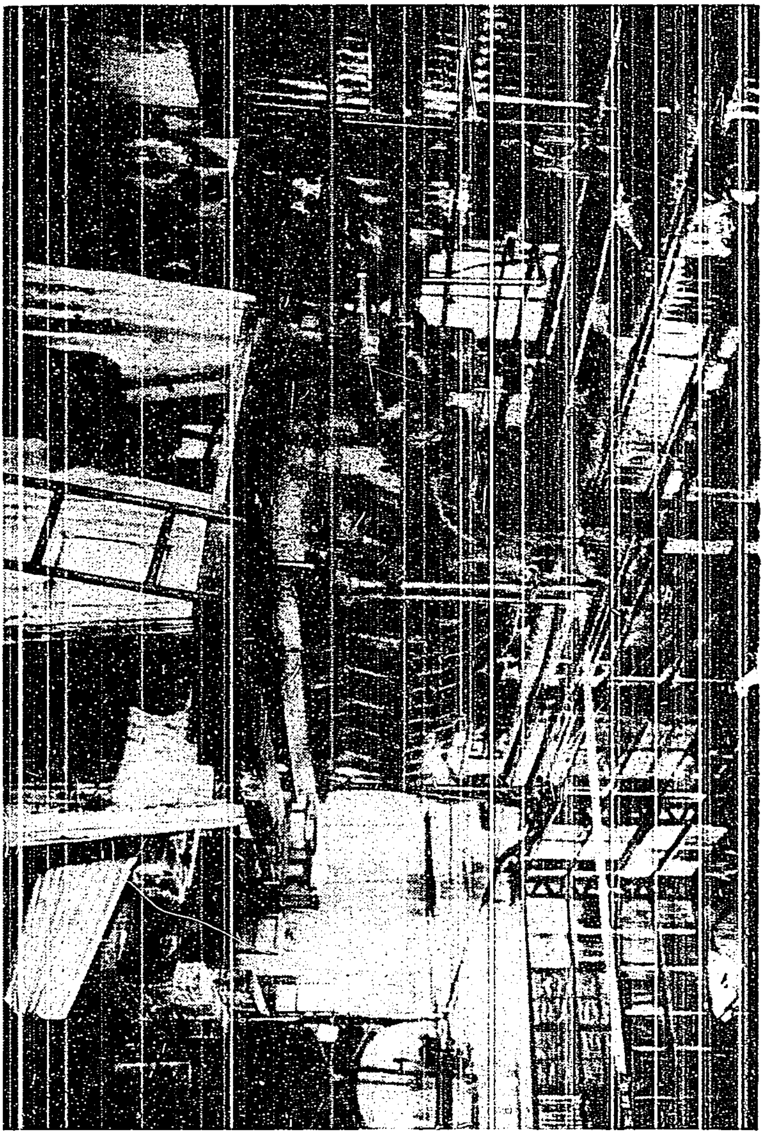

Figure 6(B)19
CLAY FILTRATION UNIT FOR LUBRICANTS

ENCLOSURE (B)19

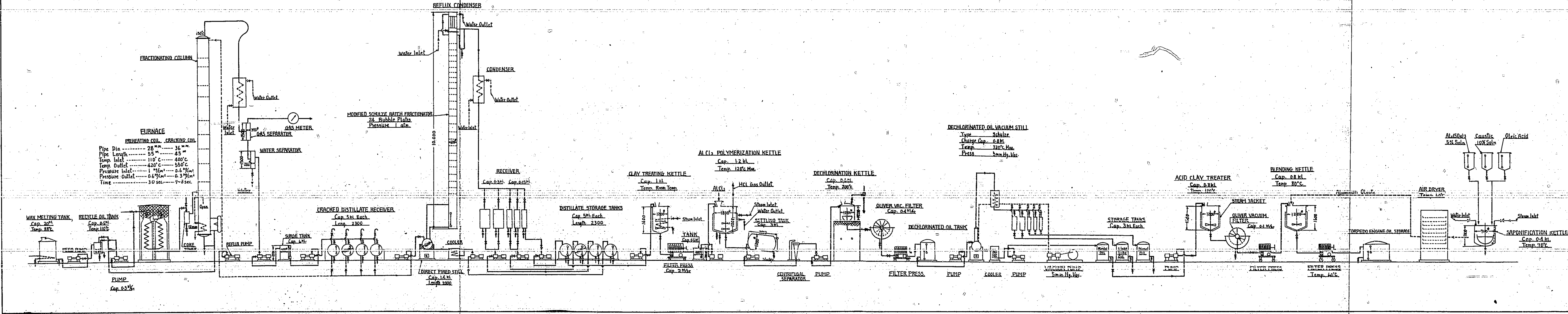

PLATE I(B)19

FLOW SHEET OF PILOT PLANT
OF TORPEDO ENGINE LUB OIL

ENCLOSURE (B) 20

STUDIES ON LUBRICANTS FOR DIESEL ENGINES

by

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CHEM. ENG. LIEUT. M. HIRATA

Research Period: 1938-1944

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)20

SUMMARY

The object of this project was to obtain an excellent lubricant for diesel engines from crude oil by acid treating or solvent extraction, or by use of additives.

From OHA crude oil was prepared a good cylinder lubricant for diesel engines by vacuum distillation, phenol extraction, dewaxing, topping, and active clay treating. The yield was about 0.3%.

The result of the engine test at Yokosuka Naval Arsenal was satisfactory, but it was not used because of the insufficient amount available.

When a turbine oil was used for the diesel engine, the wear of the cylinder was very great, and this wear could not be sufficiently decreased by using additives; i.e., adding 0.5% of lecithin or 1% of tricresyl phosphate.

When aeroengine oil #80 was used for this engine, the wear of the cylinder was very slight, but the carbon deposit on the surface of the piston and the cylinder wall was great, and use of an additive, i. e., 1% of calcium phenyl stearate, did not decrease the carbon deposit sufficiently.

I. INTRODUCTION

A turbine oil has been mainly used for the marine diesel engine in the Japanese Navy, but this was not satisfactory from the view point of the cylinder wear. To avoid wear of the engine cylinder which occurred in the above case, a viscous oil such as aeroengine oil #80 was used, but hard carbon and piston lacquer were deposited, while the wear of the cylinder was decreased to about one fifth of that in the case of the turbine oil. Therefore, studies were carried from April 1938 to March 1944 to improve the properties of the oil and to manufacture a good diesel engine oil from a crude oil easily obtainable in Japan.

II. DETAILED DESCRIPTION

A. The 250-300°C (at 5mm Hg) fraction of OHA crude oil was extracted with 5 volumes of phenol and its raffinate, after dewaxing by acetone-benzene method, was topped in vacuum and the residue was treated by active clay. The characteristics of this oil were as follows:

Viscosity at 210°F	72 S.U.S.
Viscosity index	99
Conradson's carbon residue	0.05%

The results of the engine test of this oil at Yokosuka Naval Arsenal were satisfactory, using no additive.

B. The results of the engine test of aeroengine oil #80, the properties of which are shown in Table I(B)20, were somewhat the same as in the case of the above-mentioned oil, except in this case much carbon deposit and piston lacquer appeared, and it was desirable to decrease them. Therefore, another engine test was undertaken on the effect of additive in the oil.

The addition of 1% of calcium phenyl stearate* to this oil decreased carbon deposit and piston lacquer, but not sufficiently to be satisfactory.

C. The use of turbine oil, whose properties are shown in the Table II (B) 20, caused much wear of the cylinder of this engine, but practically no carbon or lacquer deposits. To decrease this wear, 0.5% of lecithin or 1% of tricresyl phosphate* was added to this oil, but the results of the engine test showed that these additives were not effective.

D. Results obtained were summarized in the Table III(B) 20.

III. CONCLUSIONS

1. The aeroengine oil #80 was not a good diesel engine lubricant from the view point of carbon deposit and piston ring sticking.

2. An excellent diesel engine lubricant was prepared from OHA crude oil by vacuum distillation, phenol extraction, dewaxing, topping, and active clay treating.

3. The use of additives in aeroengine oil #80 (Calcium phenyl stearate) and in turbine oil (Lecithin or tricresyl phosphate) showed insufficient improvement in their characteristics.

4. From these results it may be said that the lubricating oil for marine diesel engines should be a well refined distillate and have the following properties:

Viscosity in S. U.'S. at 210°F .... 70 - 80
Viscosity index .... 90 (min)
Conradson's carbon (%) .... 0.2-0.3 (max)

---

*Chem. Eng. Comdr., Dr. I. KAGEHIRA and Chem. Eng. Lieut., M. HIRATA; Studies on the Additives of the Submarine Diesel Engine Lubricant.

Table I(B) 20
PROPERTIES OF THE AEROENGINE OIL #80 USED

Density (d_4^{15})	0.8809	Conradson's carbon residue	0.47	Sap. Value	0.12
Flash point (°C)	221.0	Ash	none	Acid Value	0.05
Viscosity (S.U.S.) at 210°F	79.0	Pour point (°C)	-16.0	Stability viscosity ratio	1.47
Viscosity Index	99.1			C.C.R. After test	1.53

ENCLOSURE (B)20

Table II(B)20
PROPERTIES OF THE TURBINE OIL USED

Reaction		neutral	Pour point (°C)	-4
Density d_4^{15}		0.930	Corrosion	none
Flash point (°C)		193	Conradson's carbon residue	0.4
Viscosity R.-I. at	30°C	645	Volatility at 135°C for 6 hr	0.6%
	50°C	181	Sap. Value	0.1
	80°C	61	Acid Value	0.08

Table III(B)20
RESULTS

Name of oil	Source of oil	Compound	Ring sticking	Hard carbon	Cylinder wear
Diesel engine oil prepared by the author	Oha	None	0	least	low
Turbine oil (obtained from the market)	Perhaps Niigata	None	0	least	high
Turbine oil (obtained from the market)	Perhaps Niigata	1% of tricresyl phosphate	0	least	high
Turbine oil (obtained from the market)	Perhaps Niigata	0.5% of lecithin	0	least	high
Aeroengine oil #80	Produced by Texas oil Co. U.S.A.	None	2 (2nd & 3rd rings)	greatest	low
Aeroengine oil #80	Produced by Texas oil Co. U.S.A.	1% of Calcium phenyl stearate	1 (2nd ring)	intermediate	low

ENCLOSURE (B) 21

STUDIES ON PRECISE OILS

by

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

Research Period: 1939-1944

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)21

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)21

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. A rapeseed oil (0.2%).

Properties of No. 5 Precise Oil

Density 25/4	0.8278
Vis. in Redwood No. 1. sec	
at 10°C	457.6
a5 30°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. Precise Oils For Special Uses

   a. A special precise oil, having a very low pour point, was obtained 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 10°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

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 vacumm 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. <u>Manufacture of No. 1, No. 2, No. 3, No. 4 Precise Oil.</u> 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. <u>No. 5 Precise Oil</u>

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. <u>Polymerization Procedure</u>: 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. <u>Dechlorination Procedure</u>: 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. <u>Vacuum Fractional Distillation:</u> 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:

Density, 25/4	0.8216
Vis. in Redwood No. 1 sec	
at 10°C	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 100°-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 cut at 120°C-300°C was used for the special watch oil.

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^{20}	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 effected 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

ENCLOSURE (B)21

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
$(CH_3(CH_2)_7CH\ \ CH(CH_2)_8OCH_2CH_2CHOHCH_2OH)$
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 uses, compositions and flow characteristics of the precise oils discussed in this paper.

ENCLOSURE (B)21

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

ENCLOSURE (B)21

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	168	-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 10°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 >	250 >	90 <	-45 >	0.1 >	0.2 >	0.3 >
No. 3 Precise Oil	0.9169	562.6	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 Niizu'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	$d^{25}/_{4}$ 0.7681	d^{20}_{4} 0.7590
Refractive index	n^{20}_{D} 1.4342	n^{20}_{D} 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	18.4	0.7615	-	-37	7.40
140°C-160°C	1.7		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	59.0	0.8083	52.1	-70	14.67
200°C-220°C	9.6		0.8148	68.5	-71	16.42
220°C-240°C	13.2		0.8217	95.7	-70	17.08
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		0.8399	437	-56	21.74
300°C-18	18.2		0.8508	325.9	-38.5	21.34

ENCLOSURE (B)21

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

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

ENCLOSURE (B)21

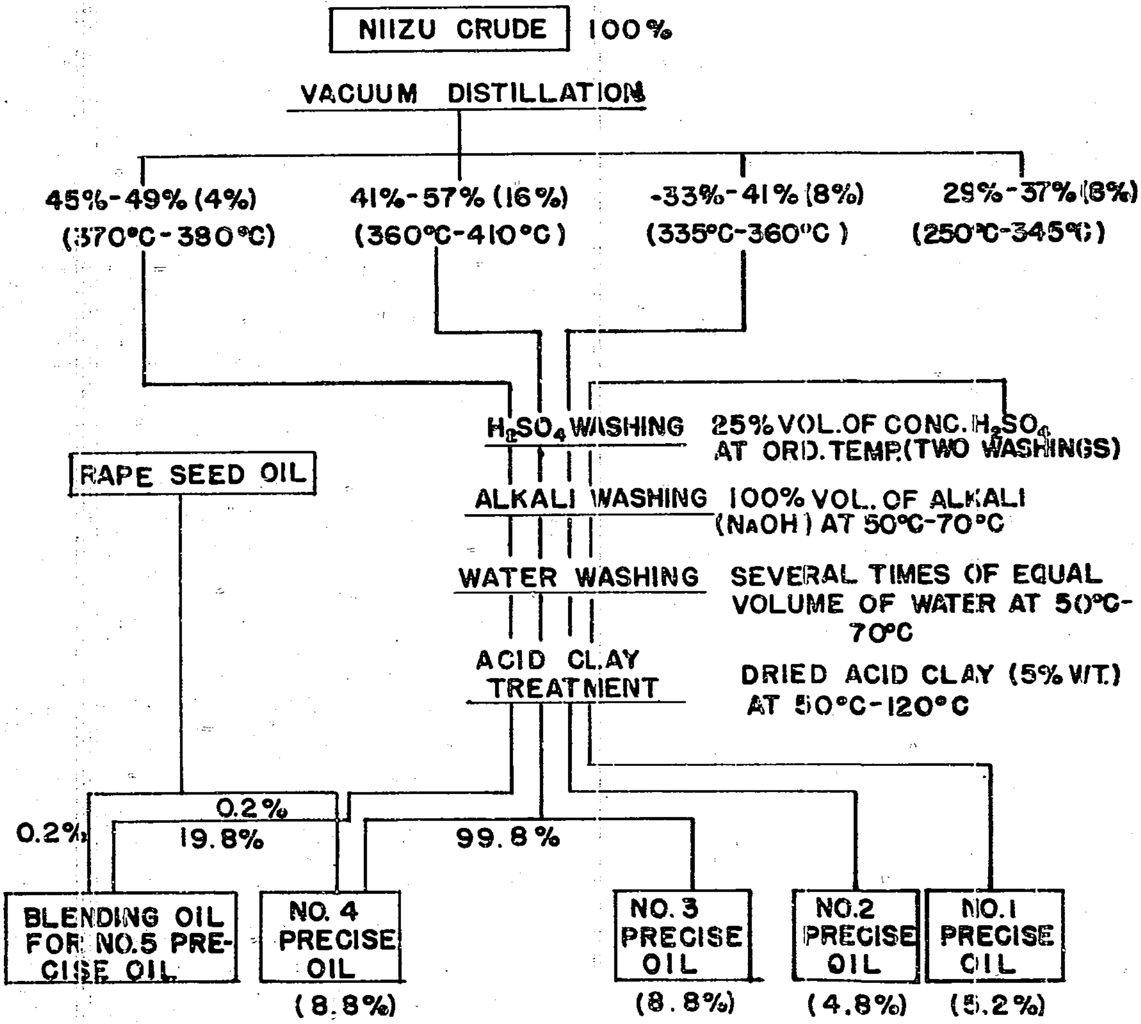

Figure 1(B)21
MANUFACTURE OF PRECISE OILS FROM NIIZU CRUDE

ENCLOSURE (B)21

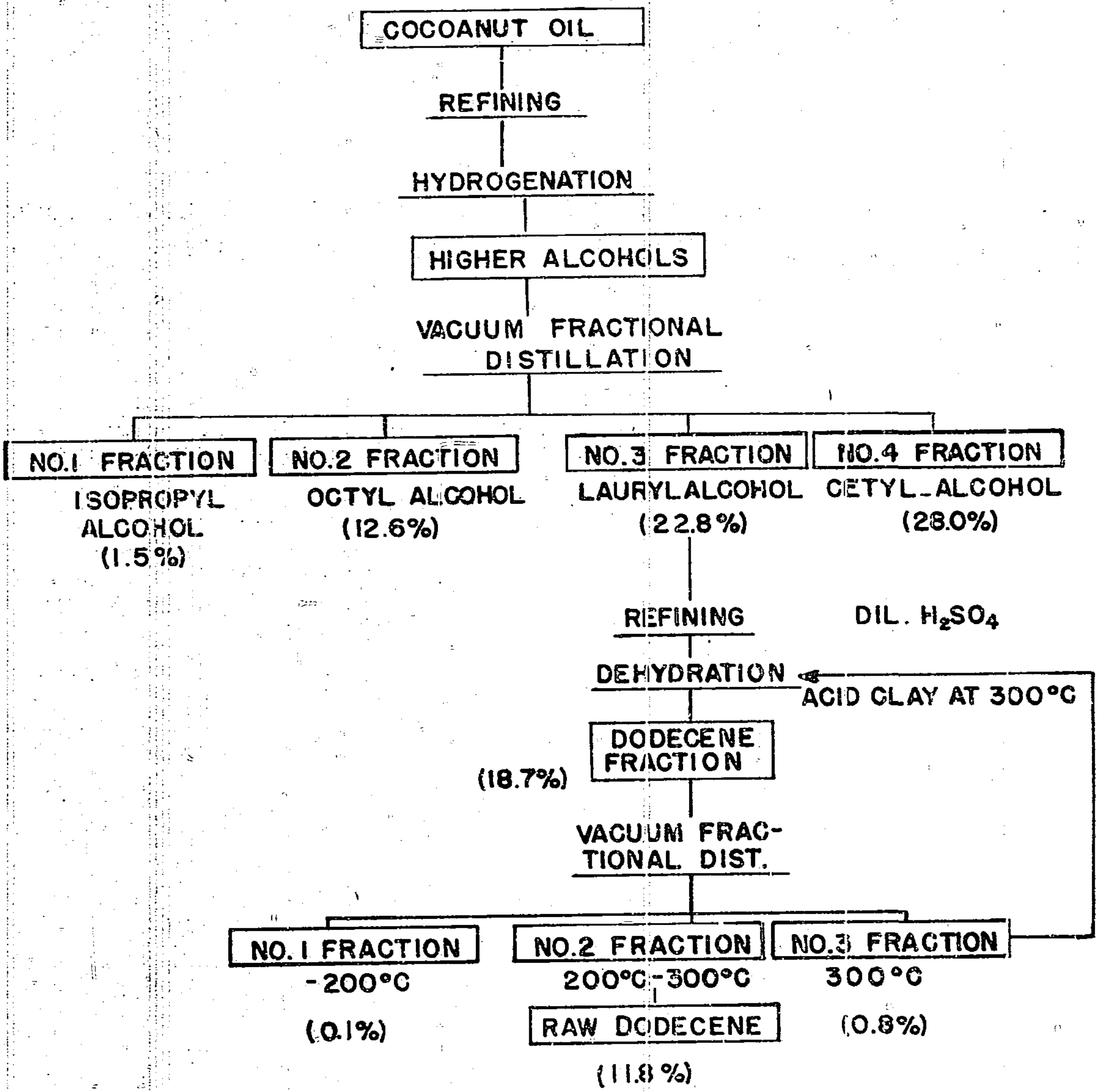

Figure 2(B)21
PREPARATION OF DODECENE

ENCLOSURE (B)21

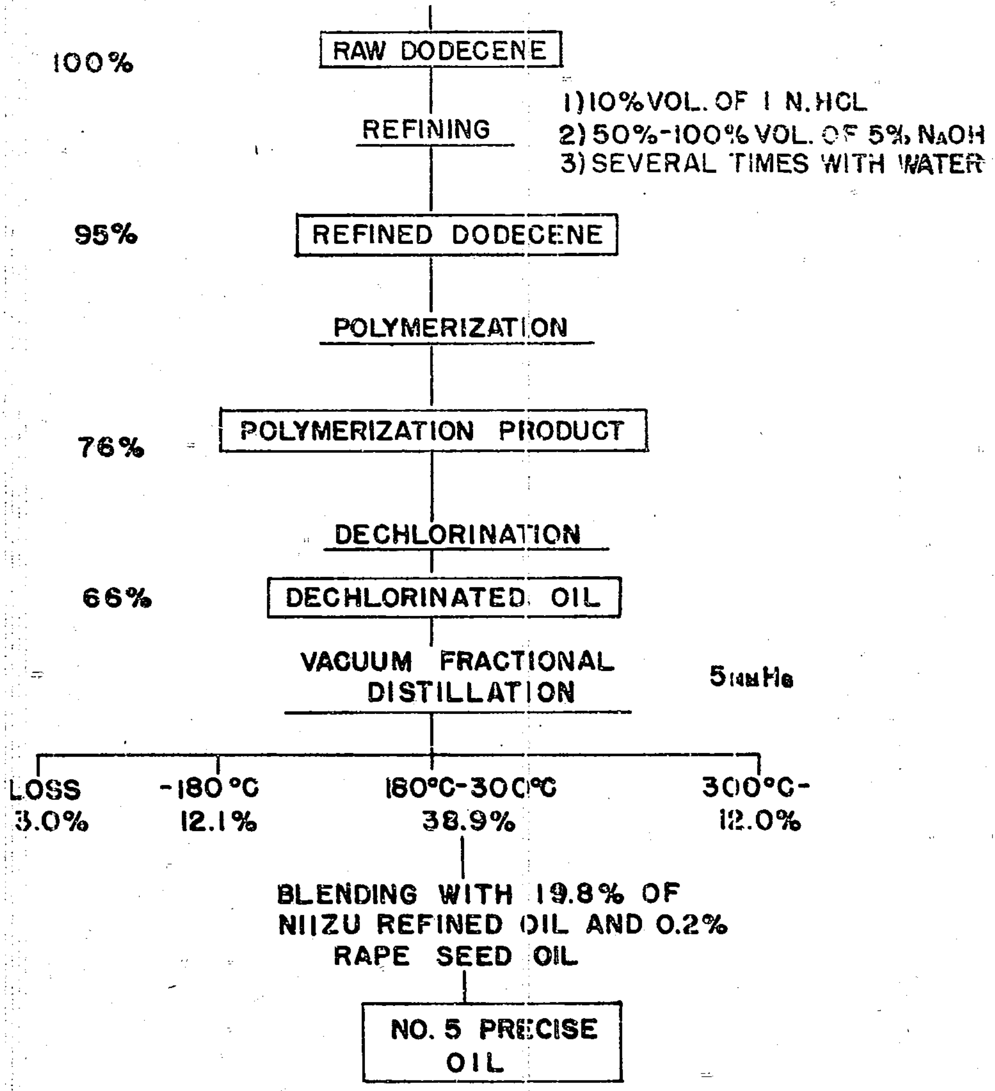

Figure 3(B)21
STEPS IN MANUFACTURE OF NO. 5 PRECISE OIL FROM RAW DODECENE

ENCLOSURE (B) 22

EXPERIMENTAL MANUFACTURING METHOD FOR PRECISE OILS

by

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Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)22

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)22

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^{15}_{4})	0.945
Flash Point (°C)	112
Viscosity (R.1.) 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.

ENCLOSURE (B)22

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 coconut 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 [illegible] using active clay catalyst. Dodecene was obtained by fractionation of the final product and had the following properties:

Density, (d^{25}_{4})	0.7631
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.

ENCLOSURE (B)22

Table I(B)22
PROPERTIES OF FRACTIONS

No.	Ranges of Fractions		Density (d^{15}_{4})	Flash Pt. (°C)	Viscosity(R.No.1)		Pour Pt. (°C)
	Vol. %	B.P.(°C)* 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.

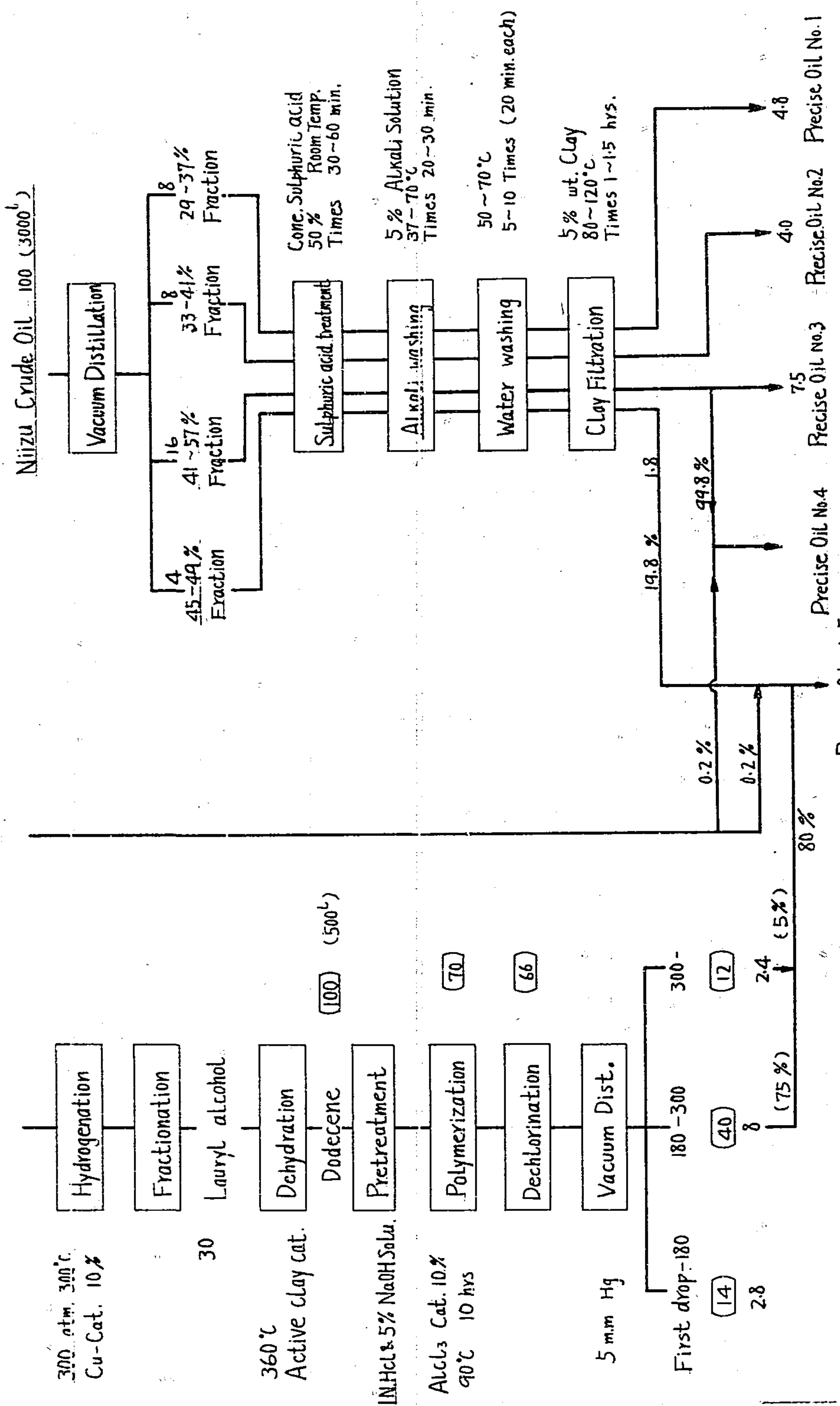
ENCLOSURE (B)22

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

	$d^{15}/_4$	Viscosity (Redwood No. I) 10°C	30°C	50°C	Acid Value	Saponification Value	Pour Point (°C)	Evap. loss wt.% 100°C 5 hrs
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	562.6	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	0.8338	457.6	154.5		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.

ENCLOSURE (B)22



Note: All yields & percentages based on weight.

Figure 1(B)22

SCHEMATIC DIAGRAM FOR PREPARING PRECISE OILS

ENCLOSURE (B)22

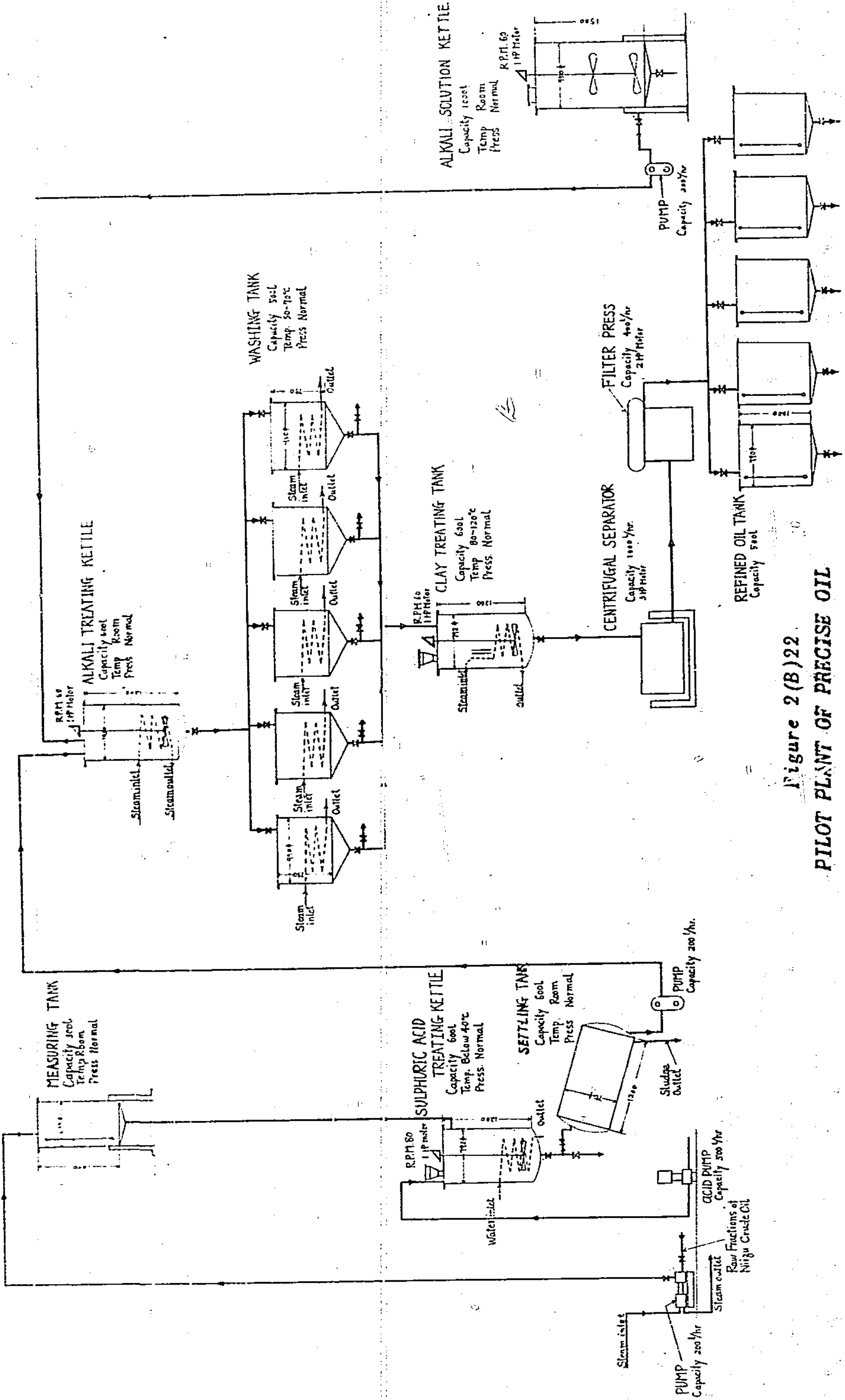


Figure 2(B)22
PILOT PLANT OF PRECISE OIL
(No. 1, 2, 3, 4)

ENCLOSURE (B)22

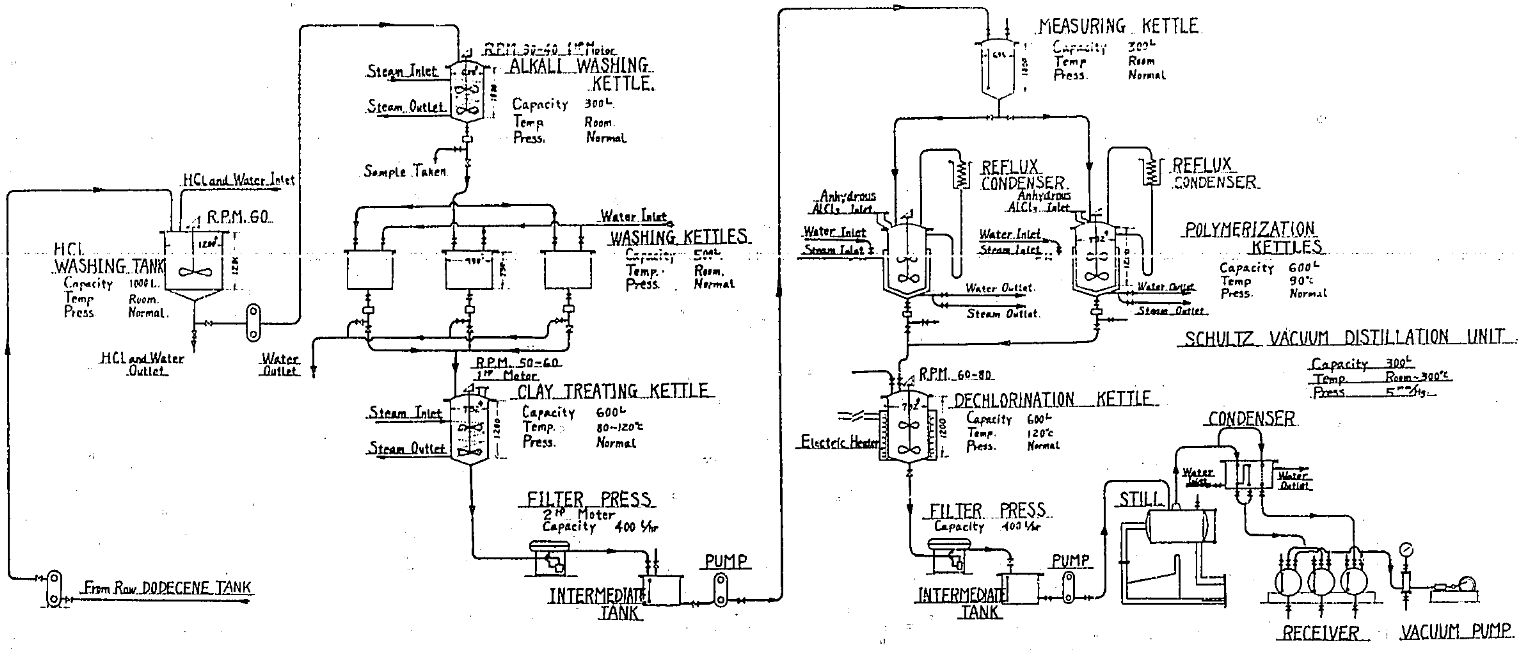


Figure 3(B)22

FLOW SHEET OF PILOT PLANT OF PRECISE OIL

(No. 5)

ENCLOSURE (B)22

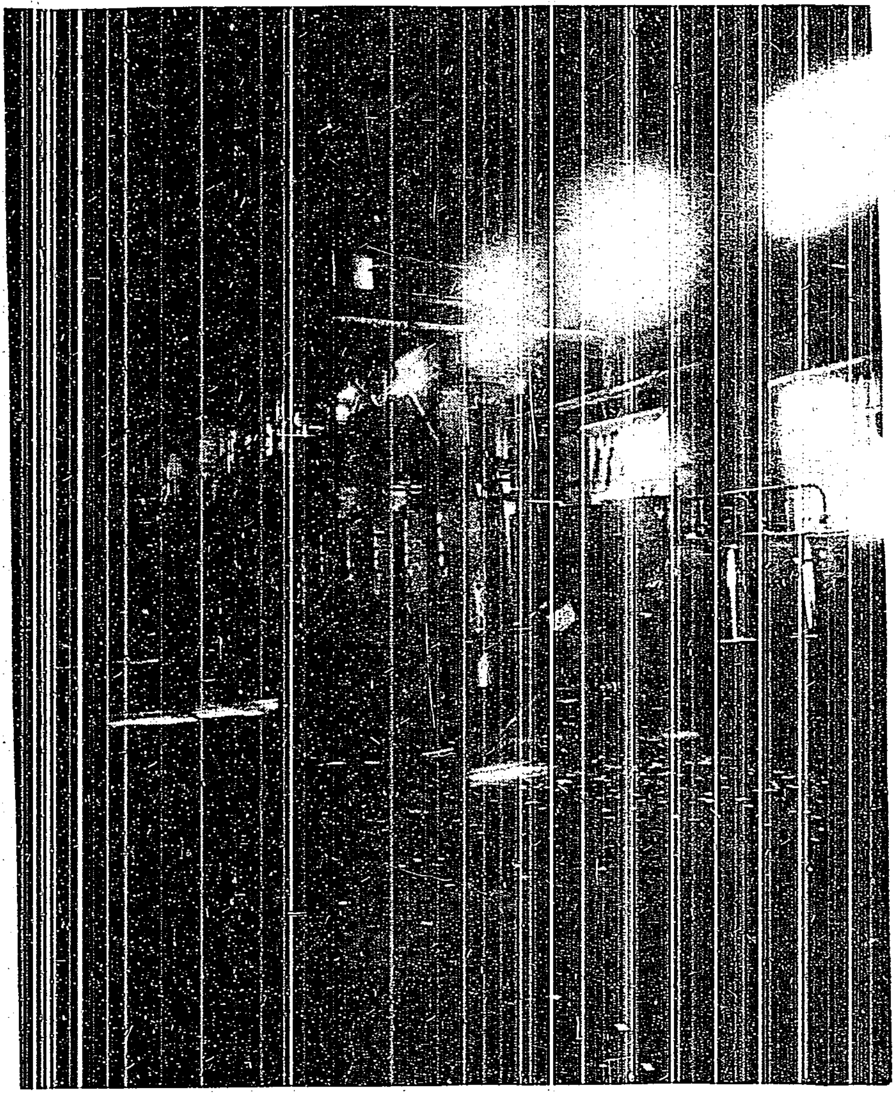


Figure 4(B)22
PILOT PLANT FOR MANUFACTURING PRECISE OILS

ENCLOSURE (B) 23

STUDIES ON ANTIOXIDANTS FOR THE AERO-ENGINE OILS

BY

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Research Period: 1940-1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)23

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)23

SUMMARY

Various antioxidants for natural and synthetic aero-engine oils were studied by the British Air Ministry Oxidation Test and the following results were obtained:

1. For natural aero-engine oil, tricresyl phosphite was the best antioxidant and a mixture 0.2% of tricresyl phosphite and 0.2% of tricresyl phosphate was actually used. To avoid sludge separation after the oxidation test, it was not necessary to use more than 0.2% of the phosphite.

2. For synthetic aero-engine oil prepared from sweated wax or Fischer Oil, copper soaps were the most effective, the viscosity ratio being lowered from 2.3 to 1.5.

3. For castor oil, p,p'-dioxy-diphenyl-amine was the best for improving oxidation stability.

4. The viscosity ratio measured by the British Air Ministry Oxidation Test had a close relation to Warburg's oxygen absorption test at 150°C.

I. INTRODUCTION

A. History of Project

The operating conditions in aero-engines had become more severe as time went on, and hence, there was a need for an effective antioxidant to decrease the carbon deposition at the top of piston and on the piston rings and the amount of sludge in engine cylinders. After referring to the literature, the authors chose several antioxidants and studied their effect on natural and synthetic aero-engine oils and castor oil.

This research covered a period extending from 1940 to August 1945.

B. Key Personnel Working on Project

Chem. Eng. Lt. Comdr. A. WAKANA
Chem. Eng. Lieut. N. KOTAKE

II. DETAILED DESCRIPTION

A. Method of Testing Oxidation of Aero-Engine Oils

In this study, the British Air Ministry Oxidation Test was adopted. Its test conditions are shown in Table I(B)23. Oils with or without antioxidants were tested under the conditions of Table I(B)23, and the viscosity and Conradson's carbons were measured. From these values, the effect of an antioxidant was determined. The viscosity ratio was calculated as the ratio of the viscosity in S.U.S. at 100°F after the test to the viscosity in S.U.S. at 100°F before the test.

B. Base Oils Used for Testing the Effect of Antioxidants on Aero-Engine Oils

Properties of the base oils for testing the effect of antioxidants are shown in Table II(B)23.

ENCLOSURE (B)23

C. Antioxidants for Natural Aero-Engine Oils

Various antioxidants were tested on the natural aero-engine oil and the results obtained are given in Table III(B)23. Tricresyl phosphite was the best antioxidant for the natural aero-engine oil, but when its concentration in oil was increased, a small amount of oily sludge was separated. A mixture of 0.2% of tricresyl phosphite and 0.2% of tricresyl phosphate to oil was actually used in service.

D. Antioxidants for Synthetic Aero-Engine Oil Prepared from Fischer Oil or Paraffin Wax

1. For a Synthetic Aero-Engine Oil Prepared from Fischer Oil. A synthetic aero-engine oil prepared from Fischer oil was highly oxidizable and its viscosity ratio after the oxidation test was 3.4. Triphenyl phosphite, tricresyl phosphite, tin oleate, chromium oleate, individually and in combinations, were tested. Results obtained are shown in Table IV(B)23 and, in these experiments, a mixture of triphenyl phosphite and chromium oleate was found to be the best.

2. For Synthetic Aero-Engine Oil from Paraffin Wax. A synthetic oil from the cracked distillate of sweated paraffin wax was comparatively easily oxidized and the viscosity ratio was 2.1 in the oxidation test. The effects of triphenyl phosphite, copper oleate and elemental sulphur were tested for the above oil. Results obtained are given in Table V(B)23. In spite of the fact that copper soap is, in general, thought of as an accelerator for the oxidation of lubricating oils, copper oleate showed a remarkable retarding action on the oxidation of the synthetic oil from the sweated wax. Other copper soaps, i.e. copper stearate, laurate, benzoate, etc., were tested and also found effective as shown in Table VI(B)23. However, copper stearate was not effective as an antioxidant for the synthetic aero-engine oils prepared from the crude wax as shown in Table VII(B)23. These same phenomena were clearly shown in the case of a mixture of natural and synthetic aero-engine oil. This contrary chemical reaction of copper soap was attributed to the difference in activity towards paraffinic and cyclic hydrocarbons, in that they are thought to inhibit peroxide formation in paraffines.

E. Antioxidants for Castor Oil

P,p'-dioxydiphenylamine and phenyl-b-naphthyl-amine were tested as antioxidants for castor oil. Results obtained are shown in Table VIII(B)23 and p,p'-dioxydiphenylamine was found to be the most effective, although it was not actually used.

F. Oxygen Absorption Test of Aero-Engine Oil

To elucidate the effect of antioxidants on engine oils, the absorption of oxygen in aero-engine oils was measured by Warburg's apparatus. The results obtained are given in Figure 1(B)23, and it can be seen that the viscosity ratios using the British Air Minstry Test had a marked correlation to the amount of oxygen absorbed in the oil. The effect of copper stearate on synthetic polymerized oil prepared from Fischer oil was also tested and its effect in preventing oxygen absorption at 150°C was observed as shown in Figure 2(B)23.

III. CONCLUSIONS

Tricresyl phosphite was the most effective antioxidant investigated for natural aero-engine oil and has been used in actual service. Copper soaps were markedly effective for synthetic aero-engine oils prepared from the cracked distillate of sweated wax or by polymerization of Fischer oil.

For castor oil, p,p'-dioxydiphenylamine was most effective in improving the oxidation stability.

The results of the oxygen absorption test of oils using the Warburg's apparatus paralleled those of the British Air Ministry Oxidation Test, and, with further studies, the oxygen absorption method should be found to be a simple oxidation test procedure.

Table I(B)23
CONDITIONS OF BRITISH AIR MINISTRY OXIDATION TEST FOR AERO-ENGINE OILS

Oil sample (cc)	45
Temperature ($^{\circ}$C)	200
Time (hr)	12
Rate of air blowing (liter/hr)	15
Material of test tube	glass

ENCLOSURE (B)23

Table II(B)23
GENERAL PROPERTIES OF SOME AERO-ENGINE OILS

		Phillips #120	Texaco #120	Polymerized Oil from Cracked Distillate of Sweated Wax	Polymerized Oil from Cracked Distillate of Crude Wax	Blend of Natural and Synthetic Oils*	Polymerized Oil of Fischer Oil
Specific Gravity (d_4^{15})		0.8965	0.8938	0.8534	0.8782	0.8820	0.8653
Flash Point (°C)		240	230	-	224	232	-
Viscosity (S.U.S., 100°F)		1794.2	1649	1187.3	1440.2	1573.2	790.6
Viscosity (S.U.S., 210°F)		121.1	117	137.6	123.0	125.4	79.2
Viscosity Index		93.4	95.4	127.9	110.0	106.9	100.8
Conradson's Carbon (%)		0.70	1.06	0.10	0.47	0.46	0.09
Pour Point (°C)		-13	-11	-25	-34	-27	-22
Stability, Viscosity Ratio		1.33	1.17	2.13	1.78	1.64	3.43
Stability, Conrad. C. (%)		1.80	1.60	0.7	1.58	1.50	1.0
Elemental Analysis	C%	80.00	85.83	80.14	86.01	86.22	84.20
	H%	12.80	13.38	13.88	13.39	13.65	13.56
	S%	0.15	0.05	0.02	-	-	0.02
Mean Molecular Weight		614	694	1095	865	740	684
Empirical Formula		$C_{44}H_{88}$	$C_{50}H_{92}$	$C_{78}H_{151}$	$C_{62}H_{115}$	$C_{53}H_{100}$	$C_{48}H_{92}$

* 10% Natural Mineral Oil
90% Synthetic Oil (Polymerized Oil from Cracked Distillate of Crude Wax)

ENCLOSURE (B)23

Table III(B)23
THE EFFECT OF ANTIOXIDANTS ON OXIDATION STABILITY OF AERO ENGINE OIL

Addition Compounds	Amount(%)	Viscosity Ratio	Conradson Carbon(%)
None	0	1.56	1.90
Tricresylphosphite	0.5	1.17	1.23
Tricresylphosphate	1.0	1.23	0.84
Dibenzyldisulphide	0.5	1.49	1.34
Copper oleate	0.1	1.70	-
Copper stearate	0.1	1.58	1.96
Stearonitrile	0.5	1.26	0.96
Stearophenone	1.0	1.25	0.96
Trilaurylphenylphosphate	1.0	1.57	1.74
Tricresyl phosphite Tricresyl phosphate	0.5 0.5	1.22	-
Tricresyl phosphite Tricresyl phosphate	0.3 0.7	1.25	-
Tricresyl phosphite Tricresyl phosphate	0.2 0.2	1.24	-
Tricresyl phosphite Tricresyl phosphate	0.1 0.2	1.33	-

ENCLOSURE (B)23

Table IV(B)23
THE EFFECT OF ANTIOXIDANTS ON SYNTHETIC AERO ENGINE OIL FROM FISCHER OIL

No.	Addition Compound	Concentration (%)	Oxidation Test	
			Viscosity Ratio	Conradson Carbon(%)
1	None	0	3.43	1.1
2	Triphenyl phosphite	0.5	2.60	1.1
3	Tricresyl phosphite	0.5	2.63	1.4
4	Triortho cresyl phosphite	0.5	2.64	1.3
5	Tin oleate	0.5	3.00	1.5
6	Chromium oleate	0.5	2.79	1.4
7	Triphenyl phosphite Tin oleate	0.5 0.5	2.71	1.6
8	Triphenyl phosphite Chromium oleate	0.5 0.5	1.87	1.2
9	Tin oleate Chromium oleate	0.5 0.5	2.62	2.2

Table V(B)23
THE EFFECT OF OXIDATION INHIBITORS ON OXIDATION STABILITY OF SYNTHETIC AERO ENGINE OIL PREPARED FROM SWEATED WAX

Addition Compound	Amount of Compound Added (%)	Viscosity Ratio	Conradson Carbon(%)
None	0	2.13	0.72
Triphenylphosphite	0.5	1.51	0.95
Copper oleate	0.1	1.32	0.73
Sulphur	0.1	1.43	0.80
Tetraphenyl tin	0.1	1.65	--

Table VI(B)23

INFLUENCE OF COPPER SOAPS ON THE OXIDATION CHARACTERISTICS OF SYNTHETIC AERO ENGINE OIL PREPARED FROM SWEATED WAX

Names of Additives	Amount (%)	Viscosity Ratio				Acid Value				Saponification Value			
		150°C	200°C	230°C	250°C	150°C	200°C	230°C	250°C	150°C	200°C	230°C	250°C
	no.	1.47	1.70	2.04	3.82	3.75	3.88	4.53	4.76	14.8	16.98	14.58	29.33
Cu-Stearate	0.1	1.08	1.27	1.76	2.74	1.35	2.35	2.87	2.91	6.9	3.2	10.17	14.49
Cu-Oleate	0.1	1.09	1.27	1.76	3.27	1.65	3.33	3.6	3.3	8.0	—	11.2	12.2
Cu-Laurate	0.1	1.07	1.26	1.62	2.25	1.55	2.71	3.47	3.43	6.5	10.45	10.33	10.94
Cu-Benzoate	0.1	1.13	1.27	1.99	2.55	—	—	—	—	—	—	—	—
Cu-Naphthenate	0.1	1.09	1.24	1.76	2.68	—	—	—	—	—	—	—	—
Cu-Whale Oil Fatty Acid Soap	0.1	1.13	1.36	1.76	2.31	—	—	—	—	—	—	—	—
Cu-Cyanate	0.1	13.2	1.52	1.78	2.55	—	—	—	—	—	—	—	—

ENCLOSURE (B)23

Table VII(B)23
THE EFFECT OF OXIDATION INHIBITORS ON OXIDATION STABILITY OF SYNTHETIC AERO ENGINE OIL PREPARED FROM CRUDE WAX

Base Oil	Addition Agent	Amount (%)	Viscosity Ratio	Conradson Carbon(%)
Synthetic aero engine oil prepared from crude wax	None	0.0	1.78	1.58
	Triphenyl phosphite	0.5	1.40	1.55
	Copper stearate	0.1	1.75	1.82
	Elemental sulphur*	0.1	1.65	-
Blended oil of natural and synthetic aero engine oil (natural 10%, synthetic 90%)	None	0.0	1.64	1.50
	Triphenyl phosphite	0.5	1.30	1.54
	Copper stearate	0.1	1.80	2.07
	Elemental sulphur	0.1	1.56	-

*Added at 80°C

Table VIII(B)23
SOME PROPERTIES OF CASTOR OIL CONTAINING OXIDATION INHIBITORS

		Castor Oil	Castor Oil +0.5% A	Castor Oil +0.5% B	Castor Oil +0.5% C
Specific Gravity		0.9616	0.9645	0.9640	0.9645
Viscosity 100°F		1211.4	1290.8	1260.6	1259.6
Viscosity 210°F		95.9	98.0	98.4	98.2
Viscosity Index		91.9	89.7	92.9	92.3
Stability	Viscosity Ratio	4.39	2.53	3.29	3.35
	Conradson's Carbon	0.61	0.88	0.61	0.65
Acid Value		3.07	2.47	2.75	2.52
Saponification Value		180.8	187.7	187.2	180.7

A : P,P'-Dioxydiphenylamine
B : Phenthiazine Thiodiphenylamine
C : Phenyl-b-Naphthylamine

ENCLOSURE (B)23

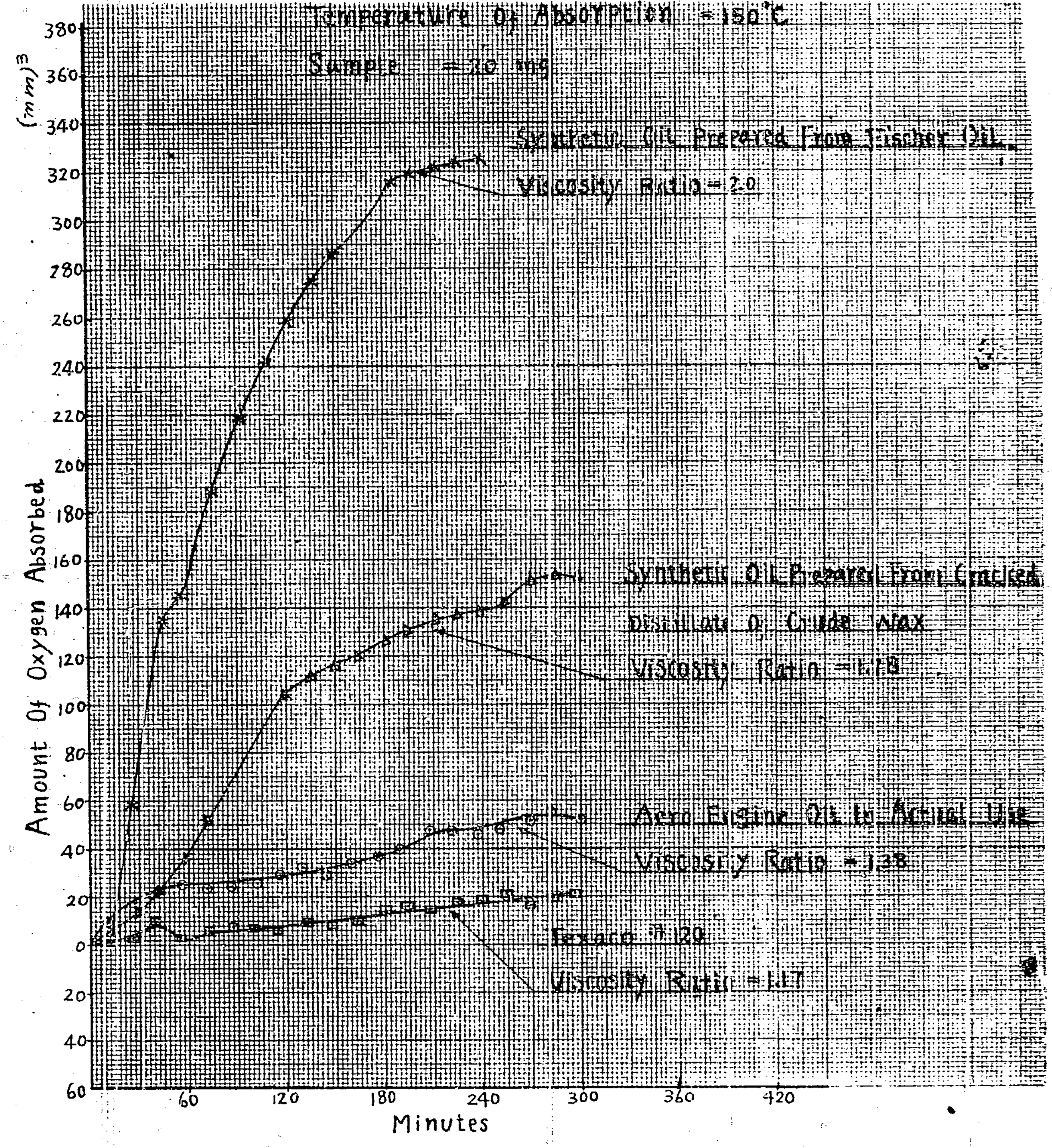

Figure 1(B)23

OXYGEN ABSORPTION TEST ON THE AEROENGINE OIL

ENCLOSURE (B)23

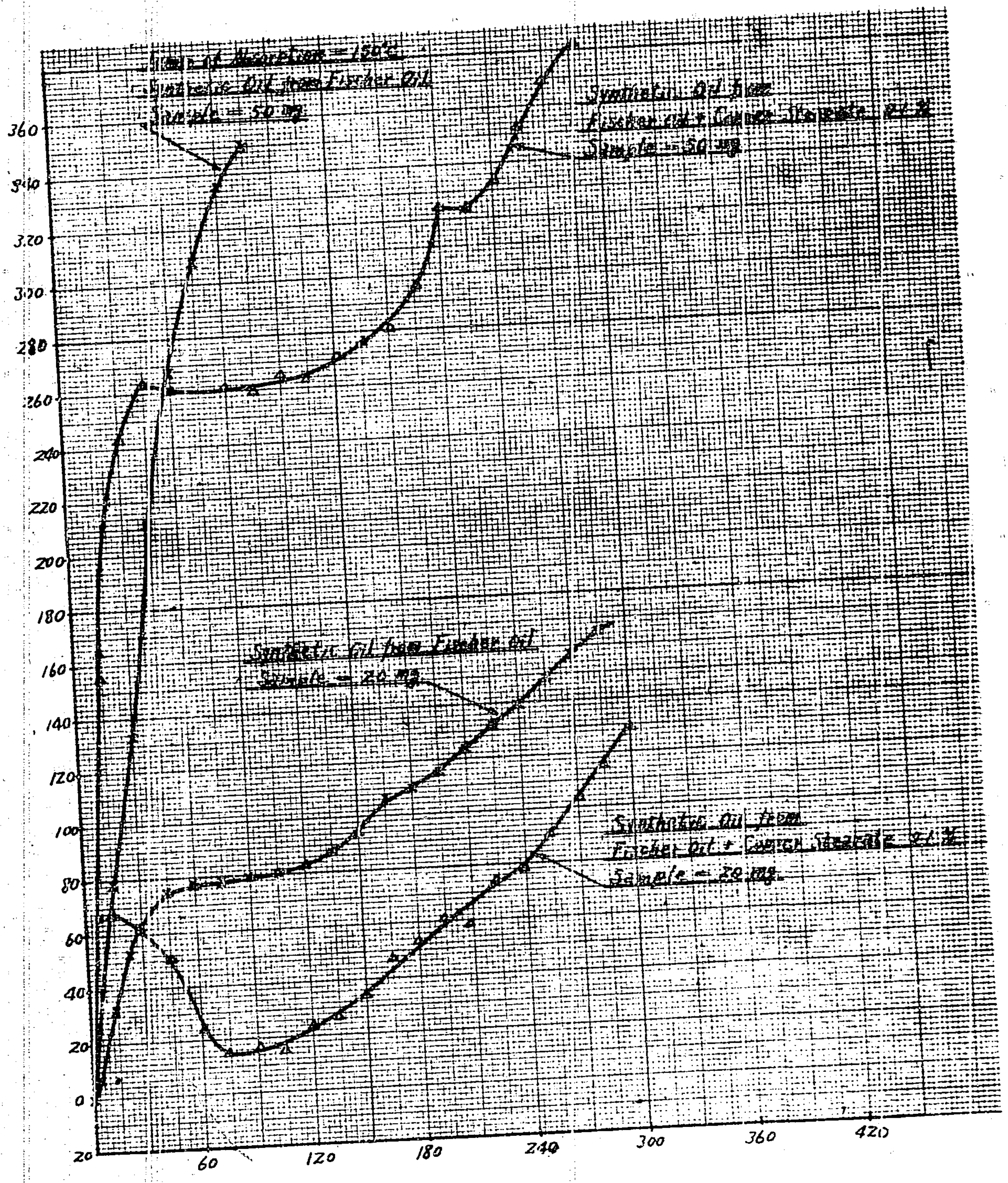

Figure 2(B)23
INFLUENCE OF COPPER STEARATE ON THE ABSORPTION
OF OXYGEN IN AEROENGINE OIL

ENCLOSURE (B) 24

EXPERIMENTAL METHOD FOR MANUFACTURING ADDITIVE AGENTS

By

NAV. CHEM. ENG. N. MATSUO
CHEM. ENG. LT. COMDR. M. HIRATA

Research Period 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)24

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)24

I. TRICRESYL PHOSPHITE

Phosphorous tricholoride (30% wt.) is slowly added to cresol (70% wt.) with sufficient stirring at room temperature. The condensation reaction shown below takes place:

$$PCl_3 + 3CH_3C_6H_4OH = (CH_3C_6H_4O)_3P + 3HCl$$

The resulting product is then slowly heated to about 200-250°C, leading inert gas (carbon dioxide or nitrogen) through the medium, in order to remove hydrogen chloride gas and to complete the condensation reaction. The product is finally fractionated in vacuum, and the fraction boiling from 223 C to 227°C at 5mm Hg is taken.

The process is schematically shown in Figure 1(B)24.

Density (d_4^{24})	1.1283
Ref. Index (n_D^{25})	1.5695
B.P. (°C/10mm Hg)	240-243

II. TRICRESYL PHOSPHATE

Phosphorous oxychloride (33% wt.) is slowly added to cresol (67% wt.) at room temperature. Anhydrous aluminium chloride (2-5% wt. of the mixture) is added little by little, and then heated to about 130-150°C, and maintained at that temperature for 7 hrs. A condensation reaction takes place according to the following equation.

$$POCl_3 \quad 3CH_3C_6H_4OH \quad (CH_3C_6H_4O)_3PO \quad 3HCl$$

The reacted mixture is washed with water and, after being dried by heating, is fractionated in vacuum of 5mm Hg. The fraction boiling from 240°C to 250°C at 5mm Hg pressure is taken.

The process is schematically shown in Figure 2(B)24.

Density (d_4^{20})	1.1718
Ref. Index (n_D^{25})	1.5010
B.P. (°C/760mm Hg)	425-435

III. A detailed flow sheet of the pilot plant for production of additives is shown in Figure 3(B)24.

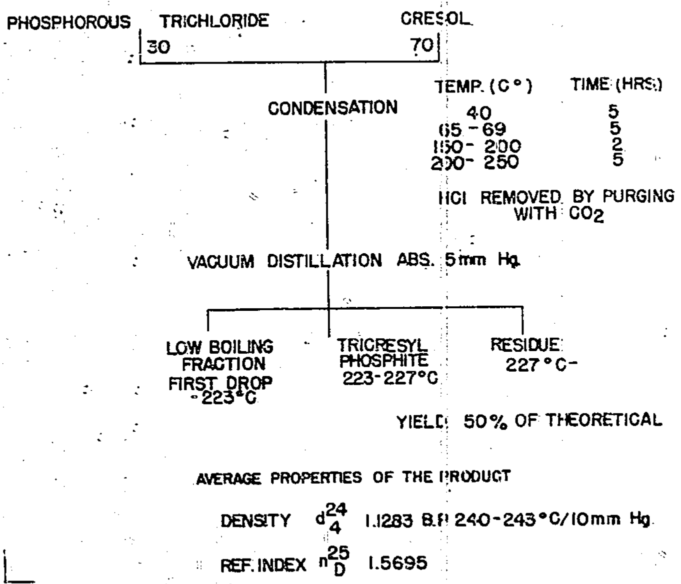

Figure 1(B)24

PROCESS FLOW SHEET FOR

MANUFACTURING TRICRESYL PHOSPHITE

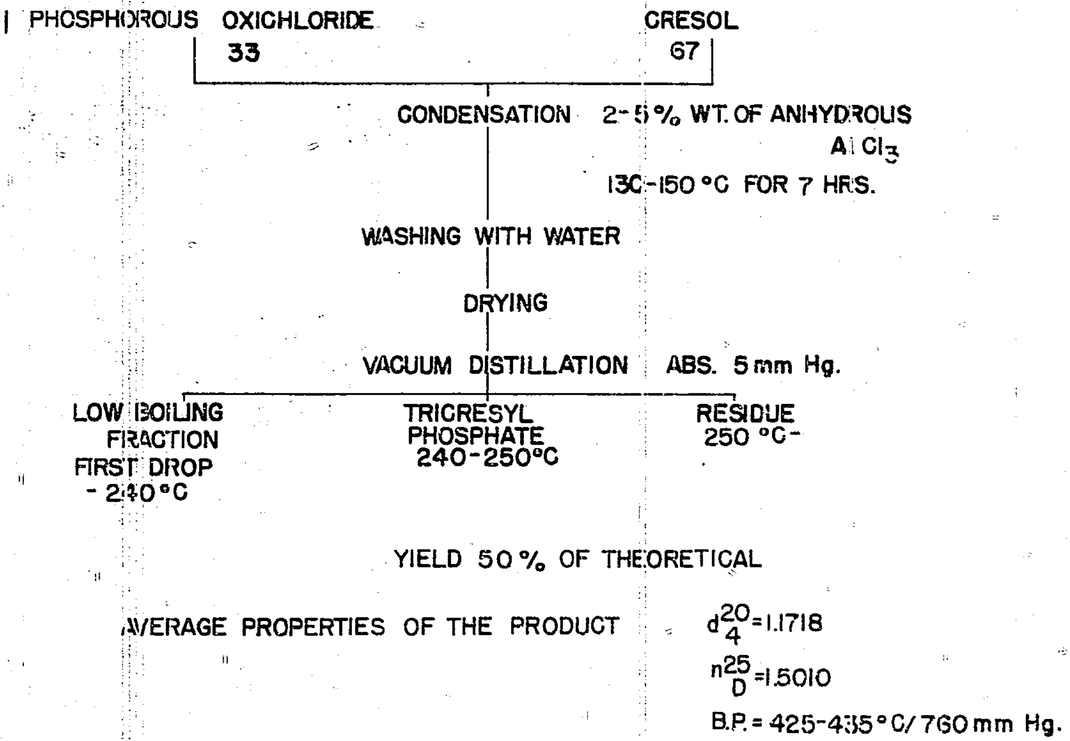

Figure 2(B)24

PROCESS FLOW SHEET FOR

MANUFACTURING TRICRESYL PHOSPHATE

ENCLOSURE (B)24

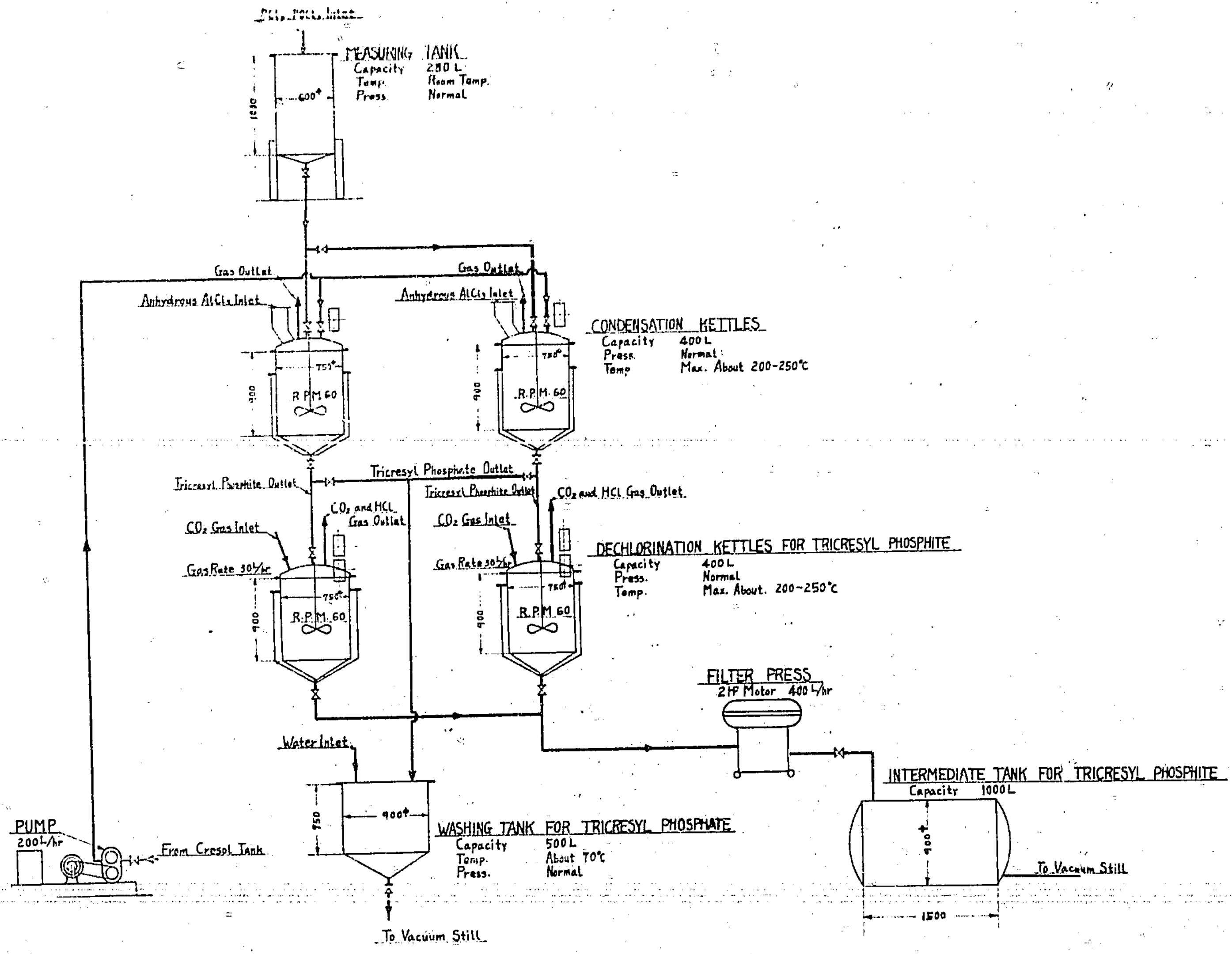

Figure 3(B)24

FLOW SHEET OF PILOT PLANT OF ADDITIVE AGENTS

ENCLOSURE (B)24

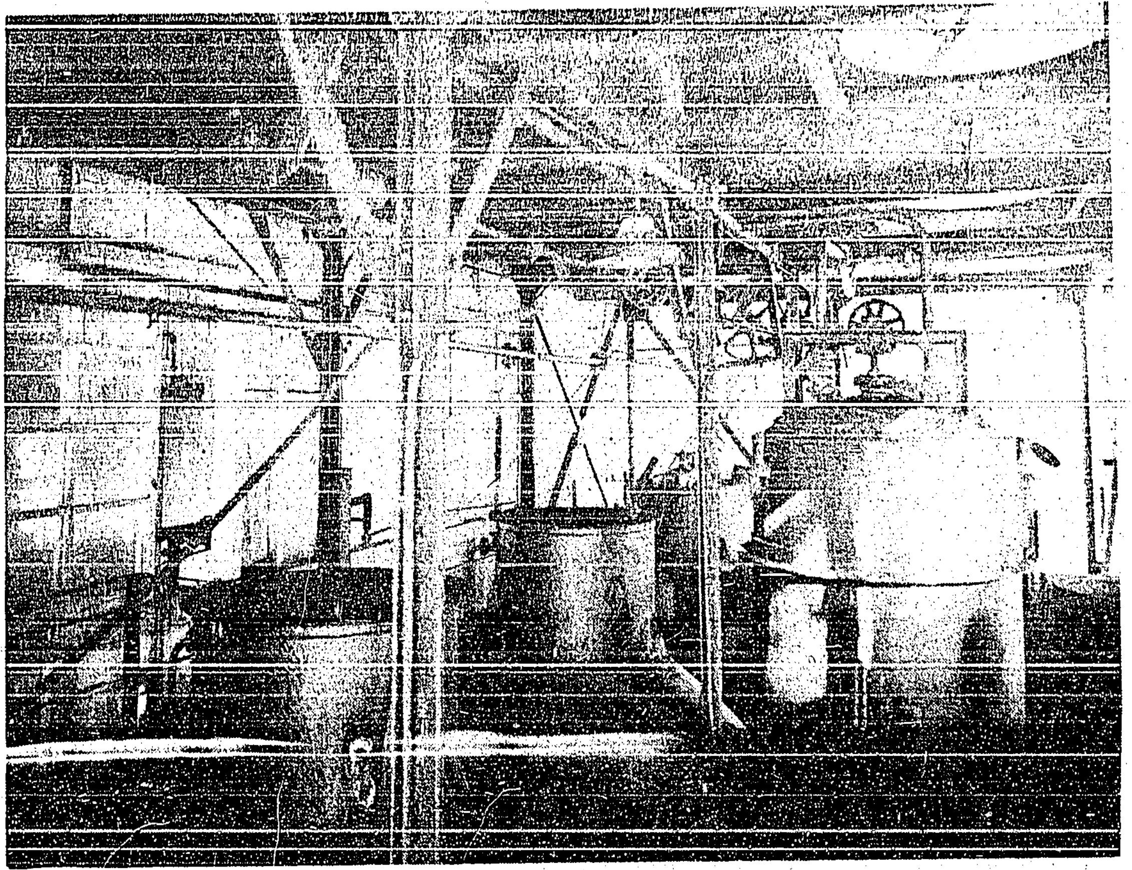

Figure 4(B)24

PILOT PLANT FOR MANUFACTURING
ADDITIVE AGENT OF LUBRICANT

ENCLOSURE (B) 25

ENGINE TESTS OF COMPOUNDED AIR CRAFT ENGINE LUBRICATING OIL, RELATIVE TO THE INFLUENCE OF TRICRESYL PHOSPHITE AND TRICRESYL PHOSPHATE AS ADDITION AGENTS

by

CHEM. ENG. LIEUT. T. FUJIMOTO

Research Period: 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)25

SUMMARY

As the horsepower of the engine of an aeroplane is increased, the bearing loads and temperature are raised. So the film strength or oiliness of the engine lubricant must be improved and added protection from oxidation must be provided for.

From chemical and physical tests, made in America and England, tricresyl phosphate had been found effective for oiliness improvement and tricresyl phosphite for protection against oxidation. Therefore these two compounds (T. C. Pi. 0.2%,T. C. Pa. 0.2% by wt.) were added to K-120-K (the oil used in Japanese Naval Air Fleet), and sent to Nakashima, Mitsubishi, and Aichi factories to test their effect in full scale aircraft engines for long operating periods. Their tests were supervised by men of The First Naval Technical Department. In these tests, this compounded oil foamed excessively. It was thought that the tricresyl phosphite caused the foaming.

I. INTRODUCTION

A. History of Project

At the First Naval Fuel Depot, the addition agents were made by Chem. Eng. Lt. Comdr. WAKANA and Chem Eng. Lt. Comdr. HIRATA. Chem. Eng. Lt. FUJIMOTO blended this agent in K-120-K oil, and sent to The First Naval Technical Depot at YOKOSUKA for testing. This Depot at YOKOSUKA, in turn, sent it to Mitsubishi, Nakashima, and Aichi.

B. Key Research Personnel on Project

Chem. Eng. Lt. Comdr., A. WAKANA
Chem. Eng. Lt. Comdr., M. HIRATA
Chem. Eng. Lt. Comdr., P. NAKAYAMA
Chem. Eng. Lt., T. FUJIMOTO
Chem. Eng. Lt., N. KOTAKE

II. TESTING

A. Blending of Sample

Tricresyl phosphite	0.2%
Tricresyl phosphate	0.2%
Blending Temperature	120°C
BlendinggPeriod	6 hr

The acid value of the compounded oil was a little lower than the base oil when stirred under the same conditions.

B. Tests Engine Used

Homare	III	Nakashima (Ogikubo)	18-cylinder air-cooled
Kasei	IIV	Mitsubishi (Nagoya)	14-cylinder air-cooled
Atsuta	IIO	Aichi (Nagoya)	12-cylinder water-cooled

C. Duration of Engine Tests

Each test was about 80 hours, using regular 91 O.N. gasoline as fuel.

These tests were made in connection with duration tests of Non-Chrome Carbon Steel crankshafts in all three engines and the test of oil was secondary.

D. Engine Test Method

1. The operating condition was at full power.

2. When the testing was completed, the engine was opened and examined, particularly the bearing surfaces, and other engine parts, on which sludge stuck such as on cylinders, superchargers, and connecting rods.

3. The chemical properties of the used oil were obtained and compared with those of the base oil.

4. The piston rings were weighed and cylinders examined after testing.

E. Summary of Data

Exact data cannot be remembered by the author but the findings it is believed, were as follows:

1. The operating condition was at full rated power.

2. The amount of sludge which stuck to the engine surfaces was smaller than that of the base oil.

3. The wearing surfaces were generally good.

4. In the case of the Homare engine the amount of foam in the oil tank was much more than with the base oil.

5. The used compounded oil was equal to or somewhat superior to the base oil when tested in the same way.

III. CONCLUSIONS

The effect of the addition agents on the engine was slight, and considered of little practical value. This experiment was completed in July, 1945, so the production of the addition agent was not in time to be of much practical use. Nevertheless, these compounds were used in the Sakae engine in Zero-Fighter during July and August, 1945. This was done in view of connecting rod (Copper-lead) bearing failures attributable to increased engine speed. About 50% of these engines showed bearing failure.

This report was obtained by the author in June, 1945 at Kasahara airfield located in KYUSHU. The author did not, however, see any of these bearings which had failed. There is no information regarding practical results obtained with this compounded oil during July and August.

ENCLOSURE (B) 26

ENGINE TEST WITH PROPOSED LUBRICANT OIL ADDITION AGENTS

by

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NAVAL MECH. ENG. CIVILIAN K. SHIMURA

Research Period:
from October 1943 to August 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)26

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)26

SUMMARY

In Japan there was a sufficient supply of aeroplane engine lubricants until about 1943. This supply consisted principally of Texaco Oil No. 120. However, in 1943 it became necessary for the Japanese Navy to use "K-120-K". This oil was prepared in Japan from Philipps Osage crude treated in the Duo-Sol plant at TOKUYAMA. This product, however, was not quite equal to Texaco No. 120 in quality. With increase in power output, it was necessary to have oil at least as good as Texaco No. 120, and to meet this requirement, tricresyl phosphite (T.C.Pi) & tricresyl phosphate (T.C.Pa) were tested by the First Naval Fuel Depot to examine their utility in full scale engines. These addition agents were found beneficial in regard to sludge formation and for frictional surfaces, particularly master rod bearing and piston rings.

I. INTRODUCTION

This K-120-K oil in which these addition agents were blended in the ratio of 0.2% by wt of each compound at the First Naval Fuel Depot, was sent to the Mitsubishi, Nakajima, and Aichi Companies, and tested.

All these tests were undertaken in connection with endurance tests of substitute materials for connecting rod & shaft manufacture. Therefore, these oil tests were only secondary in importance.

II. DETAILED DESCRIPTION

A. Test Engines and Performance Data

HOMARE II-I Type (Nakajima Co.)

Engine Data

No. of cyl...............	18
Dia. of cyl..............	1200mm (about)
Wt. of cyl...............	800kg (about)
Bore x Stroke............	130 x 150
Stroke Vol...............	36 lit (about)
Compression ratio........	7
Fuel.....................	91 O.N. gasoline
Oil......................	K-120-K
Cooling..................	air cooled

Performance Data

Horsepower (hp)		Condition
Max.............	2000	3000 R.P.M.,..... 500mm
Rated...........	1900	3000 R.P.M.,..... 350mm 2000m
Rated...........	1700	3000 R.P.M.,..... 350mm 6000m

KASEI II-V Type (Mitsubishi Co.)

Engine Data

No. of cyl...............	14
Dia. of cyl..............	1300mm (about)
Wt. of cyl...............	800kg (about)

Bore x Stroke	150 x 170
Stroke Vol	42 lit (about)
Compression Ratio	6.5
Fuel	87 O.N. gasoline
Oil	K-120-K
Cooling	air cooled

Performance Data

	Horsepower	Condition		
Max	1850	2600 R.P.M.,	450mm	
Rated	1700	2500 R.P.M.,	300mm	2000m
Rated	1550	2500 R.P.M.,	300mm	6000m

ATSUTA II-0 Type (Aichi Co.)

Engine Data

No. of cyl	12
Wt. of cyl	650kg (about)
Bore x Stroke	150 x 160
Stroke Vol	34 lit
Fuel	91 O.N. gasoline
Oil	K-120-K
Cooling	inverted 60° V water-cooled

Performance Data

	Horsepower	Condition		
Max	1200	2500 R.P.M.,	300mm	
Rated	1000	2400 R.P.M.,	150mm	1500m
Rated	970	2400 R.P.M.,	150mm	4500m

B. Test Procedure

The test period was about 60 hours in each engine and under the following conditions:

Power	Duration of Operation
max. rated hp	30^{h} {(5^{m} + 5^{m}) X 180 times}
rated hp 1st step	10^{h} (5^{h} X 2 times)
2nd step	10^{h} (5^{h} X 2 times)
high oil temp.* operation (10° higher than ordinary operation)	10^{h} {(30 min X 10 1st step) (30 min X 10 2nd step)}

C. Determination Method

After testing was completed, the engine was opened and the surface condition of the inner parts were examined.

1. Examination of dirt on the surfaces of the inner parts of engine, crankcase and reduction gear box.

---

* Usual oil inlet temp.: <75°C

2. Examination of the frictional surfaces of crankshaft, main bearing, connecting rod, piston side, cylinder and piston ring.

3. Examination of sludge on crank pin and super charger shafts.

4. Examination of carbon on piston and cylinder.

5. Examination of wear of piston side, crankpin, crankshaft, bearing metal, etc.

6. Examination of oil after use (viscosity, dilution, Conradson's test).

The sample was collected every 10 hours, during the engine test.

D. Summary of Data

General results of these tests were as follows:

1. Dirt on inner parts of engine was less than that when base oil was used alone.

2. Frictional surface conditions were better.

3. Adherent sludge on all inner parts of the engine was less than that when base oil was used alone.

4. Adherent carbon in piston and cylinder was less than when base oil was used alone.

5. Sticking of piston rings which was due to the addition agents was not recognized at all and operation conditions were very good.

6. Corrosion of bearing surfaces was not generally recognized.

7. Wear in piston, crankpin, main bearing, analysis of used oil and analysis of adherent sludge on supercharger shaft are shown in Table I(B)26. (Data are from memory.)

III. CONCLUSIONS

These addition agents were concluded to be effective by these tests, and seem to have given satisfactory service in the following planes:

Aeroplane	Engine
Zero-Fighter	Sakae II 0
SAIUN	Homare II 0
GINGA	Homare II 0
RAIDEN	Kasei II 0
SIDEN	Homare

ENCLOSURE (B)26

Table I(B)26
ENGINE WEAR AND ANALYSIS OF USED OIL

	Base Oil	
	(K - 12 - K)	Addition agent (T.C.Pi 0.2, T.C.Pa 0.2)
Viscosity (210°F) Seybolt second	(110-130)*	(115-125)*
Conradson's Test (carbon)(%)	(1.0-2.0)*	(0.8-1.5)*
Dilution (%)	<1.0*	<1.0*
Degree of wear mean value	100%	80%
Inorganic material of adherent sludge (%)	70-80	50-65

* Show the range of variation of the oil used during operation.

ENCLOSURE (B) 27

STUDIES ON THE OILINESS CHARACTERISTICS OF PURE HYDROCARBONS BASED ON STATIC FRICTION DETERMINATIONS FOR STEEL ON STEEL

by

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CHEM. ENG. LIEUT. M. HIRATA

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)27

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)27

SUMMARY

The oiliness of various cyclic hydrocarbons and a few chain hydrocarbons were measured and the following results were obtained.

1. If aromatic hydrocarbons are hydrogenated step by step, the oiliness of the compounds becomes first poorer and then better.

2. Qualitative correlations seem to exist between the oiliness of the compounds and their molecular volumes and molecular cohesion, i.e., melting point, boiling point, viscosity, etc.

3. The compounds in which the benzene nuclei are combined by single bonds were better lubricants than these having the benzene nuclei combined in condensed form.

4. The oiliness of a cyclic compound was better than that of a chain compound having the same number of carbon atoms.

I. INTRODUCTION

It has been reported in the literature that paraffinic hydrocarbons have better oiliness characteristics than naphthenes (Ref. 1.), and that in the case of straight chain hydrocarbons the oiliness improves as the molecular weight increases (Ref. 2), and that chain hydrocarbons are better lubricants than cyclic compounds (Ref. 3), but almost no systematic studies on the oiliness of pure cyclic hydrocarbons have been published. The molecules of mineral lubricants are said to have a cyclic structure with side chains of various lengths, and a systematic study of the oiliness of the pure cyclic hydrocarbons is important in this branch of the investigation of lubricants.

II. DETAILED DESCRIPTION

Studies on these problems were conducted during 1944.

A. Test Procedure and Samples Used in the Test

1. Test Apparatus. The three test pieces of the Deeley machine were changed and three steel balls (dia. ½ inch) were substituted. The test plate was made of cast steel.

2. Preparation of the Test Plate and the Test Pieces. The test pieces and the test plate were first washed with pure petroleum ether and ethylether, polished with 0.5 emery paper, and then washed with distilled water.

They were next purified by means of electrolytic reduction, applying 20 mA. current, for 30 minutes in a 2% NaOH solution using a carbon anode. Thus treated, the test plate and pieces were washed with water and alcohol, and dried in vacuum.

The oil test sample was rubbed on the surface with a piece of filter paper, and measurement was made 30 minutes after the test pieces were wetted with the oil.

3. Test Procedure. Static coefficients of friction of various

pure hydrocarbon oils, alone and in 5% benzene solution, were measured at room temperature or at temperatures higher than their melting points.

4. Compounds Used for the Test. Marketed samples of benzene, cyclohexane, naphthalene, tetralin, decalin, and anthracene were purified and used in the test.

Diphenyl and diphenyl benzene were prepared through the thermal condensation of benzene (Ref. 4), and the hydrogenation products of diphenyl, anthracene, and diphenyl benzene were prepared by high pressure hydrogenation (Ref. 5).

The compounds used and their characteristic properties are summarized in Table I(B)27.

E. Results

The results are summarized in Table II(B)27 and are represented graphically in Figure 1(B)27.

1. The substances which had better oiliness were also better oiliness compounds in a benzene solution containing 95% by volume of benzene.

2. Benzene Series:- Benzene, cyclohexane. Cyclohexane had better oiliness than benzene as already reported (Ref. 6).

3. Naphthalene Series:- Naphthalene, tetralin, decalin. Contrary to the case of the benzene series, naphthalene had better oiliness than tetralin. Such results may be due to the greater molecular cohesion of naphthalene. In the case of the benzene series, benzene has a greater molecular cohesion than cyclohexane, but the former had poorer oiliness, and such results are attributed to the smaller molecular volume of benzene. Decalin, however, had better oiliness than tetralin. This is similar to the relationship between cyclohexane and benzene. In brief, if naphthalene is hydrogenated step by step, its oiliness becomes first poorer and then better.

4. Other Series

   a. Diphenyl Series:- Diphenyl, phenylcyclohexane, dicyclohexyl.

   b. Anthracene Series:- Anthracene, tetrahydroanthracene, decahydroanthracene, perhydroanthracene.

   c. Diphenyl Benzene Series:- Diphenyl benzene, perhydrodiphenyl benzene.

   The change of oiliness resulting from stepwise hydrogenation of these other compounds gave results which resembled those of the naphthalene series.

5. General Remarks on the Above Results

   a. From the above results, it may be said that, in general, if aromatic hydrocarbons are hydrogenated step by step, the oiliness of the compounds becomes poorer at first and then improves when hydrogenation is complete. Also, qualitative correlations seem to exist between the oiliness of the compounds and their molecular volumes and molecular cohesion, i.e. melting point, boiling point, viscocsity, etc. Such relations are given in Figures 1(B)27 and 2(B)27,

b. The oiliness of the hydrocarbons becomes gradually better in the following order:

Benzene series → Naphthalene series → Diphenyl series → Anthracene series → Diphenyl benzene series.

c. The compounds having the benzene nuclei combined with single bonds were better lubricants than the compounds having the same number of nuclei combined in condensed form.

6. Comparison With Chain Compounds. The oiliness of n-hexane, i-hexane, and n-octadecane were measured and the results were compared with those of cyclic compounds having the same number of carbon atoms.

The characteristics of the compounds and the results are given in Table III(B)27 and Figure 3(B)27.

It appears that the oiliness of a cyclic compound is better than that of a chain compound having the same number of carbon atoms.

III. CONCLUSIONS

From the above results, it was concluded that naphthalene, diphenyl, anthracene, diphenyl benzene, perhydrodiphenyl benzene had good oiliness characteristics, and of these, completely hydrogenated diphenyl benzene was the best.

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2. Hardy, Proc. Roy. Soc., A 101, 561 (1922)
   J. Chem. Soc., 77, 1219 (1925)
3. AKAMATSU, Bl. Chem. Soc. Japan, 9, 288 (1940)
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6. cr. (3)

ENCLOSURE (B)27

Table I (B)27
PROPERTIES OF THE RELATED COMPOUNDS

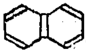
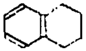
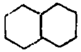
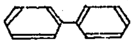
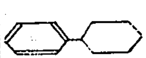
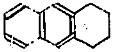
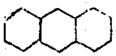
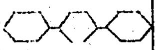
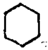
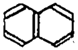
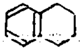
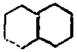
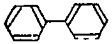
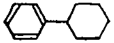
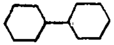
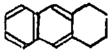
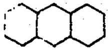
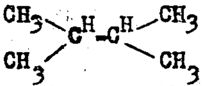
Group	Compounds	Molecular Structure	M.	P.	B.	P.	Elementary Analysis			
							C		H	
			Obs.	Lit.	Obs.	Lit.	Obs.	Cal.	Obs.	Cal.
Benzene Series	Benzene		5.4	5.5	79-80	79.6				
	Cyclohexane		4.5	4.5	80-81	80.7				
Naphthalene Series	Naphthalene		79-80	80	217-219	218				
	Tetralin		liq.	-31	204-200	206				
	Decalin		liq.	-125	188-193	189-191				
Diphenyl Series	Diphenyl		69-70	68.5-69.5	-	248-249				
	Phenylcyclohexane		liq.	7	234-236	234-236				
	Dicyclohexyl		liq.	4	229-235	225-233				
Anthracene Series	Anthracene		217-218	217-218	-	351-342				
	Tetrahydro-anthracene		104.5-107	103-105	-	309-313	92.86	92.26	6.76	7.74
	Octahydro-anthracene		39	73-79	-	292-295	89.31	90.25	9.63	9.75
	Perhydro-anthracene		liq.	liq.	-	270 272-277	86.42	87.41	13.26	12.59
Diphenyl-benzene Series	Diphenyl benzene		211.5-212	212-213	-	253	-	-	-	-
	Perhydro diphenyl benzene		160-161.5	162-163	-	-	85.32	87.03	12.36	12.97

Table II(B)27.
STATIC FRICTION COEFFICIENTS AND OTHER PROPERTIES

Compounds	Molecular Structures	Percentages of Compounds				$\frac{1}{M.W.}$	$\frac{1}{M.P.}$ (°C)	$\frac{1}{Vis.}$ (Poise) of 5 mol solution in benzene
		100%		5% Solution in benzene				
		Static C.F.	Temp. (°C)	Static C.F.	Temp. (°C)			
Benzene		0.170	13	0.168	22	0.0127	0.00358	164.5
Cyclohexane		0.153	13	0.160	22.5	0.0118	0.00358	168.1
Naphthalene		0.144	90	0.147	22.5	0.00980	0.00272	140.5
Tetralin		0.159	90	0.159	24.2	0.00956	0.00413	145.1
Decalin		0.154	90	0.153	23.2	0.00723	0.00676	148.5
Diphenyl		0.134	75	0.152	25.2	0.00649	0.00292	132.0
Phenylcyclohexane		0.149	14	0.155	22.8	0.00625	0.00357	138.9
Dicyclohexyl		0.156	75	0.153	23.0	0.00601	0.00361	141.1
Anthracene		0.121	230	0.129	17.8	0.00561	0.00204	—
Tetrahydro-anthracene		0.135	105	0.153	18	0.00557	0.00204	122.1
Decahydro-anthracene		0.139	105	0.156	9.8	0.00536	0.00302	123.9
Perhydro-anthracene		0.142	105	0.162	27.8	0.00520	0.00370	129.9
Diphenyl benzene		0.122	160	0.141	23.5	0.00442	0.00206	—
Perhydro diphenyl benzene		0.104	170	0.128	25.2	0.00403	0.00230	105.2

ENCLOSURE (B)27

Table III(B)27
COMPARISON OF OILINESS OF CHAIN AND
CYCLIC COMPOUNDS

Name	Chemical Structure	Density (d_4^{20})	M.P. (°C)	B.P. (°C)	Static Coef.*	Temp. (°C)
n-Hexane	$CH_3(CH_2)_4CH_3$	0.6592		68-70	0.161	12.8
i-Hexane		0.6630		57-59	0.160	12.6
Cyclohexane		0.7783		79-81	0.153	13.0
n-Octadecane	$CH_3(CH_2)_{16}CH_3$		28	158-162 15.5mm	0.132	45.0
Perhydrodiphenyl benzene			160-161		0.104	170

*By modified Deeley machine. Steel ball on steel plate.

ENCLOSURE (B)27

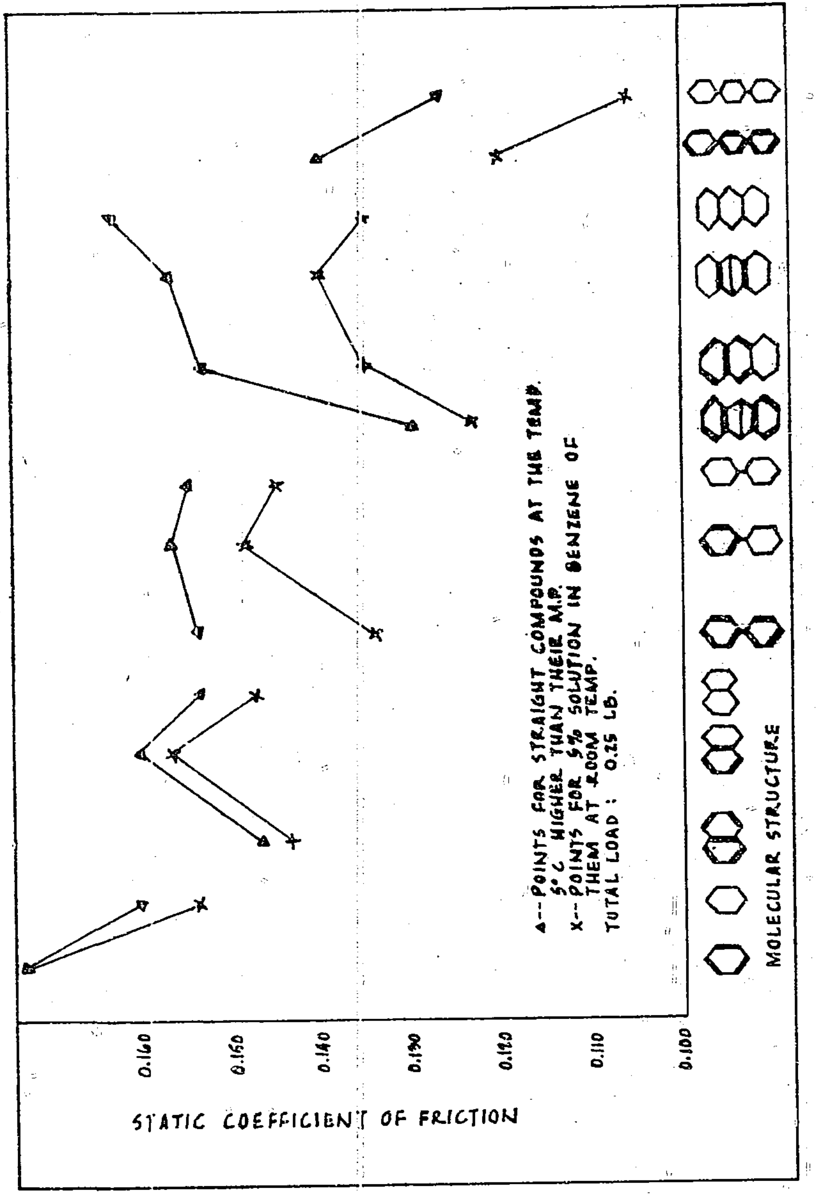


Figure 1(B)27

STATIC COEFFICIENT OF FRICTION BY MODIFIED DEELEY MACHINE

(Point Contact, Steel on Steel)

ENCLOSURE (B)27

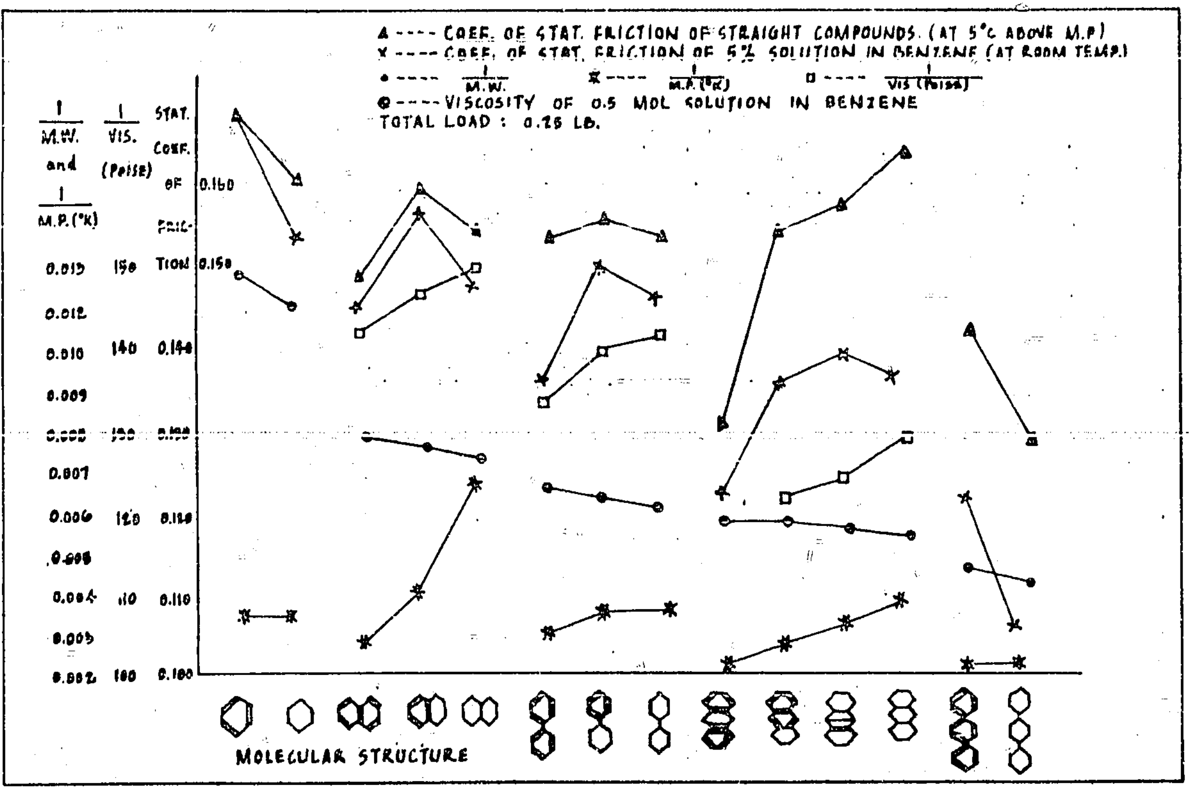


Figure 2(B)27

CORRELATION OF THE STATIC COEFFICIENTS OF FRICTION BY DEELEY (MODIFIED) MACHINE

(Point contact, steel on steel--with the molecular weight and viscosity of the compounds).

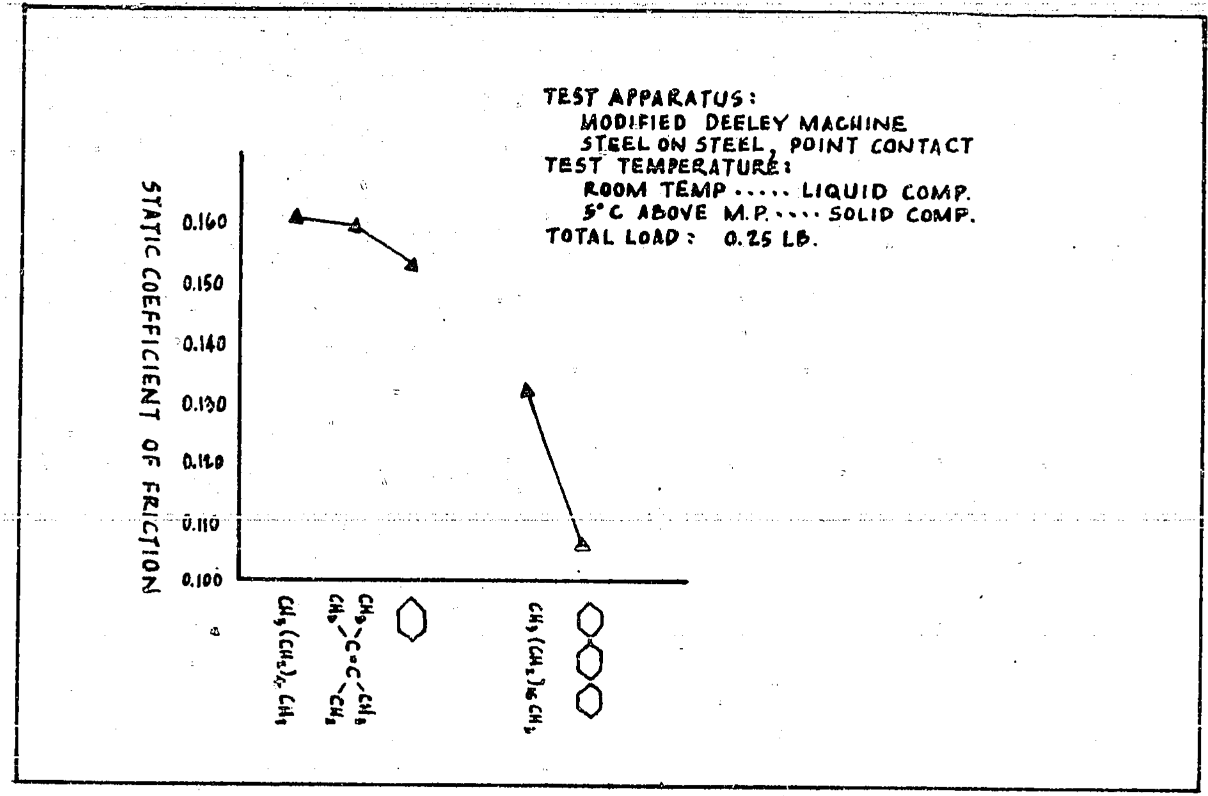


Figure 3(B)27

COMPARISON OF CHAIN COMPOUNDS WITH CYCLIC COMPOUNDS

(Static Coefficient of Friction)

ENCLOSURE (B) 28

STUDIES ON THE OILINESS CHARACTERISTICS OF STEARIC ACID, BENZENE AND THEIR DERIVATIVES BASED ON STATIC FRICTION DETERMINATIONS FOR STEEL ON STEEL

By

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CHEM. ENG. LT. M. HIRATA

Research Period: 1942-1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)28

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)28

SUMMARY

The oiliness characteristics of stearic acid, benzene and their derivatives were measured, and the effects of the polar group on oiliness were compared with each other. The results were as follows:

1. The $-NH_2$ and $-COOH$ groups were the most effective in regard to oiliness, the $-OH$ group was the next, and the $-COCH_3$, $-OCH_3$, $-CN$ were comparatively less effective.

2. The derivatives of stearic acid were better oiliness carriers than the corresponding derivatives of benzene.

I. INTRODUCTION

A great number of substances which are said to be effective as "Oiliness carriers" are known,* but the quantitative relationship between the oiliness and the chemical nature of the substances are only partly known. Accordingly, it may be important to clear up the relationship between the oiliness and the chemical structures of various compounds. With this object, studies were made of the oiliness of stearic acid, benzene and their derivatives during the period from March, 1942 to October, 1944.

II. DETAILED DESCRIPTION

A. Samples Used

1. The method of preparation and the physical and chemical properties of stearic acid, benzene and their derivatives are summarized in Table I(B)28.

2. The white oil used in making blends was prepared by treating a commercial liquid paraffin with concentrated sulphuric acid, and its properties are as follows:

Reaction	Neutral
Density (d_4^{20})	0.8856
Viscosity (Redwood No. 1 sec)	
at 10°C	775
at 30°C	262
Pour Point (°C)	-16
Acid Value	0.03
Saponification Value	0.34
Corrosion	None

B. Test Procedure

The test procedure comprised a static friction determination for steel on steel using a modified Deeley machine as in the case of the Research Project No. 57.

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*Byers J.H. Nat. Pet. News July 14 (1937)
ibid Dec. 16 (1936)
Ralston A.W. ibid Dec. 9 (1936)

C. Results

The results are summarized in Table II(B)28 and Table III(B)28 and graphically represented in Figures 1(B)28 and 2(B)28.

1. Oiliness of Stearic Acid and its Derivatives. The oiliness of octadecane, octadecyl alcohol, stearic acid, methyl stearate, methyl octadecyl ether, methyl heptadecyl ketone, stearonitrile, stearoamide were measured, and were found to fall in the following order in regard to their effectiveness:

   a. In the case of the straight compounds (not is solution): Stearoamide, stearic acid, octadecyl alcohol, staronitrile, octadecane, methyl heptadecyl ketone, methyl stearate.

   b. In the case of 1% solution in the white oil, stearoamide, stearic acid, octadecane, stearonitrile, octadecyl alcohol, methyl stearate, methyl octadecyl ether, methyl heptadecyl ketone: Generally speaking, $-CONH_2$ and $-COOH$ groups were most effective to oiliness, $-CH_3$, $-OH$, $-CN$ the next, and $-COOCH_3$, $-COCH_3$, $-OCH_3$ were least effective.

2. Oiliness of Benzene and its Derivatives. The oiliness of benzene, phenol, benzoic acid, methyl benzoate, anisol, acetophenone, benzonitrile aniline were measured, and were found to be in the following order:

   a. In the case of the straight compounds (100%): Benzoic acid, anisol, phenol, aniline, methyl benzoate, acetophenone, benzene.

   b. In the case of 1% solution of the compounds in the white oil: Phenol, methyl benzoate, benzonitrile, benzoic acid, acetophenone, aniline, benzene, anisol.

   Generally speaking, $-OH$, $-COOH$, $-COOCH_3$ groups were comparatively effective.

III. CONCLUSION

The authors made a survey on the oiliness of ordinary polar groups and found that $-OH$, $-COOH$ groups were the best and $-OH$, $-COOCH_3$ were next.

Table I(B)28
PROPERTIES AND METHODS OF PREPARATION OF COMPOUNDS

Name	Chemical Structure	M.P. (°C)	B.P. (°C)	Other Characteristics		Method of Preparation
				d_4^{20}	n_D^{20}	
Octadecane	$CH_3(CH_2)_{16}CH_3$	28	162-164/5.5mm			Prepared by means of hydrogenation of ethyl stearate.
Octadecyl Alcohol	$CH_3(CH_2)_{17}OH$	58.5	153-155/5.5mm			A marketed sample was fractionated and recrystallized with alcohol.
Stearic Acid	$CH_3(CH_2)_{16}COOH$	69~70	218-220/9mm	SV 197		A marketed sample was fractionated in vacuum and recrystallized with 95% alcohol.
Methyl Stearate	$CH_3(CH_2)_{16}COOCH_3$	38~39	166-168/1.3mm			Purified stearic acid was esterified with methanol by an ordinary method. The raw ester was washed with 2% sodium hydroxide solution and water and then recrystallized with 60% alcohol.
Methyl Octadecyl Ether	$CH_3(CH_2)_{17}OCH_3$					Octadecyl iodide was prepared from the above mentioned octadecyl alcohol and iodine, using red phosphorous as catalyst, and then it was reacted with sodium ethylate in the medium of ether.
Methyl Heptadecyl Ketone	$CH_3(CH_2)_{16}COCH_3$	55~56	170-182/4mm			Barium stearate (353gm) and barium acetate (128gm) were mixed and brought to dry distillation. The fraction distilled from 300°C to 390°C was taken. (449gm) The raw product was washed with hot solution of 2% sodium hydroxide and fractionated in vacuum. The fraction boiling from 170°C to 182°C in vacuum of 4mm Hg was taken (50gm) and recrystallized with alcohol.
Stearonitrile	$CH_3(CH_2)_{16}CN$	41	185-190/3mm			Stearoamide (128gm) and phosphorous pentoxide (60gm) were mixed and maintained at 200°C in vacuum of 1mm Hg. The distillate (103gm) was fractionated in vacuum and recrystallized with methanol.
Stearoamide	$CH_3(CH_2)_{16}CONH_2$	104	250-251/12mm			Stearyl chloride prepared from stearic acid and phosphorous trichloride was brought to reaction with 30% ammonia cooling with ice water. The raw product was recrystallized with alcohol. The yield was 57% of stearyl chloride.
Benzene	C_6H_6	5.5	80-80.5	0.8739	1.5015	A marketed benzene was treated with concentrated sulphuric acid and recrystallized.
Phenol	C_6H_5OH		178~179			A marketed phenol was fractionated.
Benzoic Acid	C_6H_5COOH	121~122				A marketed pure sample was used.
Methyl Benzoate	$C_6H_5COOCH_3$		198~200			
Anisol	$C_6H_5OCH_3$		150~160	0.9950	1.5170	A marketed sample was washed with 2% solution of sodium hydroxide and fractionated.
Acetophenone	$C_6H_5COCH_3$		199~203	1.0295	1.5337	A marketed sample was fractionated.
Benzonitrile	C_6H_5CN		188~190	1.0020	1.5285	A marketed pure sample was used.
Aniline	$C_6H_5NH_2$		183~185			A marketed sample was fractionated.

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Table II(B)28
STATIC COEFFICIENTS OF FRICTION OF STEARIC ACID AND ITS DERIVATIVES

Names of Samples	Chemical Formula	Straight Compounds		1% Solution Compounds in the White Oil	
		Static Coef. of Friction	Temp.* (°C)	Static Coef. of Friction	Temp (°C)
White Oil		0.121	25		
Octadecane	$CH_3(CH_2)_{16}CH_3$	0.109	35	0.108	25
Octadecyl Alcohol	$CH_3(CH_2)_{17}OH$	0.102	63	0.113	25
Stearic Acid	$CH_3(CH_2)_{16}COOH$	0.074	75	0.105	25
Methyl Stearate	$CH_3(CH_2)_{16}COOCH_3$	0.120	45	0.115	25
Methyl Octadecyl Ether	$CH_3(CH_2)_{17}OCH_3$			0.115	25
Methyl Heptadecyl Ketone	$CH_3(CH_2)_{16}COCH_3$	0.111	60	0.119	25
Stearonitrile	$CH_3(CH_2)_{16}CN$	0.105	45	0.111	25
Stearoamide	$CH_3(CH_2)_{16}CONH_2$	0.067	114	0.100	25

*The temperature was raised by means of a heater, up to about 5°C above the M.P. of the compounds.

Table III(B)28
STATIC COEFFICIENTS OF FRICTION OF BENZENE AND ITS DERIVATIVES

Names of Samples	Chemical Formula	Straight Compounds		1% Solution Compounds in the White Oil	
		Static Coef. of Friction	Temp.* (°C)	Static Coef. of Friction	Temp. (°C)
White Oil		0.121	25		
Benzene	$C6H6$	0.170	13	0.118	25
Phenol	$C6H5OH$	0.145	50	0.110	25
Benzoic Acid	C_6H_5COOH	0.141	126-128	0.114	25
Methyl Benzoate	$C_6H_5COOCH_3$	0.146	21.5	0.113	25
Anisol	$C_6H_5OCH_3$	0.143	25.8	0.119	25
Acetophenone	$C_6H_5COCH_3$	0.153	25.8	0.116	25
Benzonitrile	C_6H_5CN	0.162	23	0.113	25
Aniline	$C_6H_5NH_2$	0.145	22.5	0.117	25

*The temperature was raised by means of a heater, up to about 5°C above the M.P. of the compounds.

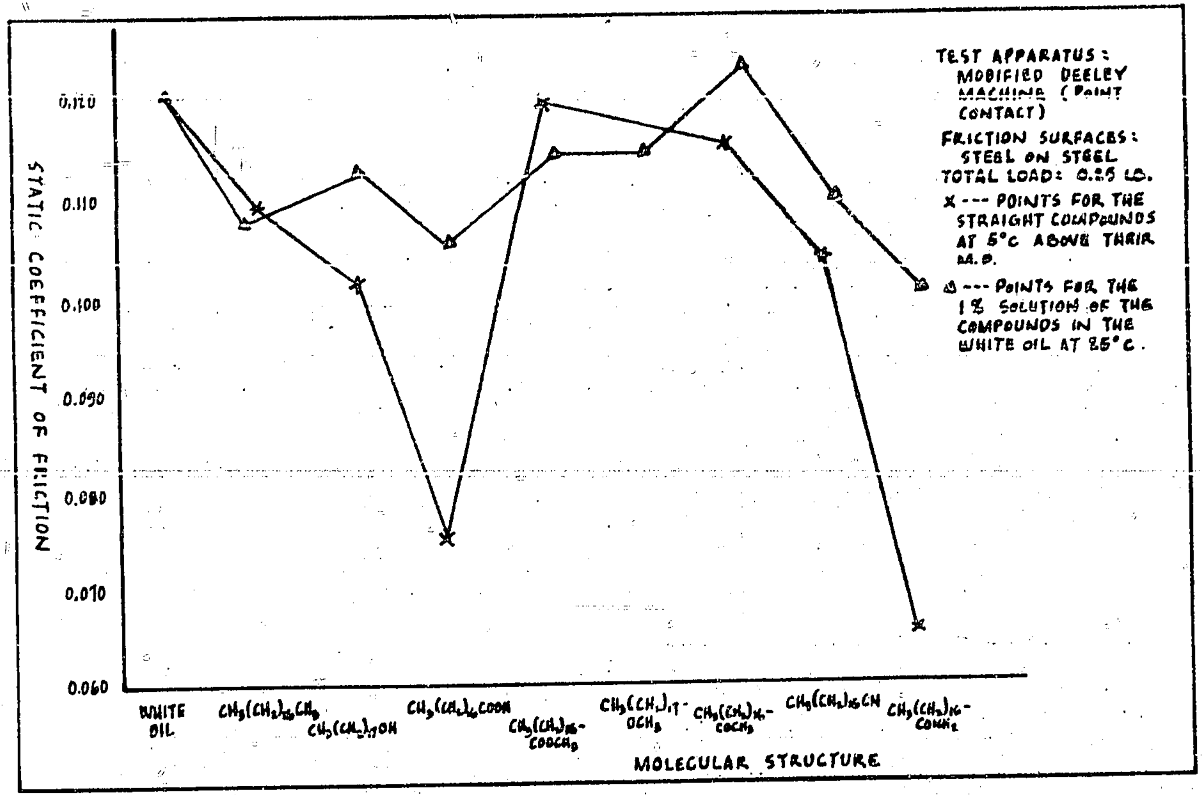

Figure 1(B)28

STATIC COEFFICIENTS OF FRICTION OF STEARIC ACID AND ITS DERIVATIVES

ENCLOSURE (B)28

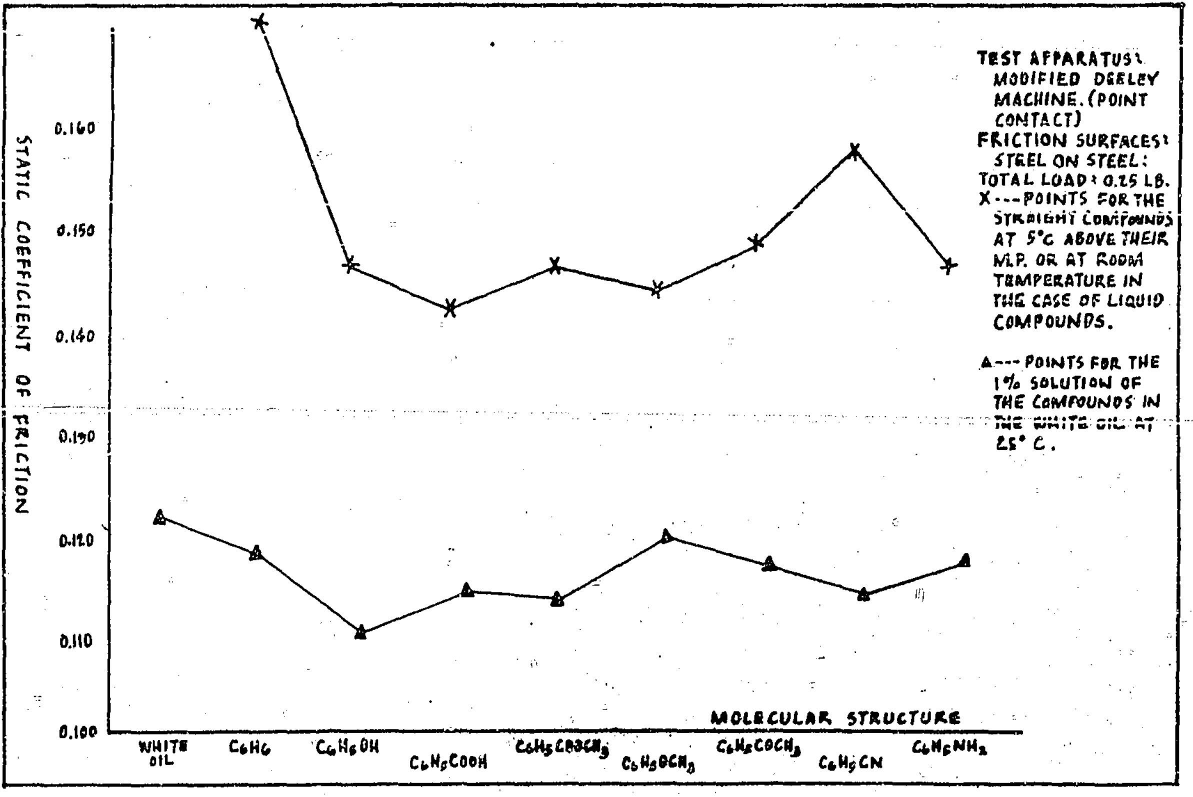

Figure 2(B)28

STATIC COEFFICIENTS OF FRICTION OF BENZENE AND ITS DERIVATIVES

ENCLOSURE (B) 29

STUDIES ON SOYA BEAN PHOSPHATIDES AS ADDITIVES FOR LUBRICATING OILS

by

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ENG. LIEUT. M. HIRATA

Research Period: 1943-1944

Prepared for and Reviewed with Authors by
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December 1945

ENCLOSURE (B)29

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)29

SUMMARY

The authors studied the soya bean phosphatides as lubricant additives, especially the relation between the oiliness and stability improving ability and the purity and chemical constituents of lecithin and cephalin.

The results were as follows:

1. The soya bean phosphatides were effective as oiliness agents for lubricants and the higher their acid values, the better the oiliness characteristics.
2. The soya bean phosphatides were effective as antioxidants.
3. No remarkable difference was found between lecithin and cephalin (from soya beans) as lubricant additives.

I. INTRODUCTION

It had already been reported in the literature that the phosphatides had some effect on the oxidation of animal and vegetable bodies.* Another reference** showed that the piston ring sticking in aero engines was inhibited by addition of 0.2% of phosphatides to the lubricant. The authors also recognized the effectiveness of phosphatides on the aircraft engine lubricant,***but the raw material had very complex chemical nature and it was thought necessary to study the relation between effectiveness and purity, and therefore, researches were carried on from 1943 to 1944.

II. DETAILED DESCRIPTION

A. Characteristics of Raw Phosphatides and Their Purification

1. Raw Phosphatides. The characteristics of raw phosphatides are given in Table I(B)29.

2. Separation of Lecithin and Cephalin

a. Separation of alcohol and acetone. The phosphatide prepared at Takeda Chemical Co. Ltd. was treated with alcohol and acetone as follows on the next page.

B. Results

1. Soya Bean Phosphatides as the Oiliness Agents. 1% of Takeda phosphatide was added to several oils and the low speed kinetic coefficients of friction were measured using the Deeley machine, (point contact, steel on steel). It was found that these phosphatides were very good oiliness agents. (See Table II(B)29.)

2. The Relation Between the Purity of the Phosphatides and Their Ability as Oiliness Agents. Studying the relation between purity of the phosphatides and their ability as oiliness agents, it was found that the purer phosphatides were the poorer oiliness agents. The results are given in Table III(B)29.

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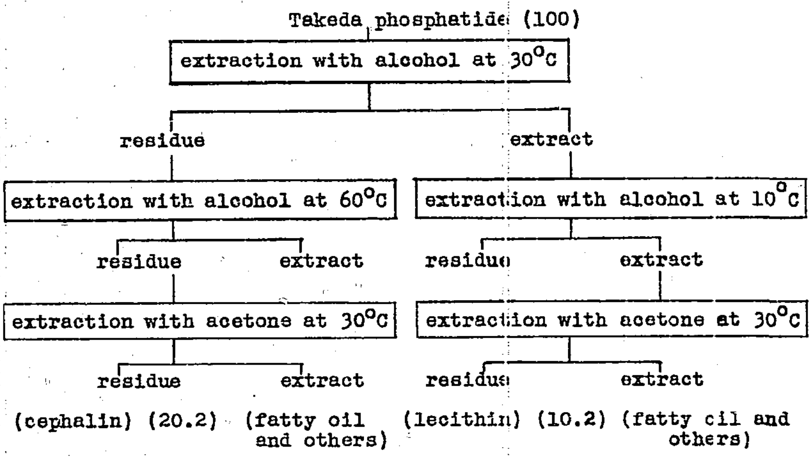
*Czapeck F. Biochemi der Pflanzen I. 773.
**U. S. Patent 2,166,286: 2,211,163: 2,212,020.
***Ser. No. 085. Enc. B-23

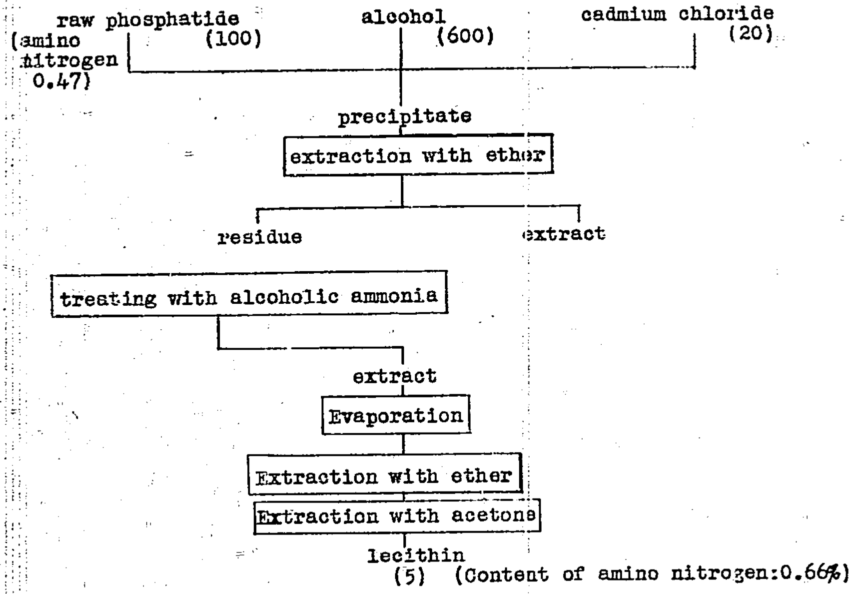


The percent content or amino nitrogen was as follows:

Raw Phosphatide : 1.71
Lecithin : 1.01
Cephalin : 1.92

The separation was unsatisfactory.

b. Purification by cadmium chloride. Comparatively pure lecithin was obtained from the phosphatide prepared at Manchurian Soya Bean Co. Ltd. by cadmium chloride as follows:



From the foregoing results the oiliness of the phosphatides were concluded to depend upon the free acid contained in them.

3. <u>Suitability of the Soya Bean Phosphatides as Antioxidants for Lubricants</u>. The stability of lubricants was improved by means of addition of phosphatides, when using the British Air Minstry Oxidation Test. Results are given in Table IV(B)29.

4. <u>The Relation Between the Purity of the Phosphatides and Their Value as Antioxidants</u>. It was found that the purer the phosphatides, the greater the stability improving ability. The results are given in the Table V(B)29.

5. <u>Effects of Combination of Phosphatides with Tricresyl Phosphate</u>. Phosphorous compounds such as triphenyl phosphite, triphenyl phosphate, tricresyl phosphate,etc. are effective as antioxidants of lubricants. Generally speaking, the phosphites are better antioxidants than phosphates, but the former are unstable to water, so we thought that the combination of phosphates and phosphatides might be a good antioxidant. This attempt was successful in the case of mineral oil base, but it failed when the base oil was made synthetically from paraffine wax.

6. <u>Difference of the Effects Between Lecithin and Cephalin</u>. Two samples of phosphatides were prepared by the authors, one lecithin rich, another cephalin rich, and the difference of the effects between the two was investigated but no remarkable difference was found as shown in the Table VII(B)29. Cephalin was only slightly soluble in the oils, and we used its saturated solution. -- mixing at a temperature of 60°C-70°C. However separation did not occur at low temperature.

IV. CONCLUSION

A. The soya bean phosphatides were effective as oiliness agents and which may be attributed mainly to the free acids (organic) present.

B. The soya bean phosphatides were good antioxidants for lubricants, and the in-purification produced improved results.

C. There was no marked difference between the effectiveness of lecithin and cephalin as oiliness agents and antioxidants for lubricants.

ENCLOSURE (B)29

Table I(B)29
CHARACTERISTICS OF RAW PHOSPHATIDES

Names of samples	Acid Value	Water(%)	N(%)	P(%)	N:P
The phosphatide prepared at Manchurian Soya Bean Co.Ltd. (Purity, 40%)	77.3	14.55	0.52	1.28	0.91
Manchurian (Purity, 50%)	55.0	11.55	0.94	1.56	1.34
Manchurian (Purity, 60%)	23.3	6.66	1.00	1.76	1.25
The phosphatide prepared at Honen-seiyu Co. Ltd. (Sample C.)	81.4	15.20	0.82	2.23	0.82
Honen-seiyu (Sample E.)	127.8	8.76	1.04	2.48	0.93
Honen-seiyu(Sample EA.)	54.9	7.24	1.30	2.82	1.00
The phosphatide prepared at Takeda Chemical Co. Ltd.	53.9	8.06	1.04	2.81	0.83
The phosphatide prepared at Tokyo Institute of Industrial Research	22.5				

Table II(B)29
KINETIC COEFFICIENTS OF FRICTION BY MODIFIED DEELEY MACHINE

Names of base oils	Kinetic coef. of friciton of base oil.			Kinetic coef. of friction of phosphatide compounded oils.		
	50°C	150°C	250°C	50°C	150°C	250°C
Aero engine oil #80	0.012	0.085	0.095	0.006	0.063	0.068
Aero engine oil #120	0.010	0.057	0.105	0.006	0.048	0.061
Turbine oil	0.010	0.098	0.116	0.008	0.090	0.086
Compressor oil	0.013	0.080	0.095	0.008	0.055	0.080

ENCLOSURE (B)29

Table III(B)29
KINETIC COEFFICIENTS OF FRICTION BY MODIFIED DEELEY MACHINE

Names of oils	Acid Values of Phosphatides	Base oil: Aero-engine oil #120			Base oil: Turbine oil		
		50°C	150°C	250°C	50°C	150°C	250°C
Base oil only		0.010	0.057	0.130	0.010	0.098	0.116
Base oil + 1% of phosphatide of purity 40%	77.3	0.008	0.051	0.068	0.008	0.071	0.072
" 55%	55.0	0.009	0.045	0.047	0.010	0.088	0.083
" 60%	23.0	0.009	0.049	0.051	0.013	0.083	0.080

Table IV(B)29
RESULTS OF BRITISH AIR MINISTRY OXIDATION TEST

Names of Base oils	Base oils only		Base oils 1% of Takeda phosphatide	
	Viscosity ratio	Carbon residue after test (%)	Viscosity ratio	Carbon residue after test (%)
Turbine oil	3.86	2.45	2.77	2.33
Aeroengine oil #80	1.50	1.72	1.29	1.27
Aeroengine oil #120	1.54	2.23	1.32	2.30
Compressor oil	2.68	2.82	2.41	2.27
Synthetic aeroengine oil #120	2.90	1.64	2.07	1.46

Table V(B)29
RESULTS OF BRITISH AIR MINISTRY OXIDATION TEST

Names of oils	Acid Values of Phosphatides	British Air Ministry Oxidation test	
		Viscosity ratio	Carbon residue in %
Aeroengine oil #120		1.54	2.23
1% of Phosphatide Purity 40%	77.3	1.35	1.65
" 55%	55.0	1.28	1.64
" 60%	23.0	1.25	1.68

Table VI(B)29
RESULTS OF BRITISH AIR MINISTRY OXIDATION TESTS

Name of oils	Viscosity ratio	Carbon residue after test (%)
Aeroengine oil #120	1.35	2.00
Aeroengine 1% of tricresyl phosphate	1.30	1.81
Aeroengine 0.5% of tricresyl phosphate 0.5% Takeda phosphatide	1.23	1.67
Synthetic aeroengine oil #120 from paraffine wax	2.90	1.46
1% of tricresyl phosphate	2.33	1.61
0.5% of tricresyl phosphate 0.5% of Takeda phosphatide	2.19	1.64

Table VII(B)29
RESULTS OF BRITISH AIR MINISTRY OXIDATION TESTS AND KINETIC COEFFICIENTS OF FRICTION

Names of oils	British Air Minstry Oxid. test.		Kinetic coef. of friction at room temp.
	Vis. ratio	Carbon residue (%)	
Aeroengine oil #80	1.47	1.53	0.087
1% of lecithin	1.23	1.14	0.079
0.53% of cephalin	1.34	1.14	0.086
Aeroengine oil #120	1.35	2.0	0.083
1% of lecithin	1.25	1.49	0.075
0.58% of cephalin	1.25	1.52	0.075
Synthetic aeroengine oil #120	2.92	1.64	0.082
1% of lecithin	2.16	1.53	0.071
0.22% of cephalin			0.073

ENCLOSURE (B) 30

STUDIES ON METHODS OF TESTING THE OILINESS OF LUBRICATING OIL

by

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Research Period: 1943-1944

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)30

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)30

SUMMARY

The authors constructed several oiliness testers, and measured the oiliness of various kinds of mineral and fatty oil with the object to establish a simple method of testing oiliness.

1. The machine constructed were two special four ball oiliness testers and a pendulum oiliness tester, and the latter was the most suitable for routine testing.

2. The numerical values of the coefficients of friction of the same lubricating oil obtained from different machines were not the same, but from the relations between the values obtained by each machine, we could determine the oiliness of a sample oil by one of the machines.

3. In the case of well refined mineral oils there was a rough parallelism between the coefficients of friction and their viscosities.

4. The coefficients of friction of fatty oils had intimate relations to their acid values as well as their viscosities.

I INTRODUCTION

In the zone fluid film lubrication, the most effective property of oil in lubrication is the viscosity and in the boundary condition, it is the oiliness of oil. The lubrication conditions of the aero engines and other machines had become more and more severe, especially in regard to the master rod bearing, and the oiliness of lubricating oil had become the most important factor. Therefore, it was necessary to establish a simple and proper method of determining it. Many reports about various types of oiliness testers are found in the literature -- static, and kinetic friction tester, point and line contact type, for example, Deeley machine, Ref. (1) Timken machine, Ref. (2) four ball machine, Ref. (3) pendulum machine, Ref. (4). From 1933 to 1934 we constructed some special types of oiliness tester referring to the literature with the object of obtaining the most simple and proper oiliness tester.

II DETAILED DESCRIPTIONS

A. The Test Apparatus and Test Procedure

1. Four Ball Tester A. It consists of three steel balls (dia $\frac{1}{2}$ inch) tightly packed in a oil cup and a rollable ball (dia $\frac{1}{2}$ inch) on the former, such as the one constructed first by O. Beeck with the object of testing high pressure lubricants. The schematic view of the apparatus is shown in Figure 1(B)30.

B, C, D. are packed balls, A is a rollable ball to which a weight carrying body E is attached, H is a mechanical device to circulate the oil, J is a heater and G is a hook for direct measurement of the frictional resistance.

a. Direct measurement of the frictional resistance: The lower part of the apparatus is revolved by a motor at a constant velocity, and the friction is measured with a spring balance or by means of a string balance device shown in Figure 2(B)30, the calculation principle is as follows:

From the balance of force at point A

$$\frac{W}{\sin\theta} = \frac{a}{\sin(\pi - \frac{\theta}{2})}; \text{ or } a = \frac{W\sin(\pi - \frac{\theta}{2})}{\sin\theta} = \frac{W\sin\frac{\theta}{2}}{\sin\theta} .(1)$$

From the balance of force at point B

$$f = a\sin\frac{\theta}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

From (1), (2)

$$f = \frac{W\sin^2\frac{\theta}{2}}{\sin\theta} = \frac{W\sin^2\frac{\theta}{2}}{2\sin\frac{\theta}{2}\cos\frac{\theta}{2}} = \frac{W}{2}\tan\frac{\theta}{2} = \frac{W}{2}\frac{1}{\sqrt{n^2-1^2}} .(3)$$

f is the force of friction, W is the weight.

b. <u>Measurement of the coefficient of friction by means of damped revolution (deceleration method)</u>: The lower part of the apparatus is revolved by a motor at gradually increasing velocity, the upper part is revolved with the lower one, and the latter is stopped, then the former begins to revolve at a decreasing velocity. The revolution velocity (deceleration ratio) is measured by means of a stroboscopic device.

The calculation principle is as follows:

It is assumed that

f : the force of friction,

γ : the distance between the point of action of the friction force and the revolution axis,

I : the moment of inertia of the revolving body,

ω : the angular velocity,

t : the time of revolution.

$$f \cdot \gamma = I\frac{d\omega}{dt} \ldots\ldots\ldots\ldots(4)$$

If n is assumed to be the revolutions per unit time,

$$f \cdot \gamma = 2\pi I\frac{dn}{dt} \ldots\ldots\ldots(5)$$

Assume f' to be the total pressure at the point of contact and the coefficient of friction, and then

$$f = \mu f \ldots\ldots\ldots\ldots\ldots(6)$$

If θ is assumed to be the angle between the straight line, connecting the center of the upper ball and that of one of the lower balls, and a plane rectangular to the revolution axis, and M to be the mass of the upper body, g to be gravity constant.

$$f' = \frac{Mg}{\sin\theta} \ldots\ldots\ldots\ldots\ldots(7)$$

from (5), (6), (7)

$$\mu = \frac{2\pi \sin\theta}{Mg\gamma}\frac{dn}{dt} \quad \ldots\ldots\ldots\ldots(8)$$

or

$$= \frac{2\pi \sin\theta}{Mg\gamma} \cdot \frac{n_1 - n_2}{t_1 - t_2} \quad \ldots\ldots(9)$$

2. Four Ball Tester B. The construction of the main parts is the same as the four ball tester A, but the weight is applied by means of a lever and it is suited for the measurement of so-called film rupture strength. The schematic view of the apparatus is shown in Figure 3(B)30.

a. Direct measurement or the coefficient of friction: The plug K and the plate L are removed, the upper part is revolved, and weight F is applied, the force of friction is measured by means of a hook G and a spring balance. H is a ball bearing device to decrease undesirable friction.

b. Measurement of the film rupture strength: The plug K and the plate L are placed in position, and the upper part is revolved and weight F is gradually increased until the film rupture occurs.

3. Pendulum Oiliness Tester. The pendulum oiliness tester is one of the most simple of the various friction testers and T. E. Stanton, J. W. Donaldson (5) used this. We made some devices for shortening the pendulum stem, as shown in Figure 4(B)30. The upper test pieces were steel balls (dia. ½ inch), and the lower was steel, white metal, or Cu-Pb alloy. The calculation method was mathematically derived by S. Kyropoulos (6) and is as follows:

$$\frac{\mu}{1+\mu^2} = \frac{A\cos\theta}{\gamma} \cdot \frac{\cos\alpha_{\gamma+1} - \cos\alpha_\gamma}{\frac{3}{2}(\alpha_{\gamma+1} + \alpha_\gamma) + \frac{3}{4}\sin 2\alpha_{\gamma+1} - \frac{1}{4}\sin 2\alpha_\gamma - 2\cos\alpha_\gamma \sin\alpha_{\gamma+1}}$$

μ: the coefficient of friction

a, γ, θ: shown in Figure 5(B)30.

$\alpha_\gamma \cdot \alpha_{\gamma+1}$: the amplitude of γth, γ+1th oscillations.

In the present experiment, $\alpha_\gamma - \alpha_{\gamma+1}$ 0.0135 radian, and the following equation was practically satisfactory:

$$\mu = 4.90 \times (\alpha_\gamma - \alpha_{\gamma+1})$$

B. Results:

We measured the oiliness of various kinds of mineral and fatty oils. Some physical and chemical properties and the test results are summarized in Table I(B)30.

The measuring conditions are shown in Table II(B)30. The following general views could be deduced, from the above experiment.

1. Relation Between Viscosity and Oiliness: The graphical representations of the relations between the oiliness (Coef. of friction and film rupture strength) and the viscosity are given in Figure 6

(B)30, 7(B)30, and 8(B)30. In the case of mineral oils, the relation between oiliness and the viscosity was roughly represented as a curve, and that of fatty oils of low acid value was also roughly on a curve lying in the zone of higher oiliness (Figure 7(B)30.). The fatty oils of high acid value were far better in oiliness, and were plotted but they did not fall on the curve for low-acid fatty oils. If we get these curves, the oiliness of any oil will be estimated from the displacement of the point for the oil from the curve. An Average of 3 or 4 determination would be required.

2. Comparison of the Data Obtained From Each Machine: The numerical values of the coefficient of friction of the same lubricating oil obtained from different machines (or from different procedures, at different conditions, with different test pieces) were not the same, but a rough parallel relation was present as shown in Figure 7(B)30 and 8(B)30, that is to say, an oil which had good oiliness by one measurement procedure also had good result in another test procedure.

3. Comparison With The Data Obtained From Deeley Machine: The data obtained from each machine had a parallel relation with that obtained from Deeley machine.(cf. Table I(B)30.)

III CONCLUSIONS

There was a relation between the coefficients of friction obtained from various oiliness testers.

To determine the oiliness of a lubricant, only one of the machines need be used.

For simple measurement, the pendulum machine is the most desirable, but for the testing of high pressure lubricants, the four ball tester B. must be used.

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(6) Kyropoulos S, Rev. Sci. Instr. 8 (1937) 151

Table I(B)30
SUMMARY OF THE TEST RESULTS

	Four Ball Tester B			Pendulum Tester									Deeley Machine		
No.	Temp.*	Viscosity	Film Rupture Strength (kg)	Steel on Steel			Steel on Brass			Steel on Copper			Temp.* (°C)	Viscostiy (S.U.S.)	Static Friction Coef.
		(S.U.S.)		Temp.* (°C)	Viscosity (S.U.S.)	Kinetic Friction Coef.	Temp.* (°C)	Viscosity (S.U.S.)	Kinetic Friction Coef.	Temp.* (°C)	Viscosity (S.U.S.)	Kinetic Friction Coef.			
1	24	4900	15	23	5000	0.086	21	6000	0.082	21	6000	0.064	25	4400	0.096
2	24	1900	12	165	5500	0.092	22	2250	0.087	22	2250	0.083	25	1550	0.097
3	22	1300	9	24	1100	0.103	26	350	0.101	26	950	0.098	24.1	1100	0.118
4	25	430	7	24	450	0.115	22	525	0.111	22	525	0.109	25	420	0.121
5	24	94	6	20	105	0.129	25	92	0.124	26	92	0.116	24	94	0.135
6	23	4300	20	19	5900	0.062	26	440	0.052	24	3350	0.046	25	3600	0.096
7	28	2600	18	28	2600	0.070							17.5		0.080
8	24 30	419 322	15 19	21	970	0.080	24	418	0.079	24	418	0.072	24.5 25.0	403 400	0.111 0.109
9	26 30	310 265	14 20	21	380	0.079	24	338	0.073	24	338	0.065	23.2 30	342 265	0.106
10	30	220	18	24.5	268	0.084							17.4 25.0	345 262	0.066 0.111
11	30	190	19	24	237	0.084							15.5 25.0	312 230	0.070 0.115
12	30	175	20	21.5	235	0.079							16.3 25.0	280 210	0.061 0.112

Table I(B)30 (Con(t)

ENCLOSURE (B)30

Table I(B)30 (Con't)
SUMMARY OF THE TEST RESULTS

No.	Samples	Viscosity (S.U.S.)		Viscosity index	Acid Value	Four Ball Tester A Direct Method			Four Ball Tester A Revolution Method		
		100°F	210°F			Temp.* (°C)	Viscosity (S.U.S.)	Kinetic Friction Coef.	Temp.* (°C)	Viscosity (S.U.S.)	Kinetic Friction Coef.
1	Aeroengine oil #120	1468.5	111.4	99.4		23	5000	0.101	27	3800	0.091
2	Aeroengine oil #80	781.0	81.0	95.5		24	1400	0.105	27	1550	0.095
3	Turbine oil	414.4	50.8	99.3		24	1100	0.110	28	820	0.097
4	Moblie oil	210.6	45.8	77.5		24	450	0.121	28	360	0.107
5	Spindle oil	67.0	37.8	152.6		24	94	0.140	28	85	0.117
6	Castor oil	1271.4	100.6	95.3	0	25	3600	0.078	27	3200	0.073
7	Polymerized Soya bean oil	1594.0	219.0	132.8	3.67				28	2600	0.069
8	Rape seed oil	242.4	60.8	153.0	0	24	419	0.092	28	360	0.087
9	Camellia oil	200.6	55.6	155.3	3.53	24	338	0.089	27	300	0.068
10	Cotton seed oil	167.4	53.0	163.2	0.34	28	228	0.091	29.5	122	0.101
11	Shark liver oil	149.4	51.7	161.2	4.28	29	200	0.089	28	210	0.072
12	Cod liver oil	139.7	51.4	169.3	4.48	28	190	0.089	29.5	220	0.073

*No additional heat applied

ENCLOSURE (B)30

Table II(B)30
CONDITIONS FOR MEASURING OILINESS
FOUR BALL TESTER

	Film rupture strength (Tester B)	Direct friction Measurement (Tester A)	Damped Oscillation method (Tester A)	Deeley Machine
Load (kg)	0 - 400	1.0077	1.0077	0.452
Sliding speed m/sec.	0.1226	0.0072	0.034	0.0362
Ambient Temperature	Room	Room	Room	Room
Test Temperature	Not controlled	Not controlled	Not controlled	Not contro

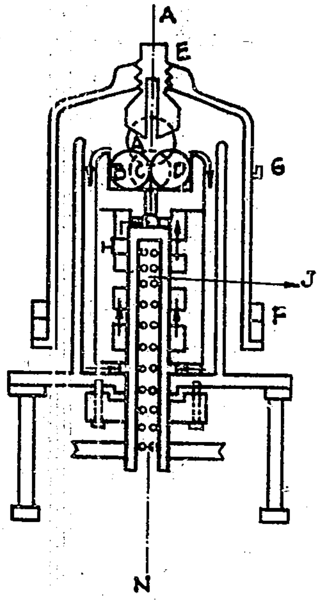


Figure 1(B)30

FOUR BALL TESTER A.

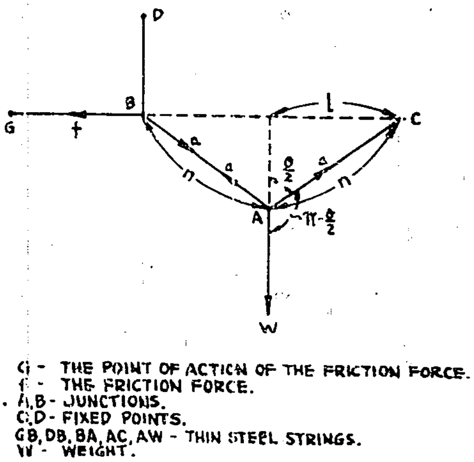


Figure 2(B)30

STRING BALANCE DIVICE FOR THE DIRECT MEASUREMENT OF KINETIC FRICTION COEFFICIENT.

ENCLOSURE (B)30

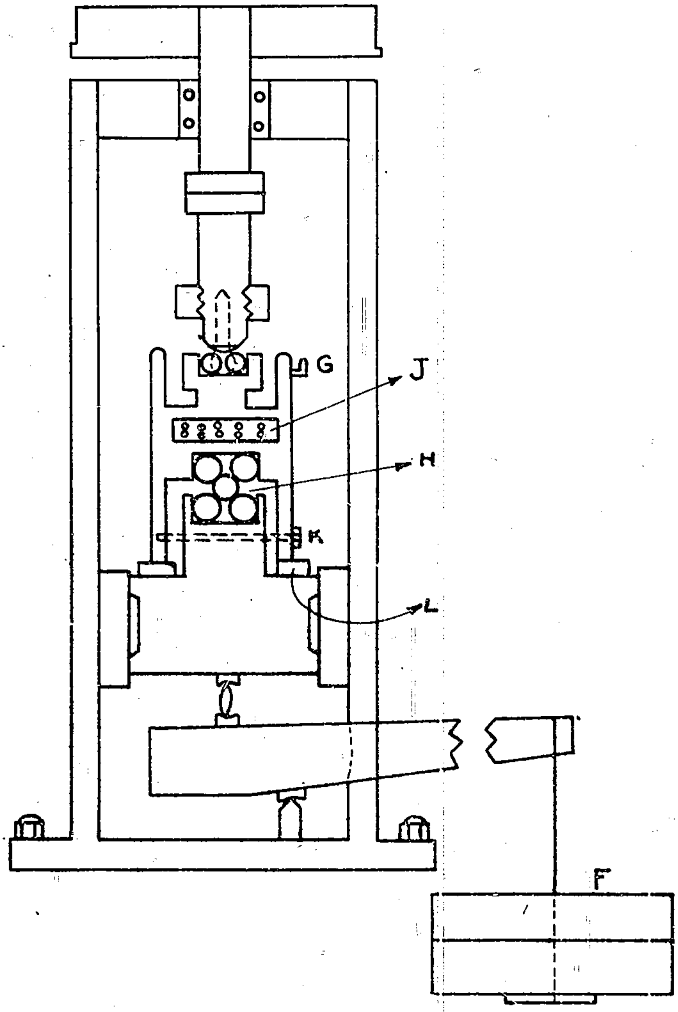


Figure 3(B)30
FOUR BALL TESTER B.

ENCLOSURE (B)30

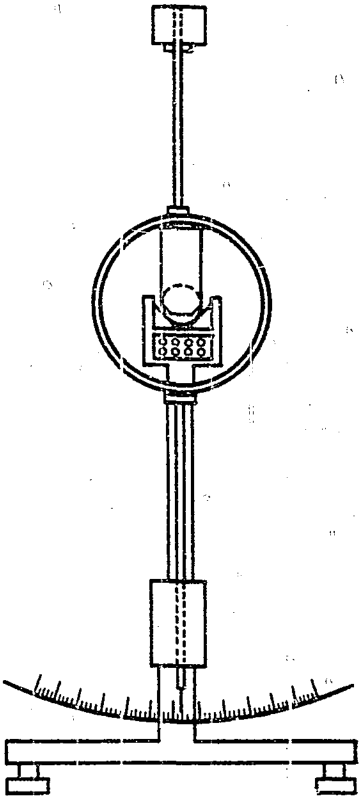


Figure 4(B(30
PENDULUM TESTER

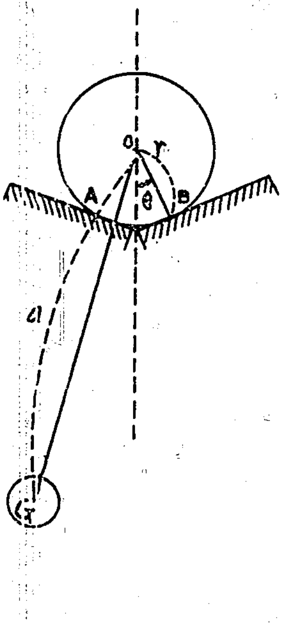


Figure 5(B)30
MAIN PARTS OF THE PENDULUM TESTER

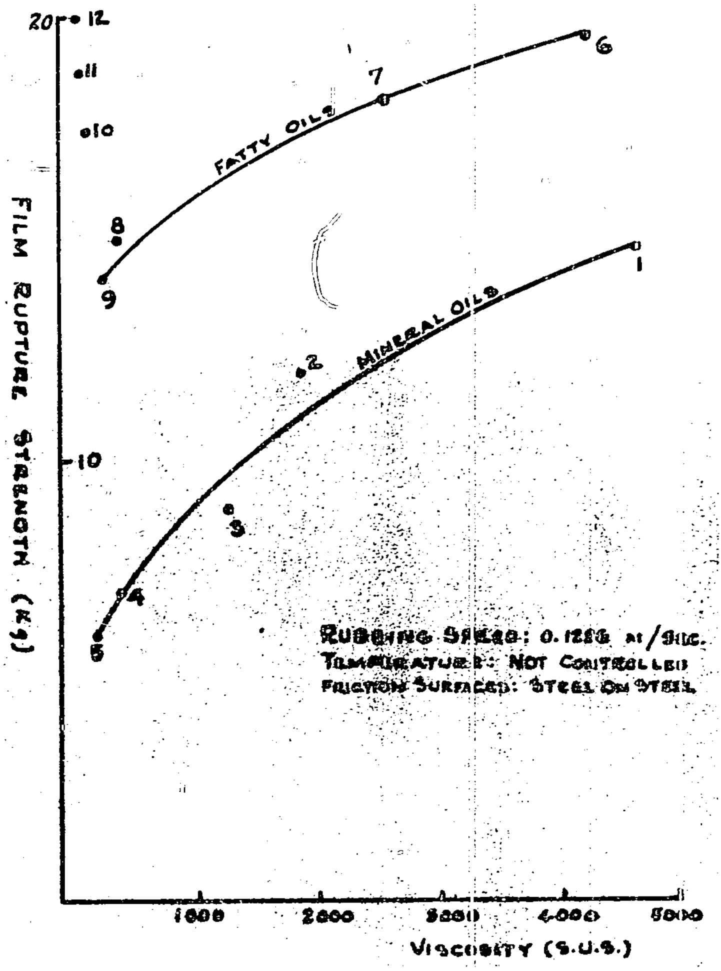


Figure 6(B)30
FILM RUPTURE STRENGTH
BY FOUR BALL TESTER B

ENCLOSURE (B)30

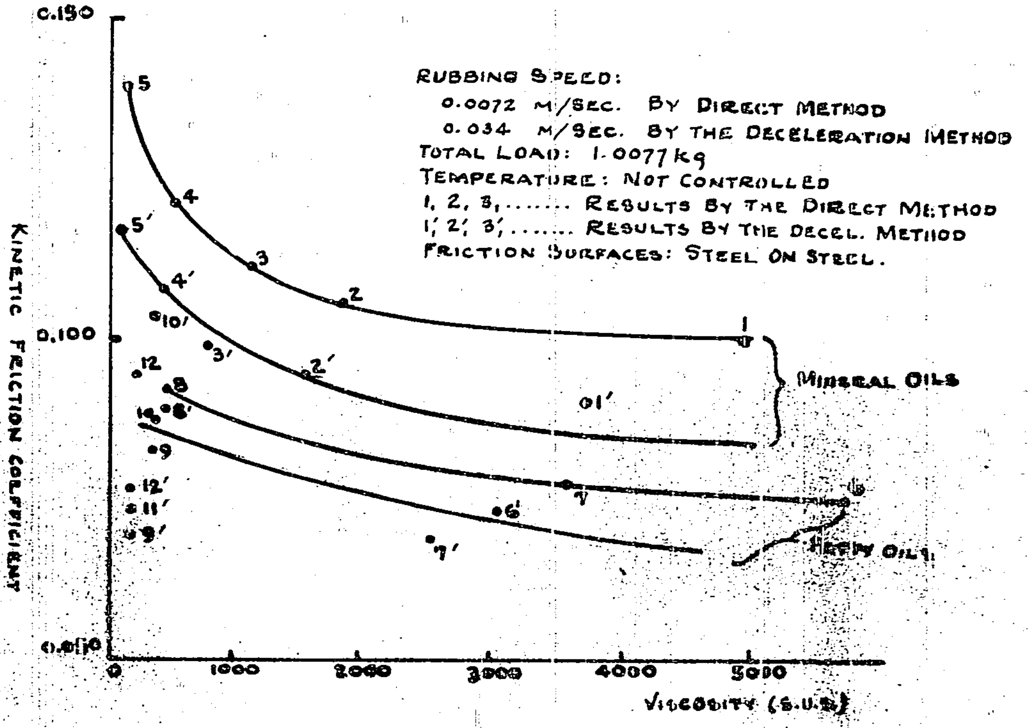


Figure 7(B)30
KINETIC FRICTION COEFFICIENT
BY 4-BALL TESTER A

ENCLOSURE (B)30

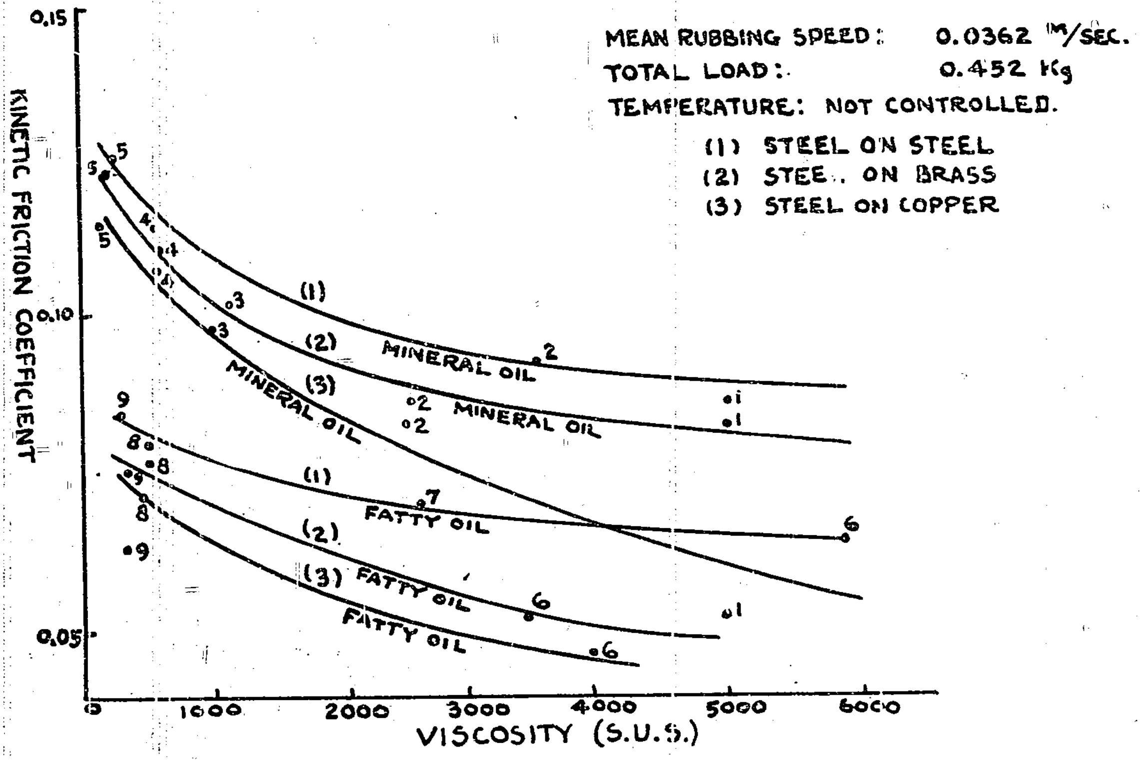


Figure 8(B)30
KINETIC FRICTION COEFFICIENT
BY PENDULUM TESTER

ENCLOSURE (B) 31

TO TEST THE LUBRICANTS UNDER EXTREME PRESSURE

by

CHEM. ENG. LIEUT. T. FUJIMOTO

Research Period: 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)31

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)31

SUMMARY

Lubricating oils were tested in a special machine under conditions comparable to those existing in the main bearings of an aeroplane engine. The test results were not usable and it would be necessary that some parts of this machine be reconstructed, particularly those parts which apply pressure to the bearing test pieces, and also means would have to be provided for preventing the hydraulic oil from mixing with the test oil.

I. INTRODUCTION

A. History of Project

This machine was brought to the OFUNA laboratory two years ago from YOKOSUKA, and remodeled here in June of 1944 and placed in operating condition in November, 1944. In January, 1945, this machine was used to test Texaxo Airplane 120# oil and was broken at that time. Since that time, every effort to repair the machine failed.

B. Key Research Personnel Working on Project

Eng. Lieut. T. FUJIMOTO

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

1. Application of the Load to the Test Pieces. The load is applied to the test pieces hydraulically, through a hole drilled in bearings such as shown in Figure 1(B)31.

2. The Measurement of the Torque. The torque of this machine is measured by magnetic striction using a coil, and tension wire which is attached just under the lower bearing.

The details of construction of the magnetic striction unit are not known and cannot be determined as the Electric Magnetic Company which constructed this apparatus was destroyed during the war.

Diameter of shaft is 1 cm., area of contact is 1 cm^2 (Figure 2(B)31)

B. Test Procedure

1. The Condition of Testing

Speed (maximum).................. 2800 RPM
Temp. of oil (Entry)................ 65 C
Pressure of supplying oil......... 5kg/cm^2
Ambient temperature.... room temperature

2. The Materials of the Test Pieces.

Shaft: Carbon Steel

Bearing: a. Carbon Steel
b. Cu-Pb Alloy (Dendritic)
c. White Metal (Not used)
d. Bronze (Not used)

ENCLOSURE (B)31

C. The Testing Method

1. The lubricating oil to be tested was circulated at the condition of no load.

2. The motor was driven slowly and gradually the speed was increased

3. The speed to be arrived at was 1000 RPM and the pressure was gradually applied, up to 100 kg/cm^2

4. In this condition, the speed was maintained about 3 hrs to wear the bearing.

5. After this, the motor was driven at various desired speeds, and pressure applied slowly.

6. The pyrometer (thermocouple) used to measure the temperature of the bearing at the point of shaft contact was carefully observed and the test was stopped when a temperature of 85° C was reached.

7. This load (pressure) which produced a temperature of 85°C was called the film strength of the oil.

8. Upon disassembly of the machine the faces of shaft and bearing were carefully inspected.

9. When the rubbing face was partially worn, the value of the unit loading was corrected accordingly by calculation.

D. Grinding of Test Pieces.

1. The shaft was ground by 0000 emery paper, and, after this, was finished, by Chrome Oxide Powder.

2. The bearing was not specially ground, but the test pieces were made very carefully.

E. Summary of Data

1. Conditions

Shaft...... Carbon Steel

Bearing .. Carbon Steel
Cu-Pb Alloy(pendritic)
Oil (tested) Texaco 120#
Maximum speed 2800 RPM

2. Data

a. Bearing: Carbon Steel. In these tests, the pressure on the test pieces was gradually increased, which caused the temperature of rubbing parts to increase gradually. As soon as the temperature reached as indicated by a pyrometer, 85°C, the test pieces generally welded to the shaft tightly.

At this time, the added (or applied) pressure calculated) was 500 kg/cm^2.

b. Bearing Cu-Pb Alloy. Next Cu-Pb alloy was used for the test pieces. At the beginning of the test, the temperature was

ENCLOSURE (B)31

gradually increased. However, the wear of the bearing was too fast to measure the film strength of the oil and the measurements were very difficult to obtain. Also the bearing surface wore badly.

Furthermore, since the upper half bearing was fixed, its wear made the centre of the shaft shift upward and become eccentric.

III. CONCLUSIONS

This testing machine was designed by Mr. FUKUSHIMA (Engineer of the First Naval Technical Depot and Eng. Lieut. Comdr. IIMURE (the Third Naval Fuel Depot). It is far from being practical, or dependable, the main defects of this machine are as follows:

1. Oil Pressure System for Loading. The mechanism of applying the oil pressure for loading is not tight, so that the hydraulic oil leaks and mixed with test oil.

2. The Vibration of Shaft. At the beginning of this test, it operated very smoothly, but afterward, as the wear of the bearing progressed, the shaft began to vibrate. The reason was that the lower bearing, and the centre of the shaft became out of alignment and vibration began.

3. Oil Supply. This test pieces have the supply hole at the centre of the groove, so, in this machine, this supports the highest load. Efforts to drill a hole at the oblique side, as shown in Figure(B)31, were unsuccessful. It is not believed that this machine is of suitable design.

ENCLOSURE (B)31

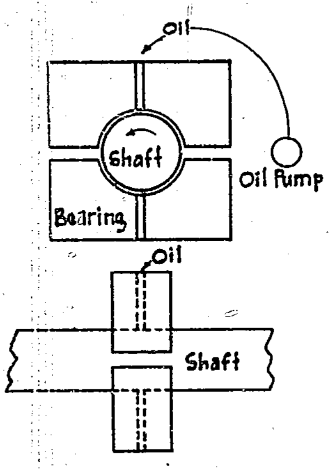


Figure 1(B)31
APPLICATION OF LOAD TO TEST PIECE

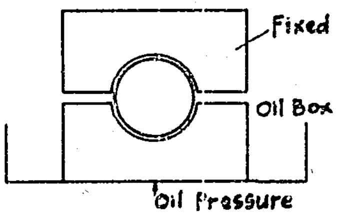


Figure 2(B)31
MEASUREMENT OF TORQUE

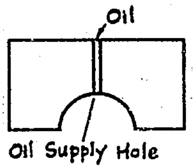


Figure 3(B)31
OIL SUPPLY
Vertical

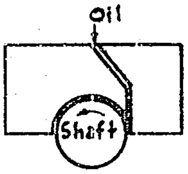


Figure 4(B)31
OIL SUPPLY
Oblique

ENCLOSURE (B)31

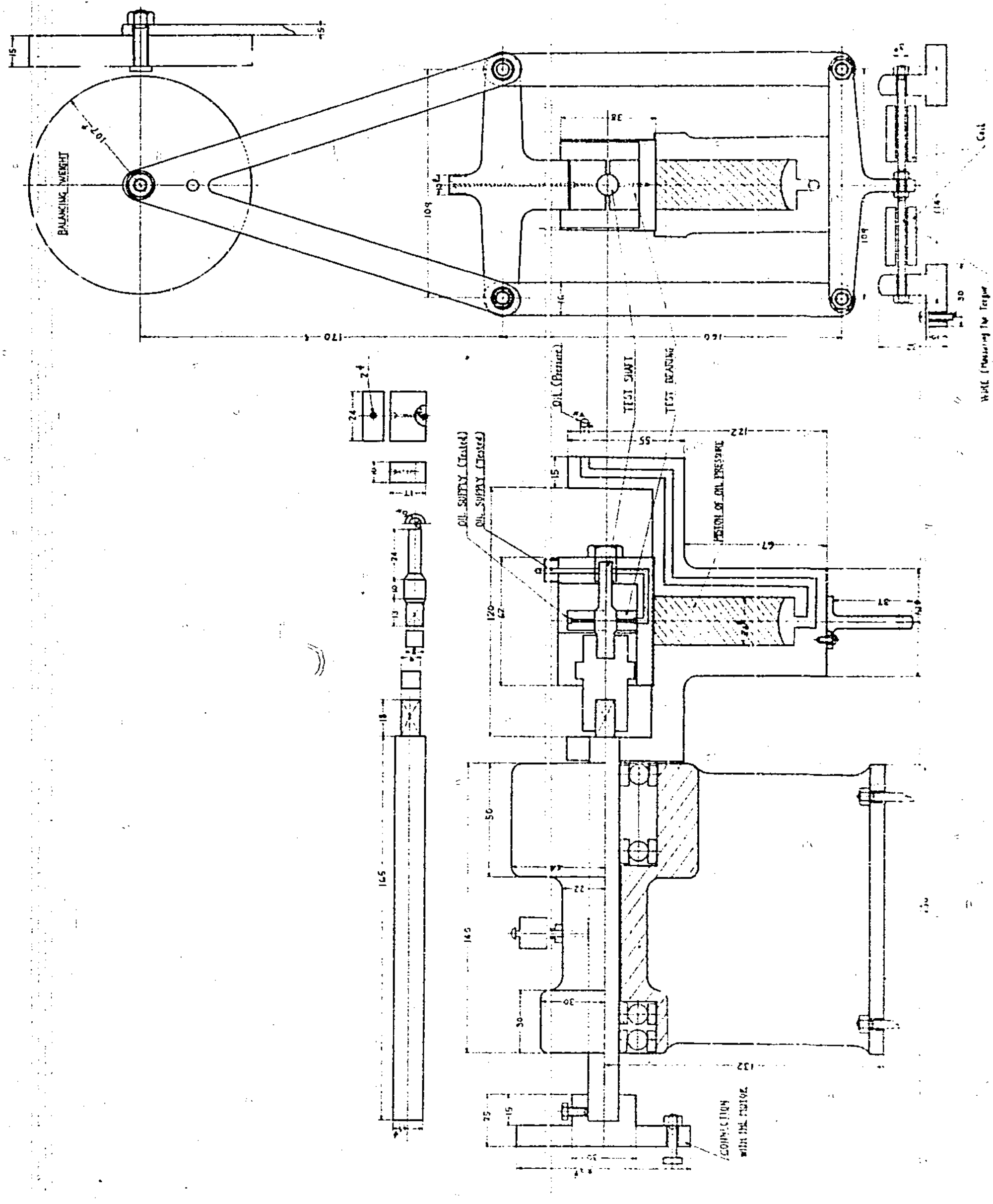


Figure 5(B)31
CROSS SECTION OF THE MAIN PARTS OF
EXTREME PRESSURE LUBRICANT TESTING MACHINE

ENCLOSURE (B)31

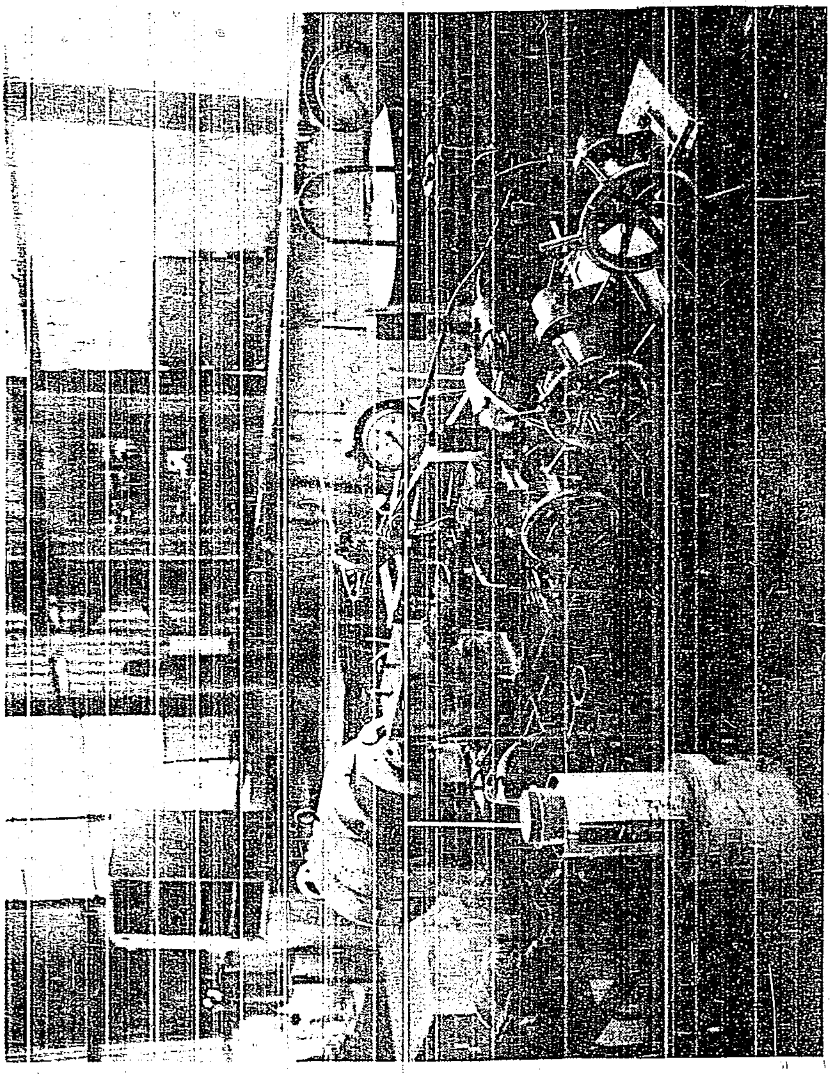


Figure 6(B)31
ALMEN'S EXTREME PRESSURE
LUBRICANT TESTING MACHINE

ENCLOSURE (B) 32

STUDIES ON ADDITIVES FOR SUBMARINE DIESEL ENGINE LUBRICANTS

by

CHEM. ENG. COMDR. DR. I. KAGEHIRA
CHEM. ENG. LIEUT. M. HIRATA

Research Period: 1942-1943

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)32

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)32

SUMMARY

With the object of determining suitable additives for submarine diesel engine oil, some compounds were studied from the standpoints of oiliness, stability, detergency and dispersion power for carbon deposits.

Some esters, soaps, and phosphorous compounds were selected for the test, and it was found that calcium phenyl stearate was the best additive from the standpoints of detergency and dispersion of carbon deposit, but lecithin and tricresyl phosphate were the most effective as the oiliness agents and the antioxidants.

I. INTRODUCTION

A turbine oil has been generally used for the submarine diesel engine lubricating oil in the Japanese Navy, but this was not satisfactory from the viewpoint of the cylinder wear. To avoid the wear of the engine cylinder which occurred in the above case, a viscous oil such as aeroengine oil #80 was used, but in this case hard carbon and lacquer were deposited, while the wear of the cylinder was decreased to about one fifth of that in the case of the turbine oil.

Such phenomena were, of course, due to the nature of the oil. Aeroengine oil #80 is a well-refined paraffinic oil which contains cylinder stock, and therefore the formation of carbon and lacquer would be greater. On the contrary, the turbine oil is made from a distillate of a naphthenic base oil by refining with sulfuric acid, and its lacquer and carbon formation would be lower. Consequently, it is desirable to find a suitable sludge disperser or carbon depressant for the aeroengine oil, and an oiliness agent for the turbine oil.

Several compounds were selected and the effectiveness of them was studied from April, 1942 to March, 1943.

II. DETAILED DESCRIPTION

A. Properties of the Base Oil and Additives and the Method of Preparation of the Latter

1. Base Oil. Aeroengine oil #80 having the following properties was used.

Density (d^{15}_4)	0.8809
Flash point (°C)	221.0
Viscosity, S.U.S. at 100°F	781.0
210°F	79.0
Viscosity index	99.1
Conradson's carbon residue (%)	0.47
Ash (%)	None
Pour point (°C)	16.0
Acid value	0.05
Saponification value	0.12
Stability---Vis. ratio	1.47
Conr. carbon res. after test	1.53

ENCLOSURE (B)32

2. Additives. Some esters, soaps and phosphorous compounds were selected for the test. The properties and the method of preparation of the additives are shown in Table I(B)32.

B. Test Procedure and Its Results

The kinetic and static coefficients of friction and stability of the samples were measured, and the most effective additives were examined for their detergency and dispersion of carbon.

1. Kinetic Friction Test

a. Test apparatus: Kinetic friction testing machine. The schematic view of the test apparatus is shown in Figure 1(B)32.

b. Test conditions:

Weight .... 2 kg at the line of contact.
Rubbing speed .... 0 - 0.35 m/sec.
Temperature (°C) .... 50, 100, 150, 200, 250.

c. Finishing method of the test piece and the test shaft: The test piece and the test shaft were polished with 04 emery paper and washed with well refined gasoline.

d. Results: One percentage of each additive was mixed with aeroengine oil #80 and the coefficient of kinetic friction was measured. The results are summarized in Table II(B)32, and graphically represented in Figures 2(B)32 to 12(B)32. From the results it was concluded that:

(1) Esters were the least effective
(2) Soaps were somewhat effective
(3) Phosphorous compounds were more effective, and among them, tricresyl phosphate and lecithin were the best.

The optimum addition percentages of calcium phenyl stearate, tricresyl phosphate and lecithin were checked and found that 1-1.5% for calcium phenyl stearate, 0.5-1% for tricresyl phosphate, and 0.2-0.5% for lecithin were desirable from the results shown in Table II(B)32 and Figure 13(B)32.

2. Static Friction Test

a. Test apparatus: The Deeley machine was used. The hardness of the test piece was 29 (Shore) and that of the test plate 66 (Shore). Both were made of steel.

b. Test apparatus: The surfaces of the test plate and the test piece were polished with 04 emery paper, and purified by means of electrolytic reduction. The test started 30 minutes after putting the oil sample under a load of 80 lbs/in^2 at 25 - 29°C.

c. Results: The static friction coefficient of 1% solution of each additive in aeroengine oil #80 was measured. From the results shown in Table III(B)32, it was concluded that:

(1) Lecithin was the most effective
(2) Soaps the next, and
(3) Phosphates, phosphites, esters were also somewhat effective.

3. Stability Test: The results of the British Air Ministry Oxidation Test shown in Table III(B)32, indicate that phosphorous compounds were good antioxidants, but soaps were not found desirable for actual use in the engine due to increase in viscosity ratio with oxidation.

4. Detergency Test: A piece of flannel was stained with soot and washed with gasoline only, or with gasoline containing 2% of each additive. Comparing these results, it was found that lecithin and calcium phenyl stearate improved the detergency of gasoline.

5. Dispersion Test: Oil sludge produced in stability tests was dispersed in a white mineral oil which also contained an additive. Increase of the transition of light in these oils was measured with a photometer, and it was found that calcium phenyl stearate improved the dispersion of sludge. The results are shown in Figure 14(B)32.

III. CONCLUSION

Calcium phenyl stearate is a suitable additive for the aeroengine oil #80 when it is used as a diesel engine lubricant. and the optimum addition quantity is 1 - 1.5%.

Lecithin and tricresyl phosphate are the suitable additives of turbine oil when it is used in diesel engines, and the optimum addition quantities are 0.2 - 0.5% for lecithin and 0.5 - 1% for tricresyl phosphate.

ENCLOSURE (B)32

Table I(B)32
PROPERTIES AND METHODS OF PREPARATION OF COMPOUNDS

Name	M.P (°C)	B.P. (°C)	Elemental Analysis		Method of Preparation
			C %	H %	
Methyl-phenyl stearate		250/2mm	obs. 79.79 cal. 79.12	obs. 11.15 cal. 11.06	Phenyl stearic acid was prepared through the condensation of oleic acid and benzene in the presence of anhydrous $AlCl_3$ as catalyst. It was then methylated and redistilled in vacuum.
Methyl dichlorostearate			obs. 60.65 cal. 62.13 cl% obs. 18.6	obs. 9.45 cal. 9.87 cal. 19.7	Marketed stearic acid was purified by means of recrystallization with 80% alcohol, and directly chlorinated with chlorine gas at 80°C, and then remaining chlorine and hydrogen chloride gas were removed by leading nitrogen gas through the medium. It was then methylated and washed with 2% sodium carbonate solution and water, and dried.
Calcium phenyl stearate					Prepared by means of double decomposition from 3% sodium phenyl stearate solution and 1% calcium chloride solution in water. The precipitated calcium phenyl stearate was purified by means of extraction with ether.
Calcium dichlorostearate					Prepared by analogous method to that mentioned above.
Triphenyl phosphite		220/1mm	obs. 68.49 cal. 69.68	obs. 4.64 cal. 4.87	Phenol and phosphorous trichloride were condensed directly, and distilled in vacuum.
Triphenyl phosphate	45-48		obs. 63.85 cal. 66.27	obs. 4.27 cal. 4.64	Marketed sample was recrystallized with alcohol.
Tricresyl phosphite		215-225/1mm	obs. 70.60 cal. 71.11	obs. 6.10 cal. 6.05	Marketed sample of ortho cresol was fractionated and a fraction taken boiling at 190-194°C. It was directly condensed with phosphorous trichloride at room temperature and distilled in vacuum.
Tricresyl phosphate		232-242/1mm	obs. 68.42 cal. 68.48	obs. 5.74 cal. 5.71	Purified cresol (ortho) was condensed with phosphorous oxychloride at 130°C using 2% by wt. of anhydrous $AlCl_3$ as catalyst. It was then washed with water and distilled in vacuum.
Lecithin					Pure soya bean lecithin prepared in Takeda Chemical Co. Ltd. was used.

Table II(B)32
COEFFICIENTS OF KINETIC FRICTION

		Aeroengine Oil #80 (Base Oil)					Base Oil plus 1% of Methylphenyl stearate					Base Oil plus 1% of Methyl dichlorostearate				
Temp. (°C)		50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)	0.35	0.010	0.025	0.070	0.083	0.086	0.013	0.044	0.066	0.081	0.083	0.010	0.030	0.063	0.071	0.082
	0.30	0.010	0.028	0.072	0.086	0.089	0.015	0.047	0.072	0.082	0.084	0.011	0.032	0.065	0.075	0.083
	0.25	0.010	0.031	0.075	0.087	0.090	0.017	0.052	0.078	0.083	0.087	0.013	0.038	0.067	0.078	0.084
	0.20	0.010	0.037	0.080	0.089	0.092	0.018	0.056	0.082	0.084	0.089	0.015	0.045	0.070	0.081	0.086
	0.15	0.012	0.043	0.085	0.091	0.094	0.020	0.065	0.084	0.085	0.091	0.022	0.052	0.078	0.082	0.088
	0.10	0.017	0.051	0.090	0.095	0.095	0.025	0.077	0.092	0.089	0.093	0.033	0.067	0.089	0.083	0.091
	0.05	0.033	0.070	0.105	0.100	0.097	0.049	0.095	0.010	0.095	0.095	0.065	0.087	0.110	0.093	0.095

		Base Oil plus 1.5% of Calcium phenyl stearate					Base Oil plus 1% of Calcium phenyl stearate					Base Oil plus 0.5% of Calcium phenyl stearate				
Temp. (°C)		50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)		0.011	0.030	0.059	0.075	0.075	0.007	0.025	0.063	0.069	0.075	0.008	0.028	0.069	0.082	0.085
		0.011	0.033	0.063	0.076	0.076	0.007	0.026	0.065	0.071	0.076	0.008	0.031	0.071	0.082	0.086
		0.011	0.037	0.068	0.077	0.077	0.008	0.032	0.068	0.083	0.077	0.008	0.036	0.075	0.084	0.086
		0.011	0.042	0.072	0.079	0.077	0.009	0.038	0.073	0.075	0.078	0.001	0.043	0.081	0.086	0.086
		0.012	0.050	0.074	0.081	0.077	0.011	0.046	0.076	0.077	0.079	0.011	0.053	0.087	0.086	0.086
		0.013	0.055	0.080	0.083	0.077	0.014	0.060	0.082	0.081	0.080	0.014	0.068	0.092	0.086	0.088
		0.030	0.073	0.088	0.086	0.077	0.020	0.075	0.087	0.086	0.083	0.038	0.087	0.098	0.088	0.090

		Base Oil plus 1% of Calcium dichlorostearate					Base Oil plus 1% of Triphenyl phosphite					Base Oil plus 1% of Tricresyl phosphite				
Temp. (°C)		50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)	0.35	0.009	0.014	0.047	0.074	0.075	0.007	0.008	0.042	0.066	0.065	0.007	0.016	0.038	0.057	0.067
	0.30	0.008	0.016	0.050	0.076	0.076	0.006	0.011	0.048	0.070	0.068	0.007	0.018	0.042	0.061	0.069
	0.25	0.008	0.022	0.057	0.078	0.077	0.005	0.015	0.057	0.075	0.071	0.006	0.020	0.047	0.064	0.072
	0.20	0.008	0.030	0.065	0.081	0.079	0.005	0.020	0.065	0.078	0.073	0.006	0.024	0.052	0.068	0.074
	0.15	0.009	0.040	0.074	0.084	0.080	0.004	0.030	0.073	0.082	0.076	0.006	0.031	0.050	0.074	0.078
	0.10	0.010	0.054	0.084	0.088	0.084	0.003	0.042	0.083	0.084	0.078	0.005	0.047	0.068	0.079	0.082
	0.05	0.022	0.071	0.097	0.094	0.085	0.007	0.067	0.097	0.088	0.085	0.005	0.070	0.078	0.084	0.090

Table II(B)32 (con't)
COEFFICIENTS OF KINETIC FRICTION

	Base Oil plus 1% of Triphenyl phosphate					Base Oil plus 1.5% of Triphenyl phosphate					Base Oil plus 1% of Tricresyl phosphate				
Temp. (°C)	50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)	0.009	0.011	0.044	0.052	0.052	0.010	0.019	0.042	0.055	0.050	0.009	0.011	0.044	0.052	0.052
	0.009	0.012	0.048	0.054	0.052	0.011	0.021	0.045	0.057	0.052	0.009	0.012	0.048	0.054	0.052
	0.009	0.014	0.052	0.058	0.054	0.011	0.024	0.049	0.061	0.053	0.009	0.014	0.052	0.058	0.054
	0.009	0.018	0.055	0.062	0.058	0.011	0.028	0.053	0.064	0.056	0.009	0.018	0.055	0.062	0.058
	0.008	0.026	0.060	0.066	0.060	0.011	0.035	0.055	0.066	0.058	0.008	0.026	0.060	0.066	0.060
	0.008	0.038	0.070	0.070	0.064	0.013	0.048	0.066	0.070	0.065	0.008	0.038	0.070	0.070	0.064
	0.020	0.057	0.082	0.076	0.074	0.025	0.062	0.079	0.080	0.074	0.020	0.057	0.082	0.076	0.074

		Base Oil plus 0.5% of Tricresyl phosphate					Base Oil plus 0.2% of Tricresyl phosphate					Base Oil plus 1% of Lecithin				
Temp. (°C)		50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)	0.35	0.012	0.025	0.044	0.052	0.061	0.010	0.021	0.066	0.066	0.063	0.020	0.016	0.043	0.064	0.068
	0.30	0.012	0.025	0.046	0.054	0.061	0.010	0.025	0.068	0.068	0.063	0.018	0.016	0.051	0.066	0.071
	0.25	0.012	0.028	0.048	0.056	0.062	0.010	0.031	0.070	0.070	0.067	0.017	0.018	0.059	0.071	0.073
	0.20	0.013	0.034	0.051	0.059	0.064	0.010	0.038	0.073	0.072	0.072	0.017	0.022	0.066	0.074	0.075
	0.15	0.016	0.040	0.056	0.064	0.068	0.012	0.052	0.078	0.075	0.072	0.016	0.027	0.076	0.078	0.078
	0.10	0.024	0.047	0.065	0.069	0.073	0.016	0.063	0.084	0.078	0.073	0.016	0.042	0.084	0.082	0.081
	0.05	0.044	0.067	0.074	0.076	0.080	0.013	0.077	0.097	0.082	0.076	0.020	0.063	0.096	0.086	0.085

	Base Oil plus 0.5% of Lecithin					Base Oil plus 0.2% of Lecithin				
Temp. (°C)	50	100	150	200	250	50	100	150	200	250
Rubbing Speed (m/sec)	0.009	0.022	0.030	0.042	0.052	0.010	0.030	0.054	0.055	0.068
	0.009	0.024	0.030	0.043	0.052	0.010	0.032	0.055	0.056	0.068
	0.009	0.027	0.033	0.047	0.053	0.009	0.035	0.058	0.057	0.069
	0.009	0.031	0.036	0.050	0.055	0.010	0.038	0.062	0.063	0.070
	0.009	0.035	0.036	0.052	0.058	0.012	0.043	0.068	0.063	0.071
	0.012	0.042	0.039	0.054	0.061	0.020	0.054	0.074	0.065	0.072
	0.019	0.055	0.052	0.064	0.063	0.039	0.070	0.083	0.070	0.073

Table III(B)32
RESULTS OF BRITISH AIR MINISTRY OXIDATION TEST
AND STATIC COEFFICIENT OF FRICTION BY DEELEY MACHINE

Sample	Brit. Air Ministry Oxid. Test		Static Coef. of
	Vis. Ratio	Conr. C. Residue *	Friction (Deeley) **
Base oil: Aeroengine oil #80	1.50	1.70	0.147
Base plus 1% Methyl dichlorostearate	1.43	1.29	0.128
Base plus 1% Methyl phenyl stearate	1.45	1.34	0.128
Base plus 1% Calcium dichlorostearate	2.10	2.13	0.111
Base plus 1% Calcium phenyl stearate	2.20	2.24	0.109
Base plus 1% Triphenyl phosphate	1.39	1.25	0.116
Base plus 1% Tricresyl phosphate	1.40	1.41	0.124
Base plus 1% Triphenyl phosphite	1.28	1.27	0.126
Base plus 1% Tricresyl phosphite	1.25	1.25	0.144
Base plus 1% Lecithin	1.29	1.27	0.097

* Results after oxidation   ** Friction surfaces: Steel on steel   Load: 80 lb/in^2 Temp.: 25-29

ENCLOSURE (B)32

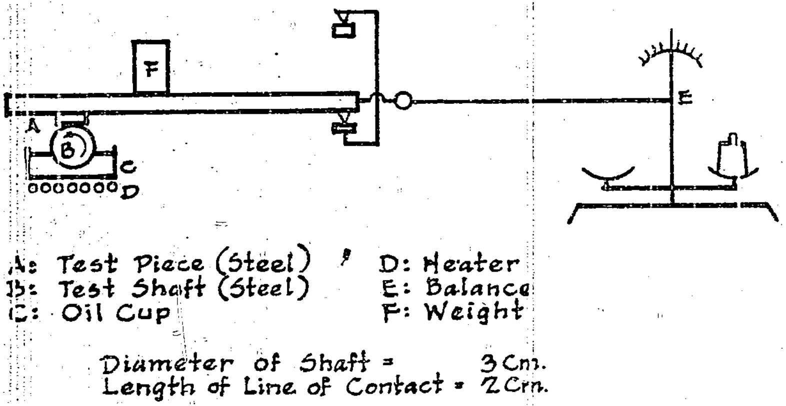


Figure 1(B)32

KINETIC FRICTION TESTING MACHINE

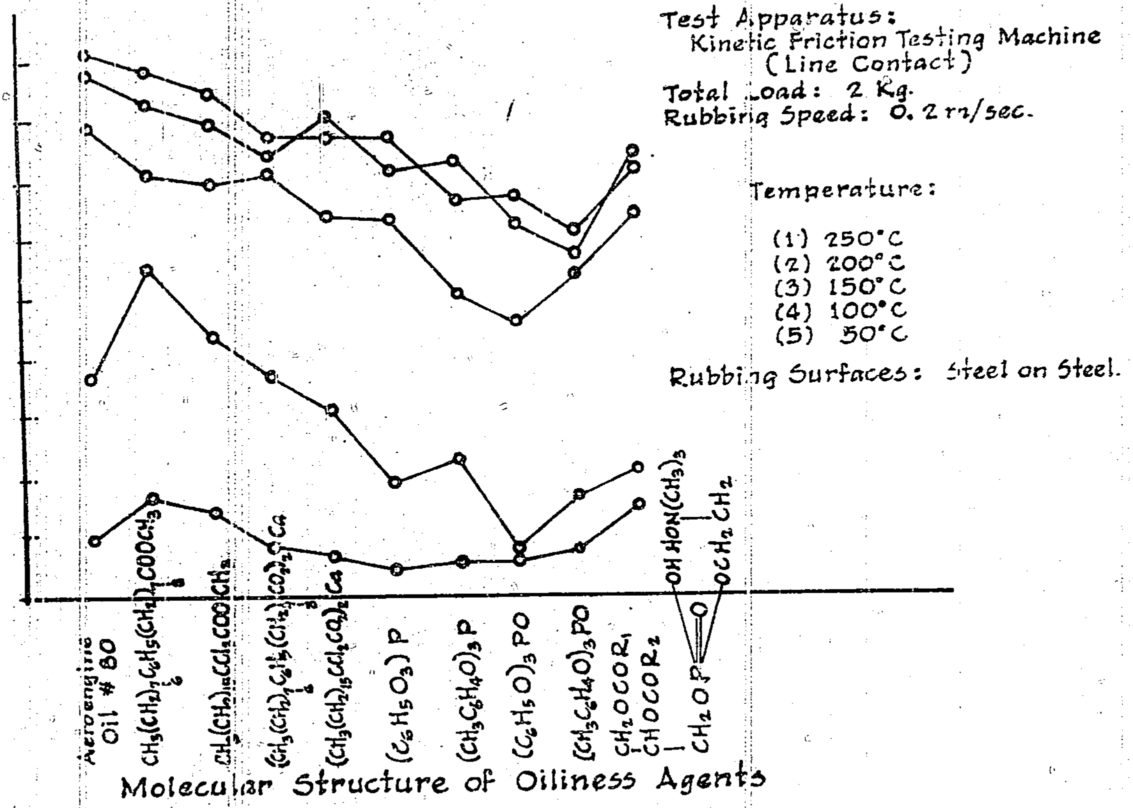


Figure 2(B)32

KINETIC COEFFICIENTS OF FRICTION OF STRAIGHT AEROENGINE OIL *80 AND THAT WHICH CONTAINS 1% WT. OF VARIOUS CILINESS AGENTS

ENCLOSURE (B)32

TEST APPARATUS

KINETIC FRICTION TESTING MACHINE (LINE CONTACT)

FRICTION SURFACES: STEEL ON STEEL

TOTAL LOAD: 2 KG.

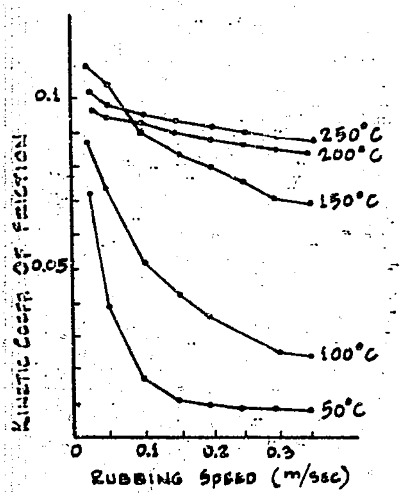


Figure 3(B)32
AEROENGINE OIL #80

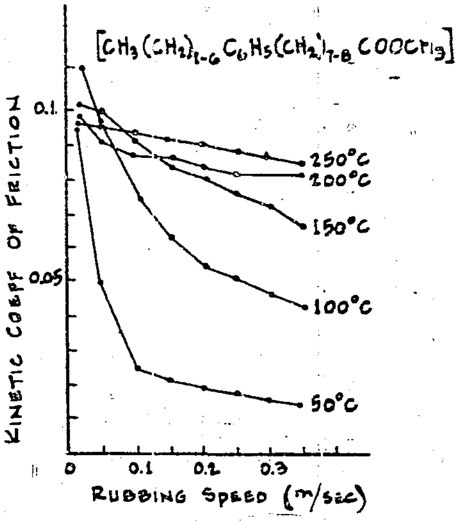


Figure 4(B)32
AEROENGINE OIL #80
METHYL PHENYL STEARATE

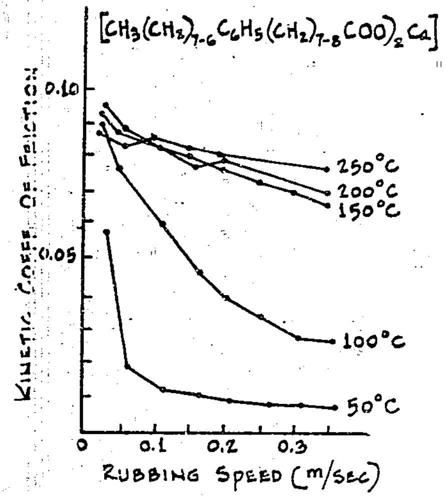


Figure 5(B)32
AEROENGINE OIL #80
METHYL DICHLOROSTEARATE

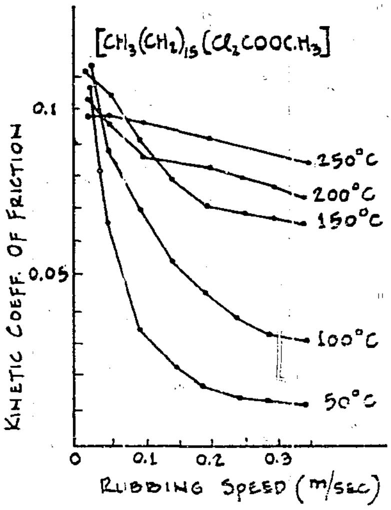


Figure 6(B)32
AEROENGINE OIL #80
CALCIUM PHENYL STEARATE

ENCLOSURE (B)32

TEST APPARATUS

KINETIC FRICTION TESTING MACHINE (LINE CONTACT)
FRICTION SURFACES: STEEL ON STEEL
TOTAL LOAD: 2 KG.

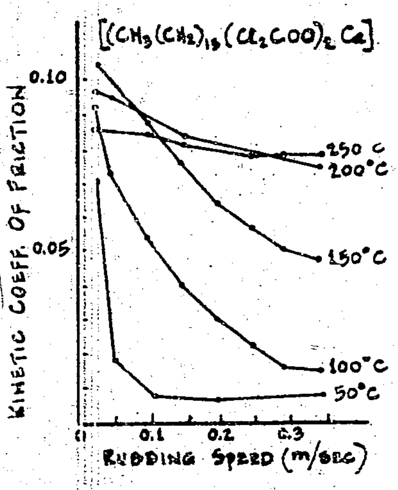


Figure 7(B)32
AEROENGINE OIL #80
CALCIUM DICHLOROSTEARATE

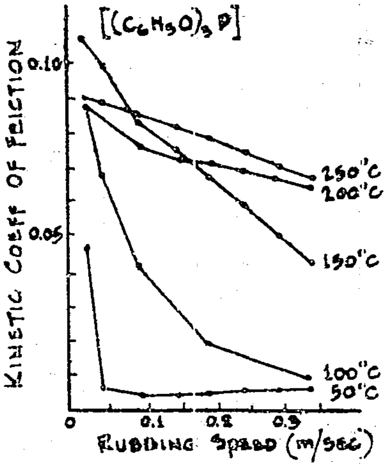


Figure 8(B)32
AEROENGINE OIL #80
TRIPHENYL PHOSPHITE

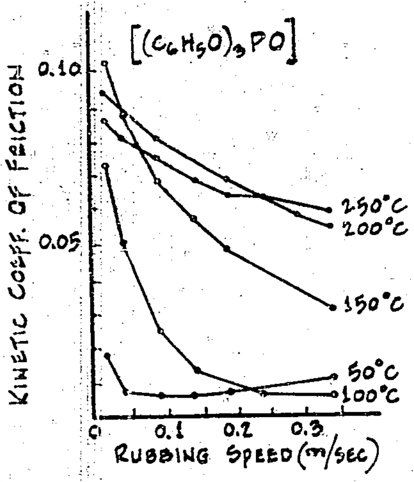


Figure 9(B)32
AEROENGINE OIL #80
TRIPHENYL PHOSPHATE

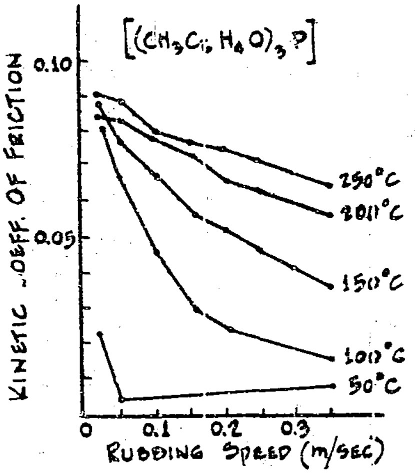


Figure 10(B)32
AEROENGINE OIL #80
TRICRESYL PHOSPHITE

ENCLOSURE (B)32

TEST APPARATUS

KINETIC FRICTION TESTING MACHINE (LINE CONTACT)

FRICTION SURFACES: STEEL ON STEEL

TOTAL LOAD: 2 KG.

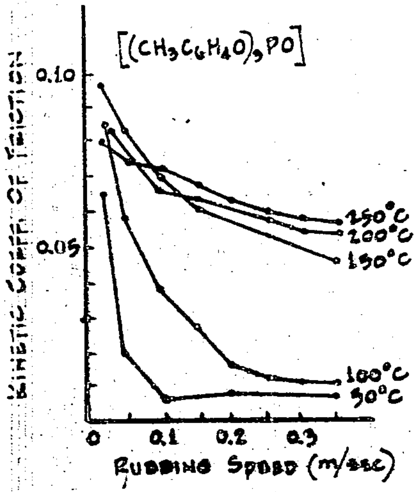


Figure 11(B)32

AEROENGINE OIL #80

TRICRESYL PHOSPHATE

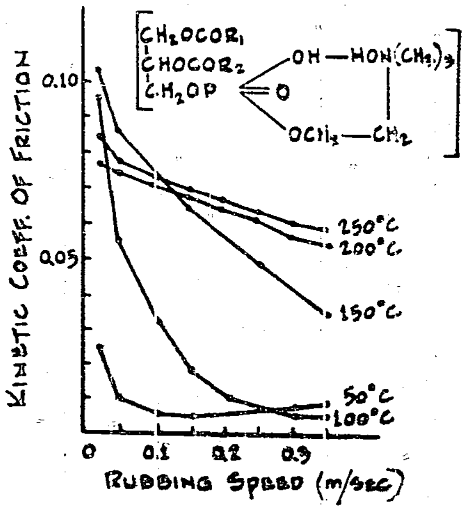


Figure 12(B)32

AEROENGINE OIL #80

LECITHIN

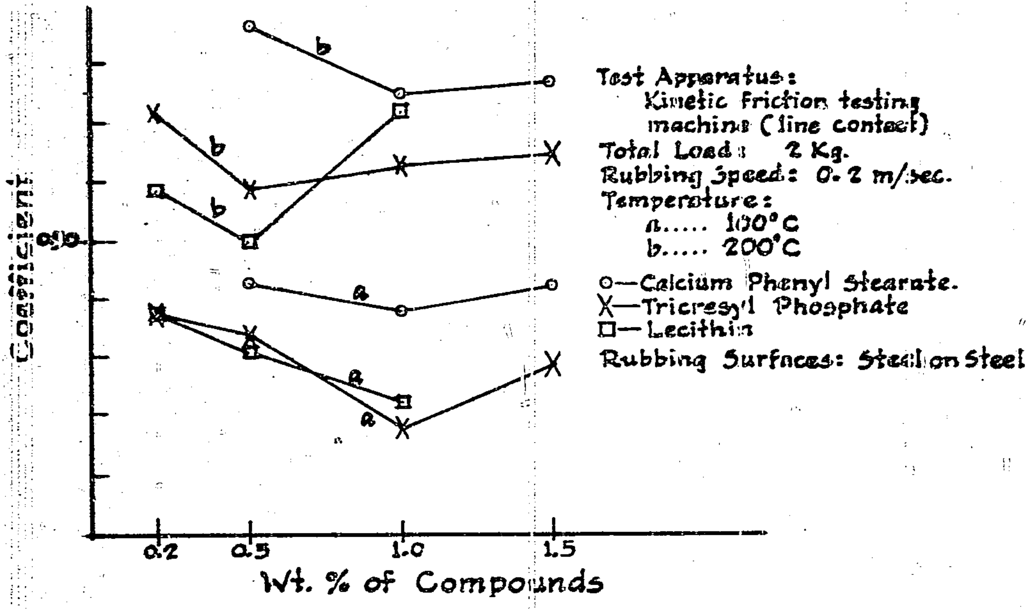


Figure 13(B)32

KINETIC COEFFICIENTS OF FRICTION OF AEROENGINE OIL #80 CONTAINING DIFFERENT WT.% OF OILINESS AGENTS

ENCLOSURE (B)32

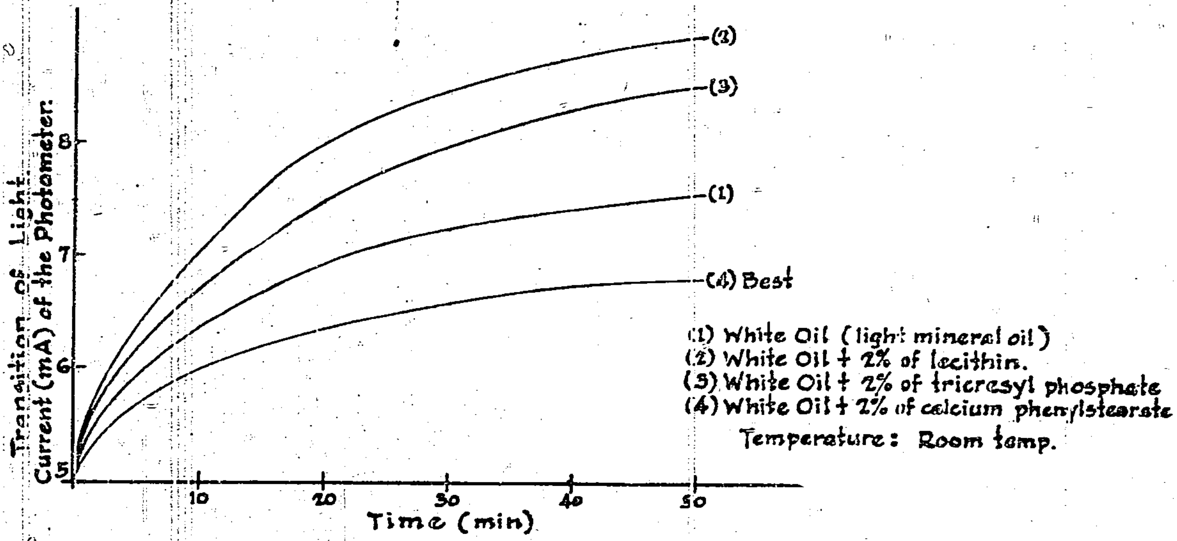


Figure 14(B)32
SEDIMENTATION VELOCITY OF SLUDGE IN OILS

ENCLOSURE (B) 33

STUDIES ON A VISCOSITY INDEX IMPROVER

by

CHEM. ENG. CAPT. DR. I. KAGEHIRA
CHEM. ENG. LT. COMDR. A. WAKANA
NAVAL ENG. I. FUJII

Research Period: 1942-1943

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)33

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)33

SUMMARY

Isobutylene, obtained by the dehydration of isobutyl alcohol at 400°C in the presence of alumina, was liquefied and diluted with gasoline and then was polymerized at (-)40°C with aluminum chloride. Topping this polymerized oil up to 250°C at 5mm of vacuum, the residual oil was obtained in 43% yield (by weight) based on isobutyl alcohol. By adding 13% of the above-mentioned residual oil to Texaco aero engine oil #80, the viscosity at 210°F was raised from 77 to 121 S.U.S. and the viscosity index was raised from 94 to 101.

This blended oil was tested twice, using the Ricardo type single-cylinder engine. One test was for 30 hours and the other for 19 hours, and it was observed that the blended oil was somewhat more subject to decomposition and gave greater wear of piston rings than the aero engine oils then in practical use.

I. INTRODUCTION

A. History of Project

The aero engine oil had been produced from Midcontinent crude oil by the solvent extraction method at the Third Naval Fuel Depot, and its yield was restricted mainly by the minimum viscosity index requirement of 90.

In April 1942, it was reported that a compound named "Exanol" was marketed as a viscosity index improver by the Standard Oil Co. In order to test the practical application of these compounds, the isobutylene polymer was prepared and blended with the Texaco aero engine oil #80 and tested by the Ricardo type single-cylinder engine in January 1943.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr. A. WAKANA
Naval Eng. I. FUJII

II. DETAILED DESCRIPTION

A. Test Procedures and Conditions

1. Preparation of the Isobutylene Polymer. Isobutylene, which was obtained from the dehydration of isobutyl alcohol at 400°C in the presence of alumina, was liquefied and diluted with gasoline which had been previously treated with aluminum chloride. The isobutylene was then polymerized at (-) 40°C with aluminum chloride in the usual manner reported in the published literature. The polymerization product was washed with water, and the gasoline and lighter fractions up to 250°C at 5mm Hg were distilled. The residual oil was pale yellow in color and sticky. The yield of the residual oil was 43% by weight based on isobutyl alcohol.

2. Engine Test. Blending 13 parts of this polymer to 100 parts of aero engine oil #80, the viscosity of the oil was raised from 77 S.U.S. to 121 S.U.S. at 210°F and the viscosity index was raised from 94 to 101. This oil was tested using the Ricardo single-cylinder engine, first for 30 hours and then for 19 hours, and these results were compared with the results obtained from the aero engine oil in actual use. Operating conditions are shown in Table I(B)33.

ENCLOSURE (B)33

B. Summary of Data

1. Properties of the oils used in the engine tests are shown in Table II(B)33.

2. Operating Conditions. As shown in Figures 1(B)33 and 2(B)33, no abnormalities were found.

3. Engine Inspection. After running, the engine inspection showed that from the standpoint of cleanliness the aero engine oil in actual use was the best, the Texaco aero engine oil #80 was next, and the blended oil was third.

4. Change in Lubricating Oils During Use. Alteration of the lubricating oils during use is shown in Table III(B)33 and IV(B)33. At five hour intervals, 500cc of the oil were removed and its properties were determined. The increase of acid value and the sludge was perceptible.

5. Wear of Piston Rings. As shown in Tables V(B)33 and VI(B)33, the piston wear with the blended oil was somewhat larger than with the aero engine oil in actual use.

III. CONCLUSIONS

It was possible to produce the aero engine oil, by adding the isobutylene polymer to the lower viscosity oil, but it will be necessary to improve its heat stability before it can be used in aircraft engines.

ENCLOSURE (B)33

Table I(B)33
TEST CONDITIONS IN THE RICARDO SINGLE-CYLINDER ENGINE

	Test No.	
	1	2
Duration of Test (hrs)	30	19
Engine Speeds (RPM)	1500	1600
Compression Ratio	4.5	5.4
Oil Temperature at Inlet (°C)	70	90
Cooling Water Temperature at Outlet (°C)	60	60-80
Air Temperature (°C)	50	30
Fuel	87 gas	92 gas
Initial Oil Charge (kg)	27*	27*

*No supply during the test.

Table II(B)33
PROPERTIES OF THE OILS USED IN ENGINE TESTS

	Specific Gravity (d^{15}_{4})	Flash Point (°C)	Conradson Carbon (%)	Viscosity S.U.S.		Viscosity Index	Acid Value	Saponification Value
				100°F	210°F			
Aero Engine Oil in Actual Use*	0.8958	261	0.7	1778	122	95	0.1	0.7
Texaco Aero-Engine Oil #80	0.8865	226	0.4	708	77	94	0.04	0.2
Above Plus Isobutylene Polymer	0.8869	220	0.4	1620	121	101	0.1	0.1

*Prepared by solvent extraction from Osage crude oil at the Third Naval Fuel Depot.

ENCLOSURE (B)33

Table III(B)33
CHANGE IN PROPERTIES OF LUBRICATING OIL DURING USE TEST

Properties	Sample	0 hr	5 hrs	10 hrs	15 hrs	20 hrs	25 hrs	30 hrs
Specific Gravity (d^{15}_4)	A	0.8958	0.8954	0.8956	0.8957	0.8960	0.8965	0.8963
	B	0.8869	0.8870	0.8877	0.8879	0.8888	0.8897	0.8908
Flash Point (°C)	A	261	156	155	151	147	141	138
	B	220	147	151	139	147	142	143
Viscosity at 210°F (S.U.S.)	A	122	121	122	124	123	123	125
	B	121	119	122	119	121	122	123
Conradson Carbon (%)	A	0.7	0.9	0.9	1.0	1.0	1.0	1.1
	B	0.5	0.5	0.6	0.6	0.6	0.7	0.7
Volatility Test (%)	A	0.007	0.2	0.2	0.3	0.3	0.3	0.3
	B	0.105	0.3	0.3	0.3	0.4	0.5	0.4
Acid Value	A	0.1	0.2	0.2	0.3	0.3	0.3	0.3
	B	0.1	0.1	0.2	0.2	0.4	0.5	0.9
Sludge (%)	A	0	0.2	0.2	0.2	0.2	0.2	0.3
	B	0	0.2	0.4	0.4	0.4	0.5	0.6

A: Aero engine oil, in actual use B: Blended oil

Table IV(B)33
CHANGE IN LUBRICATING OILS DURING USE 2ND TEST

	Aero Engine Oil in Actual Use		Oil Blended	
	Before Test	After Test	Before Test	After Test
Specific Gravity (d^{15}_4)	0.8958	0.8968	0.8869	0.8382
Flashing Temperature (°C)	261	218	220	217
Viscosity at 210°F (S.U.S.)	122	126	121	129
Viscosity Index	95	100	101	106
Conradson Carbon (%)	0.7	0.8	0.5	0.6
Sludge (%)	0	0.8	0	0.9
Acid Value	0.1	0.2	0.1	0.2
Saponification Value	0.7	1.6	0.1	1.7

Table V(B)33
WEAR IN WIDTH OF PISTON RINGS AT 1ST RUNNING (mm)

		Aero Engine Oil in Actual Use						Aero Engine Oil Prepared by the Addition of Isobutylene Polymer to the Texaco Aero Engine Oil #80					
Ring No.	Position	Before Running		After Running		Wear in Width	Mean	Before Running		After Running		Wear in Width	Mean
1	A	3.501	3.500	3.495	3.497	0.0045	0.0039	3.495	3.497	3.488	3.490	0.007	0.0048
	B	3.540	3.540	3.542	3.537	0.0015		3.542	3.537	3.543	3.533	0.006	
	C	3.501	3.500	3.493	3.501	0.0035		3.493	3.501	3.493	3.487	0.007	
	D	3.415	3.410	3.410	3.405	0.0050		3.410	3.405	3.408	3.410	0.0015	
	E	3.450	3.448	3.445	3.443	0.0050		3.445	3.443	3.443	3.440	0.0025	
2	A	3.445	3.453	3.451	3.440	0.0035	0.0038	3.451	3.440	3.436	3.439	0.008	0.0072
	B	3.500	3.500	3.492	3.495	0.0065		3.492	3.495	3.440	3.494	0.020	
	C	3.510	3.510	3.510	3.506	0.0020		3.510	3.506	3.506	3.505	0.0025	
	D	3.503	3.500	3.500	3.500	0.0015		3.500	3.502	3.498	3.795	0.0045	
	E	3.460	3.445	3.450	3.452	0.0065		3.450	3.452	3.451	3.450	0.0010	
3	A	3.476	3.472	3.470	3.474	0.0020	0.0036	3.470	3.474	3.465	3.468	0.0055	0.0045
	B	3.539	3.535	3.531	3.531	0.0060		3.531	3.531	3.529	3.527	0.0030	
	C	3.505	3.515	3.530	3.515	0.0020		3.503	3.515	3.510	3.511	0.0020	
	D	3.413	3.405	3.397	3.410	0.0050		3.397	3.410	3.394	3.399	0.0070	
	E	3.450	3.446	3.440	3.455	0.0030		3.455	3.440	3.440	3.445	0.0050	

WEAR OF RING
MEASURING POSITION
OF PISTON WEAR

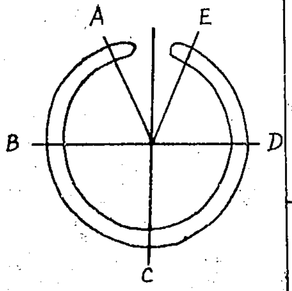


Table VI(B)33
WEAR IN WIDTH OF PISTON RINGS AT 2ND RUNNING (mm)

		Aero Engine Oil in Actual Use						Aero Engine Oil Prepared by the Addition of Isobutylene Polymer to the Texaco Aero Engine Oil #80					
Ring No.	Position	Before Running		After Running		Wear in Width	Mean	Before Running		After Running		Wear in Width	Mean
1	A	3.492	3.492	3.490	3.490	0.002	0.0019						
	B	3.460	3.460	3.457	3.453	0.005							
	C	3.490	3.489	3.489	3.450	0							
	D	3.440	3.438	3.439	3.439	0.0015							
	E	3.466	3.460	3.463	3.461	0.001							
2	A	3.462	3.469	3.460	3.460	0.001	0.001	3.460	3.460	3.452	3.450	0.009	0.0076
	B	3.415	3.413	3.410	3.410	0.004		3.410	3.410	3.403	3.405	0.006	
	C	3.461	3.478	3.478	3.481	0		3.478	3.478	3.480	3.475	0.0015	
	D	3.530	3.529	3.530	3.529	0		3.530	3.529	3.519	3.516	0.012	
	E	3.491	3.490	3.491	3.490	0		3.491	3.490	3.483	3.480	0.009	
3	A	3.499	3.450	3.499	3.499	0.0005	0.0022	3.501	3.499	3.501	3.494	0.0025	0.0107
	B	3.445	3.447	3.439	3.440	0.0065		3.439	3.440	3.434	3.435	0.005	
	C	3.479	3.480	3.479	3.479	0.0005		3.479	3.479	3.460	3.457	0.0205	
	D	3.506	3.509	3.505	3.508	0.0005		3.505	3.508	3.491	3.487	0.0175	
	E	3.536	3.524	3.518	3.520	0.003		3.518	3.520	3.510	3.512	0.008	

ENCLOSURE (B)33

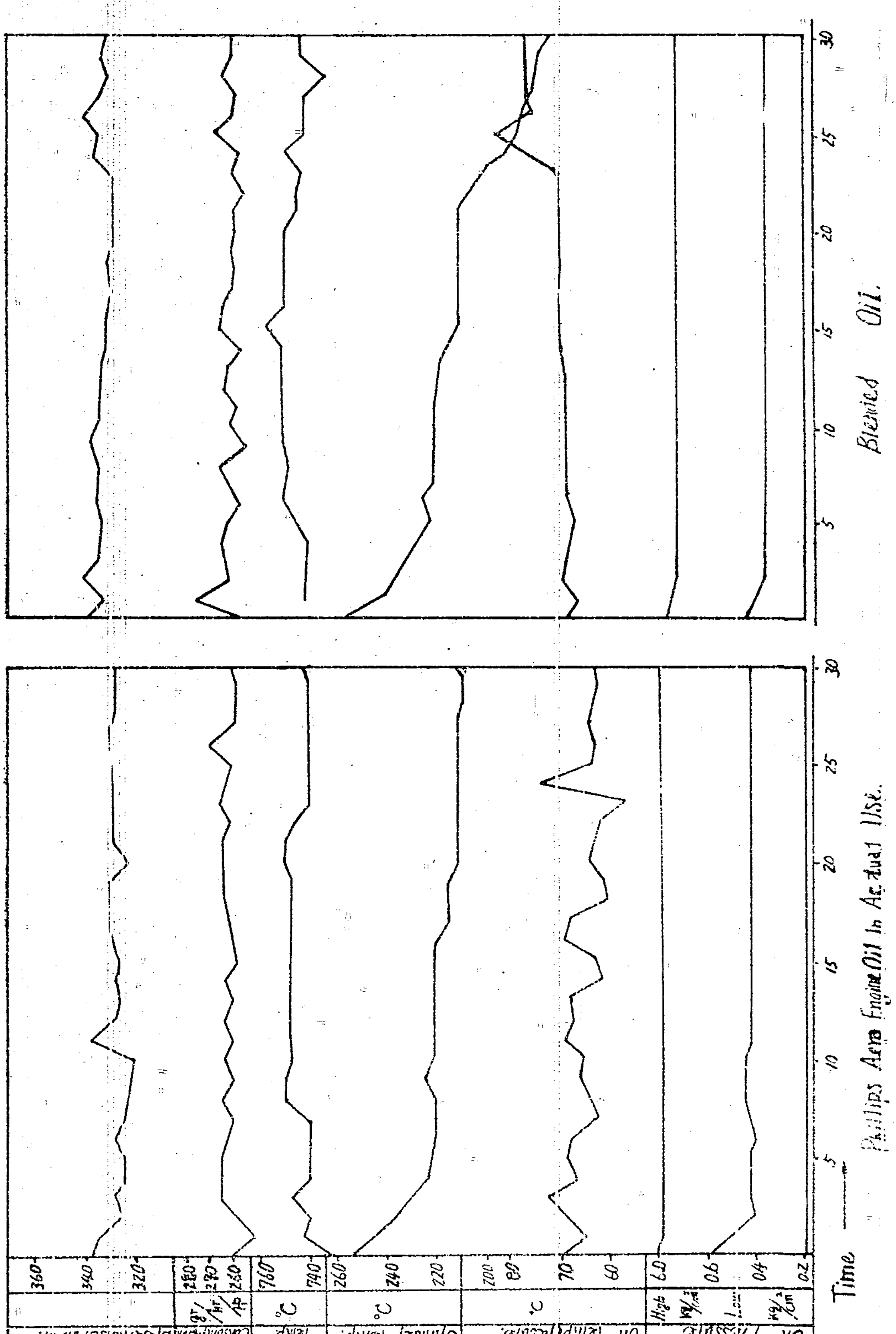
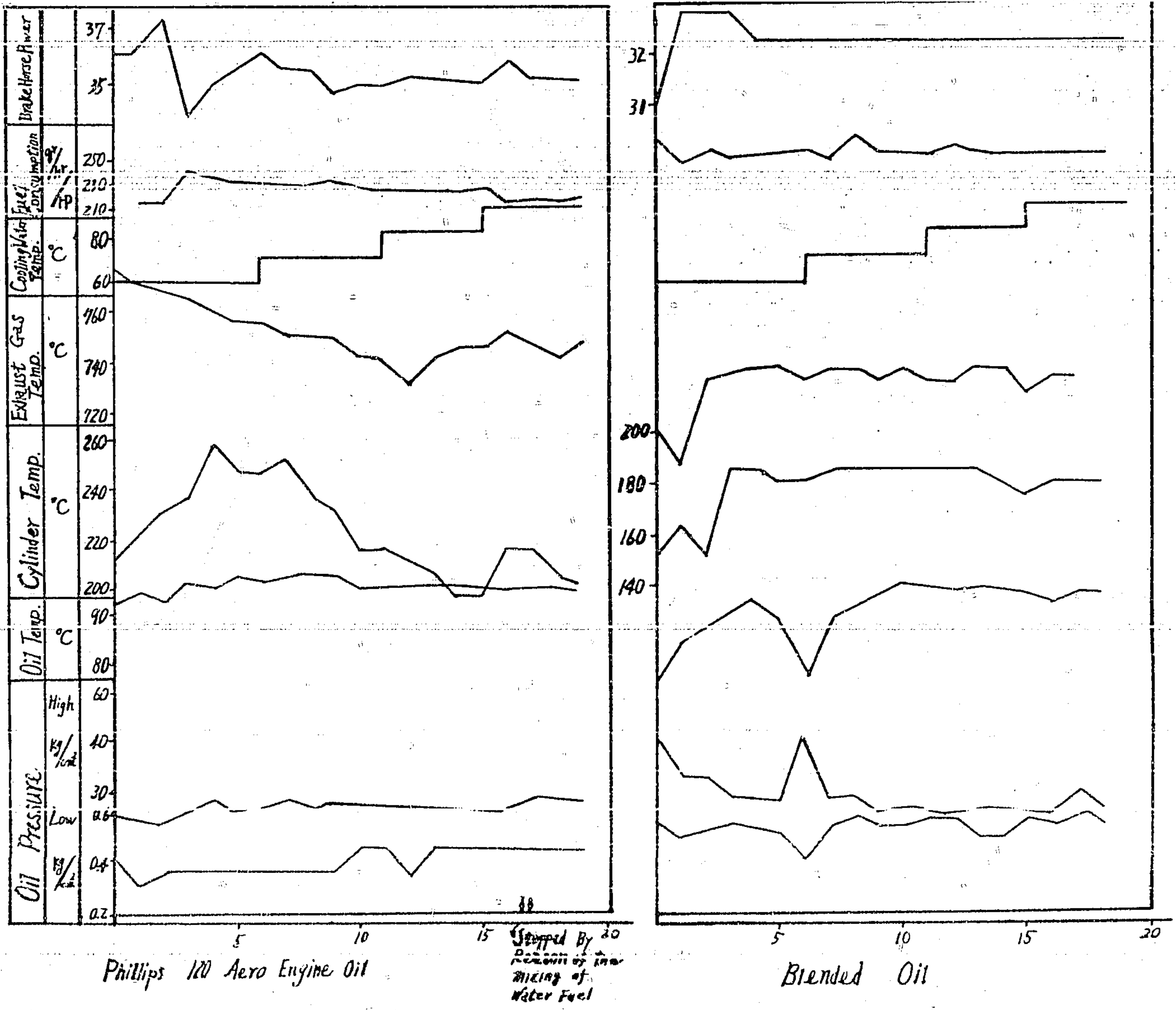


Figure 1(B)33
STATE OF FIRST RUNNING



Stopped By Reason of the Mixing of Water Fuel

Figure 2(B)33
STATE OF SECOND RUNNING

ENCLOSURE (B) 34

STUDIES ON HIGH FREQUENCY INSULATING MATERIALS

by

ENG. LT. COMDR. A. WAKANA

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)34

SUMMARY

In order to obtain isobutylene polymers as insulating materials, studies on the polymerization of isobutylene at low temperature in the presence of aluminum chloride were carried out. Isobutylene was prepared by the dehydration of tertiary butyl alcohol in the presence of anhydrous oxalic acid followed by precise distillation. Liquefied isobutylene was polymerized in liquid ethylene at (-)150°C in the presence of an ethylchloride solution of aluminum chloride and a vigorous reaction took place immediately, forming a polymer of 170,000 average molecular weight.

I. INTRODUCTION

A. History of Project

In April 1944, polyisobutylene for use as a high frequency insulating material was requested by the Second Naval Technical Depot.

According to the published literature the author studied the polymerization of isobutylene at (-)150°C in the presence of an ethyl chloride solution of aluminum chloride was carried out and a polymer, having an average molecular weight of about 170,000 was obtained in September 1944.

B. Key Personnel Working on Project

Eng. Lt. Comdr. A. WAKANA
Eng. Lieut. N. KOTAKE
H. OKA

II. DETAILED DESCRIPTION

An attempt was made to prepare an isobutylene polymer at low temperature in accordance with U. S. Patents. In the patent, BF_3 had been used mainly, but in our experiments aluminum chloride was used, since the supply of BF_3 was scarce in Japan. As a diluent, liquid ethylene was used to avoid the rapid rise in temperature due to the violent polymerization of isobutylene, and aluminum chloride was dissolved in ethyl chloride in order to make the reaction uniform and as a protection from the humidity. Isobutylene was prepared by the dehydration of tertiary butyl alcohol in the presence of anhydrous oxalic acid. After redistilling by the Podbielniak distillation apparatus, the isobutylene was stored in a 20 liter glass bottle. Ethylene was prepared by the dehydration of ethyl alcohol in the presence of an alumina catalyst and stored in a pressure bomb. Ethyl chloride was obtained in the market. A 30 gram sample of isobutylene was taken in a 1000cc beaker and diluted with 35 grams of liquid ethylene and cooled to (-)170°C with liquid air. Ethyl chloride solution (50cc) containing 1.5% $AlCl_3$ was diluted with 39 grams of liquid ethylene and cooled to (-)140°C. The solution of catalyst was poured into the isobutylene solution. At (-)165°C, reaction did not occur so the beaker was removed from the liquid air vessel, and at -145°C reaction took place. The solution was agitated with a resistance thermometer and at -100°C, a small quantity of ethyl alcohol was added and reaction was stopped. The white spongy material, (26 grams), which was floating on the surface was gathered and was dissolved in toluene. After purification by a precipitation method, the product was obtained. The average molecular weight was determined to be 170,000 by the viscosity method in normal heptane solution.

At the reaction temperature of (-)170°C, cooled by solid carbon dioxide, a polymer of 12,000 molecular weight was prepared, and at (-)100°C, cooled by

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liquid ethylene, a polymer of 31,000 molecular weight was prepared.

When isobutylene, prepared from the dehydration of isobutyl alcohol by alumina catalyst at 350°C, was used as a starting material, a polymer of 80,000 molecular weight was obtained.

It was possible to obtain a high isobutylene polymer of 170,000 molecular weight, using aluminum chloride as a catalyst.

In order to develop to a commercial scale, further experiments would be necessary in order to find economical methods.

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STUDIES ON POUR POINT DEPRESSANTS FOR LUBRICATING OILS

by

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Research Period: 1943-1944

Prepared for and Reviewed with Authors by
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ENCLOSURE (B)35

LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Turbine oil, obtained from Oha crude oil, contains about 5% wax and has pour points ranging from (+)5 to 15°C.

To depress pour points below 0°C without dewaxing the use of "Paraflow," the best known commercial pour point depressant, was tried. When added to the oil in small quantities such as 0.1 to 0.5%, these compounds effectively depressed the pour point without unfavorable effect on other properties of oil. The synthesis of "Paraflow" was studied and a most effective product was obtained by condensing naphthalene and chlorinated wax at 50-100°C in the presence of 5% of anhydrous aluminum chloride for 3 hours. It was found necessary to control the reaction by the addition of small quantities of water. The need for water was accidentally discovered, and was not mentioned in the U.S. Patent on "Paraflow."

I. INTRODUCTION

A. History of Project

Some of the turbine oils used by the Japanese Navy in 1941 were prepared from Oha crude oil. Oha crude oil had been thought to be a naphthenic base crude, but it sometimes contained a small amount of wax, and the turbine oils prepared from it had high pour points. To conform to the specifications for turbine oil, the pour point had to be below 0°C. The capacities of the dewaxing plants in Japanese refineries were too small to dewax turbine oil, since dewaxing plants were used principally for the preparation of aero engine oil.

Suida, H. and Pöll, H. (U.S.A. Text book) pointed out that the use of "Paraflow" in transformer or turbine oils had been found undesirable, due to its unfavorable effect on oxidation stability. The authors tested "Paraflow" imported from America and found it very effective as a pour point depressant and not deleterious in regard to oxidation stability.

Studies were carried out as to the optimum conditions for preparing the same compound as "Paraflow" from chlorinated wax and naphthalene. These studies began in June, 1943, and satisfactory results were obtained in March, 1944.

B. Key Personnel Working on Project

Chem. Eng. Lt. Comdr. A. WAKANA
Chem. Eng. Lt. Comdr. S. HARA

II. DETAILED DESCRIPTION

A. An outline showing the steps in the preparation of turbine oil from Oha topped crude oil is shown in Figure 1(B)35. The properties of the turbine oil are given below. The properties of its fractions are given in Table I(B)35.

	Turbine Oil
Density(d_4^{15})	0.9306
Flash Point(°C)	195
Viscosity(R.I. sec.) 30°C	631
50°C	135
80°C	63
(S.U.S.) 100°C	371.2
210°C	49.8
V.I.	26.9
Pour Point(°C)	10
Conradson's Carbon Residue(%)	0.11
Stability Test	Good
Demulsibility	54
Remain Water in Oil(%)	1.82
Acid Value	0.06
Volatility(%)	0.58
Aniline Point	74
Corrosion	Good

This oil was dewaxed by diluting with five volumes of dichlorethane at (-)15°C, and a yield of 95% of dewaxed oil was obtained. Its pour point was (-)18°C, and the yield of wax having a melting point of 39°C was 3%, as shown in Table II(B)35.

B. Properties of "Paraflow"

The properties of the imported "Paraflow," used in these experiments, are tabulated below.

Specific Gravity (d_4^{25})	0.8900
Index of Refraction (n_D^{25})	1.4985
Specific Ref.(r_D^{25})	0.3296
Aniline Pt.(°C)	112
Molecular Weight	962
Elementary C(%)	85.77
Analysis H(%)	12.42
Molecular Formula	$C_{69}H_{119}O$
Acid Value	0.05
Saponification Value	0.26
Iodine Value	14.0
Viscosity(S.U.S.) 100°F	2245
210°F	171.4
Viscosity Index	112.9
Conradson's Carbon Residue(%)	1.20
Pour Point(°C)	-11
Flash Point(°C)	248
Volatility(135°C-6 hrs) (%)	0.047
Stability(175°C-15 hrs)	Good
Oxidation Test Viscosity Ratio	1.88
Conradson's Carbon(%)	3.41
Color	Greenish Red

The results of vacuum distillation are shown in Table IV(B)35. "Paraflow" was dewaxed with five volumes of dichlorethane at (-)20°C, and it was found that only the waxy compound was effective in depressing the pour point of turbine oil, as shown in Table III(B)35.

C. Tests of "Paraflow" in Turbine Oils

"Paraflow" was tested in the laboratory at the First Naval Fuel Depot and also in several oil refineries; the results are given in Table V(B)35 and Figure 2(B)35.

A cold storage test was performed as shown on Table IV(B)35.

A turbine oil (Pour point, 8°C) and the same oil blended with 0.1% "Paraflow" (Pour point (-)10°C) were stored and thermostatically kept at 0°C and changes in their properties were determined. The results are tabulated in Table VI(B)35 and show that the pour point of the turbine oil blended with "Paraflow" was not changed while in storage at low temperatures.

D. Synthesis of "Paraflow"

Referring to U.S. Patent 1,815,022, it was attempted to synthesize a pour point depressant similar to "Paraflow." The properties of sweated wax are shown below.

Color		White
Pour Point (°C)		56
Conradson Carbon (%)		0.09
Viscosity (S.U.S.)	210°F	38.4
Elementary Analysis	C (%)	84.88
	H (%)	14.76
Mean Molecular Weight		461
Molecular Formula		$C_{32}H_{66}$
Distillation Test (at 5mm)	IBP	205
	10%	226
	20%	230
	30%	236
	40%	239
	50%	242
	60%	246
	70%	249
	80%	255
	90%	259
	98%	294

This wax was chlorinated to dichlor paraffin by chlorine gas at 80°C. The results are given in Figure 3(B)35.

A pour point depressant was prepared from this dichlor paraffin and naphthalene by the following procedure: (see Figure 4(B)35). Dichlor paraffin (300 grams) and naphthalene (150 grams) were placed in a three-necked glass flask and heated to 50°C.

After both were dissolved completely, five grams of aluminum chloride were added slowly. After 5-20 minutes a vigorous reaction took place, the reaction gas foaming up to the necks. Then three grams of water were added to control the reaction. Over a period of about 60 minutes, 16 grams of aluminum chloride were added. After maintaining a temperature of 50°C for 90 minutes, the reaction temperature was raised to 100°C and maintained for 120 minutes.

After settling, the sludge was separated and 304 grams of the condensation product were obtained. For dechlorination, nine grams of active clay were added to the condensation product which was then covered with carbon dioxide gas, and heated to 250°C for two hours. In this process 21 grams of unreacted naphthalene were distilled off. The product was then cooled to 150°C. A gas oil (1000 grams) were added for the extraction of the product, and the clay was filtered off.

After recovering the gas oil which had been added, the lighter fraction boiling up to 240°C was distilled off in a vacuum of 2mm Hg.

By adding 0.5% of this product to the turbine oil having a (+)10°C pour point, the pour point was lowered to (-)18°C. The properties of the product are shown in Table VII(B)35. The synthetic product was dewaxed and only the waxy substance was found effective.

E. Addition of Water in the Synthesis of the Pour Point Depressant

The procedure was repeated according to the patent description, but successful results were not obtained. To determine the extent of reaction, the quantity of HCl gas evolved in the condensation of dichlor paraffin with naphthalene was measured by absorption in water.

In these studies, accidentally some water flowed back, and a small quantity of water was introduced into the reaction flask.

A desirable product was thereby obtained. Then the role of water in the condensation reaction was studied, and the following results were obtained.

When 300 grams of dichlor paraffin, 150 grams of naphthalene, and 21 grams of aluminum chloride were used in the condensation reaction, the quantity of water was varied from one gram to six grams. The condensation product was tested by adding 0.5% of it to a turbine oil having a pour point of (+)10°C. The results are shown below.

Quantity of Water (grams)	Pour Point (°C)
1	11
2	-6
3	-20
4	-18
5	Filtration was impossible.
6	

Thus, the presence of water was necessary for the synthesis of the pour point depressant, and the addition of water affects the concentration of hydrogen chloride present.

F. The Effect of Pour Point Depressant on High Viscosity Lubricating Oils

The effect of this pour point depressant on high viscosity lubricating oils was tested.

As shown in Table VII(B)35, it was also effective in these oils.

G. Determination of Allowable Range of Wax Content for the Use of the Pour Point Depressant

A 54°C melting point wax was mixed in various proportions to a turbine oil having a pour point of (-)18°C, and the pour points of the oil were determined.

The results are given in Figure 5(B)35 and show that a small amount of wax markedly raised the pour point. The effect of the pour point depressant for this oil was tested and the results are shown in Figure 6(B)35.

Spindle oil was also tested and the results are given in Figure 8(B)35. The 56°C and 46°C melting point waxes were added to turbine oil, fuel oil, or normal heptane, respectively, and their pour points are shown in Figure 8(B)35. From these results it was observed that the lower the viscosity of the oil or the lower the melting point of wax contained, the greater the allowable percentage of wax for a given pour point.

H. Test Procedures Used

1. Stability. When no black sludge is formed after heating 20 grams of a sample of oil at 170°C for 15 hours.

2. Demulsibility. A sample of oil (20cc) is emulsified by means of inducing water vapor until the total volume reaches 40cc, and then settled at 95°C. Demulsibility is calculated from the rate of separation of oil using the following equation.

$$\text{Demulsibility} = \frac{\text{cc of oil separated} \times 5}{\text{time (minutes)}}$$

3. Volatility. Percentage of loss in weight of 65cc of oil after heating at 135°C for six hours.

4. Corrosion. A.S.T.M. copper strip corrosion test for three hours.

III. CONCLUSIONS

It was found that pour point depressant could be prepared which differed in physical properties from the imported "Paraflow" but was effective in depressing the pour points of oils.

It was prepared on an industrial scale and actually used.

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Table I(B)35
PROPERTIES OF EACH FRACTION OBTAINED FROM TOPPED CRUDE OIL

Volume (%)	Distillation (°C/4mm)	Temperature Converted to (°C/760mm)	Density (d^{25}_4)	Viscosity 100°F	(S.U.S.) 210°F	Viscosity Index	Pour Point (°C)
0~10	142~190	302~366	0.9091	71.1	36.1	-	-13
10~20	~198	~378	0.9172	109.8	38.5	-	-9
20~30	~210	~392	0.9205	156.1	41.2	16.0	-2
30~40	~221	~405	0.9227	239.3	44.6	17.5	3
40~50	~231	~416	0.9230	363.1	48.9	13.5	7
50~60	~241	~429	0.9277	560.8	54.5	7.0	10
60~70	~250	~438	0.9350	906.7	63.3	0.3	14
70~80	~261	~455	0.9331	1222.9	72.3	9.1	14
80~90	~278	~478	0.9273	1610.3	82.9	16.7	19
90~100	~302	~508	0.9308	2355.7	102.0	26.3	20

Table II(B)35
THE DEWAXING OF THE TURBINE OIL

Name	Yield (%)	Density (d^{15}_4)	Pour Point (°C)	Viscosity 100°F	(S.U.S.) 210°F	Viscosity Index	Aniline Point (°C)
Dewaxed Turbine Oil	95	0.9325	-18	467.2	50.8	-9.9	72
Wax	3	-	+39	-	-	-	-
Loss	2	-	-	-	-	-	-

Table III(B)35
DEWAXING OF IMPORTED "PARAFLOW"

	Yield (%)	Pour Point (°C)	Pour Point Depressing Test For Turbine Oil			
			0	0.1%	0.3%	0.5 %
Dewaxed Oil	31	-6	10	10	8	7
Waxy Compound	62.5	2	10	-5	-12	-18
Loss	6.5	-	-	-	-	-

Table V(B)35
EXPERIMENTAL RESULTS OF ADDITION OF "PARAFLOW" TO TURBINE OIL

Nihon Oil Company Ltd. Yokohama Refinery	Base Lub.	Amount of "Paraflow" (%)	Reaction	Specific Gravity	Flash Point (°C)	Viscosity (Redwood)			Pour Point (°C)	Corrosion	Volatile Material (%)	Conradson's Carbon (%)	Animal and Vegetable Oil	Acid Value	Demulsibility	Residual Water in Oil	Stability	Amount of "Paraflow"	F.P.
						30°C	50°C	80°C											
	No. 1 Turbine Oil	0		0.9277	190	573	189	63	+2	Good	0.367	0.08		0.06	73	1.062	Good		
		0.01		0.9274	190	582	187	63	+2	Good	0.362	0.082		0.06	66	1.233	Good	0.02	+2
		0.1		0.9274	190	590	185	63	-1	Good	0.360	0.088		0.06	60	1.252	Good	0.2	-5
		0.5		0.9274	190	588	183	63	-7	Good	0.360	0.093		0.06	60	1.246	Good		
	No. 2 Turbine Oil	0		0.9306	190	586	183	62.5	+9	Good	0.375	0.055		0.06	73	1.033	Good		
		0.01		0.9297	190	599	183	62.5	+9	Good	0.368	0.058		0.06	73	1.052	Good	0.02	+8
		0.1		0.9294	190	595	183	62.5	+5	Good	0.360	0.061		0.06	65	1.326	Good	0.2	+2
		0.5		0.9294	190	602	183	63	-6	Good	0.358	0.063		0.09	70	1.082	Good		
	No. 3 Turbine Oil	0		0.9297	190	593	188	63	+15	Good	0.365	0.032		0.06	60	1.422	Good		
		0.01		0.9301	190	593	187	63	+10	Good	0.358	0.043		0.06	60	1.365	Good	0.02	+8
		0.1		0.9398	190	598	187	63	+5	Good	0.363	0.041		0.06	66	1.214	Good	0.2	+2
		0.5		0.9298	190	602	185	63	-6	Good	0.362	0.063		0.09	65	1.065	Good		
Nihon Oil Company Ltd. Niigata Refinery	Light Turbine Oil	0	Neutral	0.929	181	313	109	50	+3	Good	0.488	0.135	No	0.030	80	0.448	Good		
		0.01	Neutral	0.929	181	313	109	50	-1	Good	0.462	0.135	No	0.030	80	0.448	Good		
		0.05	Neutral						-15	Good									
		0.1	Neutral	0.930	181	313	109	50	-19	Good	0.445	0.140	No	0.03	80	0.500	Good		
		0.2	Neutral						-27	Good									
		0.5	Neutral	0.930	181	314	109	50	-31	Good	0.339	0.145	No	0.035	80	0.645	Good		
	No. 1 Turbine Oil	0	Neutral	0.932	189	589	180	62.5	+5	Good	0.252	0.159	No	0.035	57	0.898	Good		
		0.01	Neutral	0.930	190	589	180	62.5	+13	Good	0.256	0.159	No	0.035	50	0.898	Good		
		0.05	Neutral						-13										
		0.1	Neutral	0.934	190	589	180	62.5	-17	Good	0.258	0.160	No	0.042	40	1.074	Good		
		0.2	Neutral						-24										
		0.5	Neutral	0.936	190	592	180	62.5	-25	Good	0.260	0.162	No	0.045	53.3	1.193	Good		
	No. 2 Turbine Oil	0	Neutral	0.932	189	610	184	62.5	+13	Good	0.258	0.160	No	0.028	57	0.988	Good		
		0.01	Neutral	0.933	190	610	184	62.5	+10	Good	0.262	0.160	No	0.028	43	1.151	Good		
		0.05	Neutral						-5										
		0.1	Neutral	0.934	190	610	184	62.5	-12	Good	0.235	0.163	No	0.035	43	1.268	Good		
		0.2	Neutral						-20										
		0.5	Neutral	0.935	190	614	184	63.0	-24	Good	0.277	0.174	No	0.040	40	1.285	Good		

Table V(B)35 Continued

EXPERIMENTAL RESULTS OF ADDITION OF "PARAFLOW" TO TURBINE OIL

	Base Lub.	Amount of "Paraflow" (%)	Reaction	Specific Gravity	Flash Point (°C)	Viscosity (Redwood)			Pour Point (°C)	Corrosion	Volatile Material (%)	Conradson's Carbon (%)	Animal and Vegetable Oil	Acid Value	Demulsibility	Residual Water in Oil	Stability	Amount of "Paraflow"	P.P.
						30°C	50°C	80°C											
Showa Oil Company Ltd. Niigata Refinery	Turbine Oil	0			180		164		+6			0.073					Good		
		0.05							+45								Good		
		0.07							+2								Good		
		0.1							-55								Good		
		0.15							-135								Good		
		0.2			181		165		-17			0.073					Good		
Showa Oil Company Ltd. Kawasaki Refinery	Turbine Oil	0	Neutral	—	195	454	150	58	+11	Good	—	0.21		0.029	109		Good		
		0.01	Neutral		195	460	151	58	+9	Good		0.21		0.29	100		Good		
		0.1	Neutral		195	479	154	59	-55	Good		0.20		0.014	92		Good		
		0.5	Neutral		193	485	155	59	-17	Good		0.20			80		Good		
Mitsubishi Oil Company Ltd. Kawasaki Refinery	Mitsubishi Turbine Oil No. 4	0	Neutral	0.932	196	605	174	61	-16	Good	0.12	0.05	No	0.006	66.6	0.72	Good		
		0.01							-16										
		0.05							-17										
		0.10							-17										
		0.20							-18										
		0.50	Neutral	0.933	196	612	176	61	-20	Good	0.12	0.05	No	0.018	66.6	0.65	Good		
	Turbine Oil	0	Neutral	0.928	182	650	190	69	+10	Good			No	0.028	66.6	1.30	Good		
		0.01							+10										
		0.05							+8										
		0.10							+6										
		0.20							0										
		0.50	Neutral	0.928	184	654	190	68	-12	Good			No	0.037	66.6	1.30	Good		
Maruzen Oil Company Ltd. Shimazu Refinery	No. 1 Turbine Oil	0	Neutral	0.928	194	604	188	63.5	+5	Good	0.150	0.05	No		77	0.886	Good		
		0.01	Neutral	0.928					+2.5	Good	0.152	0.05	No		79.3	0.907	Good		
		0.05							+1										
		0.10	Neutral	0.928					-2	Good	0.155	0.05	No		81.0	0.911	Good		
		0.20							-6										
		0.50	Neutral	0.928					-24	Good	0.160	0.05	No		83.2	0.913	Good		
	No. 2 Turbine Oil	0							+10										
		0.01							+95										
		0.05							+9										
		0.10							+6										
		0.20							-4										
		0.50							-22										
	No. 3 Turbine Oil	0							-15										
		0.01							+14										
		0.05							+12.5										
		0.1							+12									0.3	-7
		0.2							+2									0.4	-13
		0.5							-16										

Table IV(B)35
VACUUM DISTILLATION OF IMPORTED "PARAFLOW"

	Distilled Temp. (°C/1mm)	Converted to 760mm	Yield (wt. %)	Appearance
1	175-200	382-416	1.2	Pale yellow, liquid
2	-250	-483	11.7	Pale yellow, liquid mixed with crystal
3	-274	-515	16.6	Orangeyellow, liquid
4	-290	-533	17.2	Orangeyellow, liquid
5	-300	-550	4.8	Orangeyellow, liquid
6	300-	550-	48.2	Dense green, liquid

(See pages 386 and 387 for Table V(B)35.)

Table VI(B)35
STORAGE TEST OF TURBINE OILS

Time Elapsed (hours)	Turbine Oil Without Addition of "Paraflow"			Turbine Oil With Addition of 0.1% "Paraflow"		
	Viscosity (Redwood No.2) (0°C)	Pour Point (°C)	Pour Point Preheated to 50°C	Viscosity (Redwood No.2) (0°C)	Pour Point (°C)	Pour Point Preheated to 50°C
45	1357.8	+ 8	+12	1005	-20	-7
110	1590.9	+ 4	+12	995.3	-19	-10
158	1536.5	-	-	985.0	-	-
397	1569.3	-	-	998.2	-	-

Table VII(B)35
PROPERTIES OF SYNTHETIC PRODUCTS

	Specific Gravity (d_4^{15})	Ind. of Refra. (n_D^{25})	Viscosity (S.U.S.) 100°F	Viscosity (S.U.S.) 210°F	Pour Point (°C)	Conradson's Carbon	Acid Value	Saponification Value	Iodine Value	Molecular Weight	Ash	Lowering Test of Pour Point by Addition 0.5% to (+)10°C Turbine Oil
A	-	1.5335	-	423.3	29	1.16	0.62	1.01	9.61	769	-	-18
B	-	1.5400	30,000	1,067	20	0.64	0.65	0.96	5.70	962	-	-18
C	0.9279	-	-	-	25	0.33	0.47	1.30	7.47	-	0.02	-18

Table VIII(B)35
THE EFFECT OF THE POUR POINT DEPRESSANT ON HIGH VISCOSITY OILS

	Specific Gravity (d_4^{15})	Viscosity (S.U.S.) 100°F	Viscosity (S.U.S.) 210°F	Viscosity Index	Carbon Residue (%)	Acid Value	Saponification Value	Stability Test Vis. Ratio	Stability Test Conradson Carbon (%)	Pour Point (°C) Depressant Added 0	0.1	0.5	1.0
Aeroplane Oil	0.9029	1567.8	118.2	100.6	0.59	0.09	-	1.35	1.85	+7	4	-1	-4
Synthetic Lubricating Oil	0.9002	1443.0	124.7	111.7	0.82	0.32	0.58	2.10	2.93	10	10	8	0
Natural Lubricating Oil	0.9342	2849.6	126.2	66.3	1.59	0.11	0.34	2.70	5.27	8	5	3	-3

ENCLOSURE (B)35

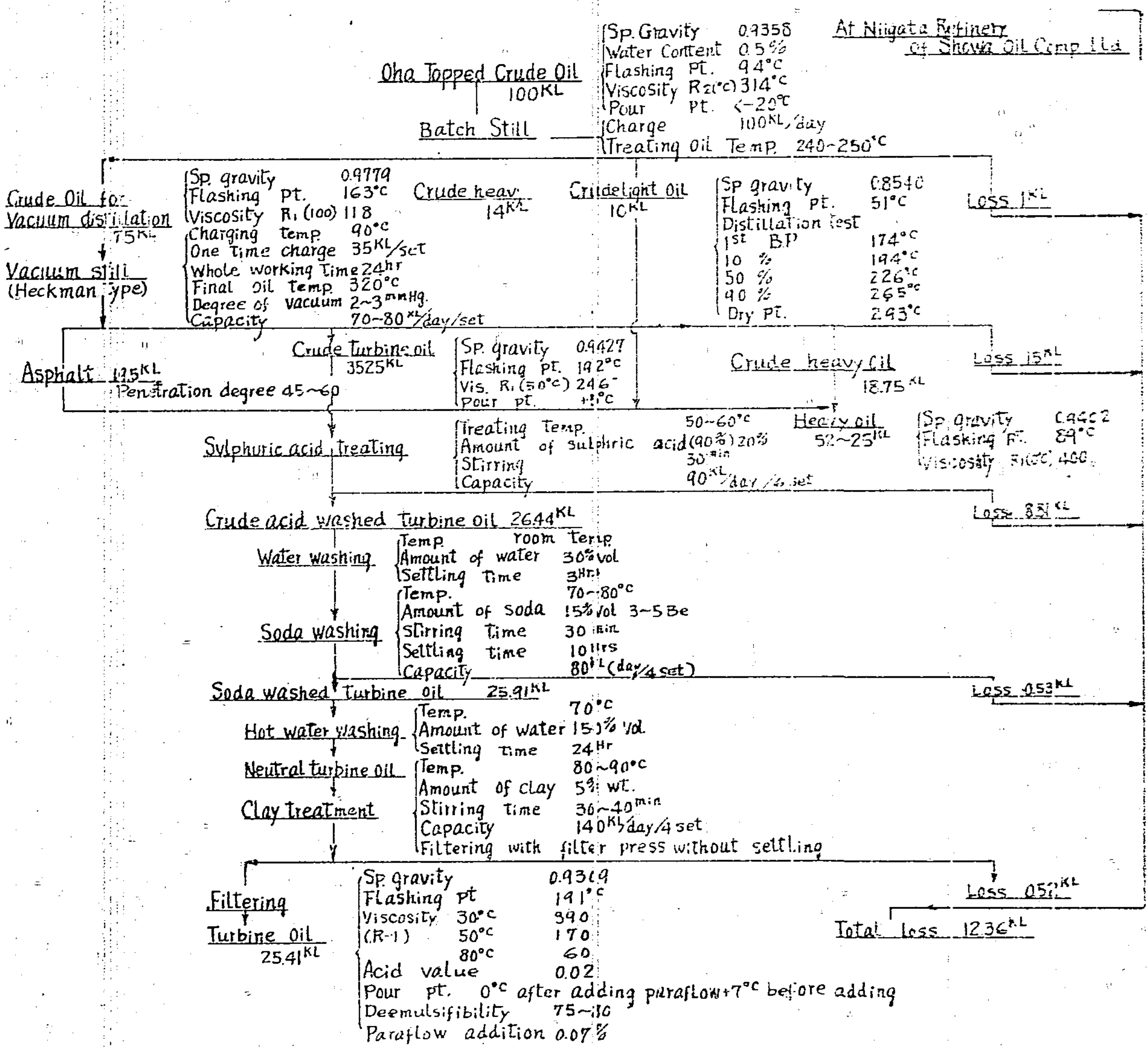

Figure 1(B)35
FLOW SHEET OF PRODUCTION OF TURBINE OIL FROM OHA CRUDE OIL

ENCLOSURE (B)35

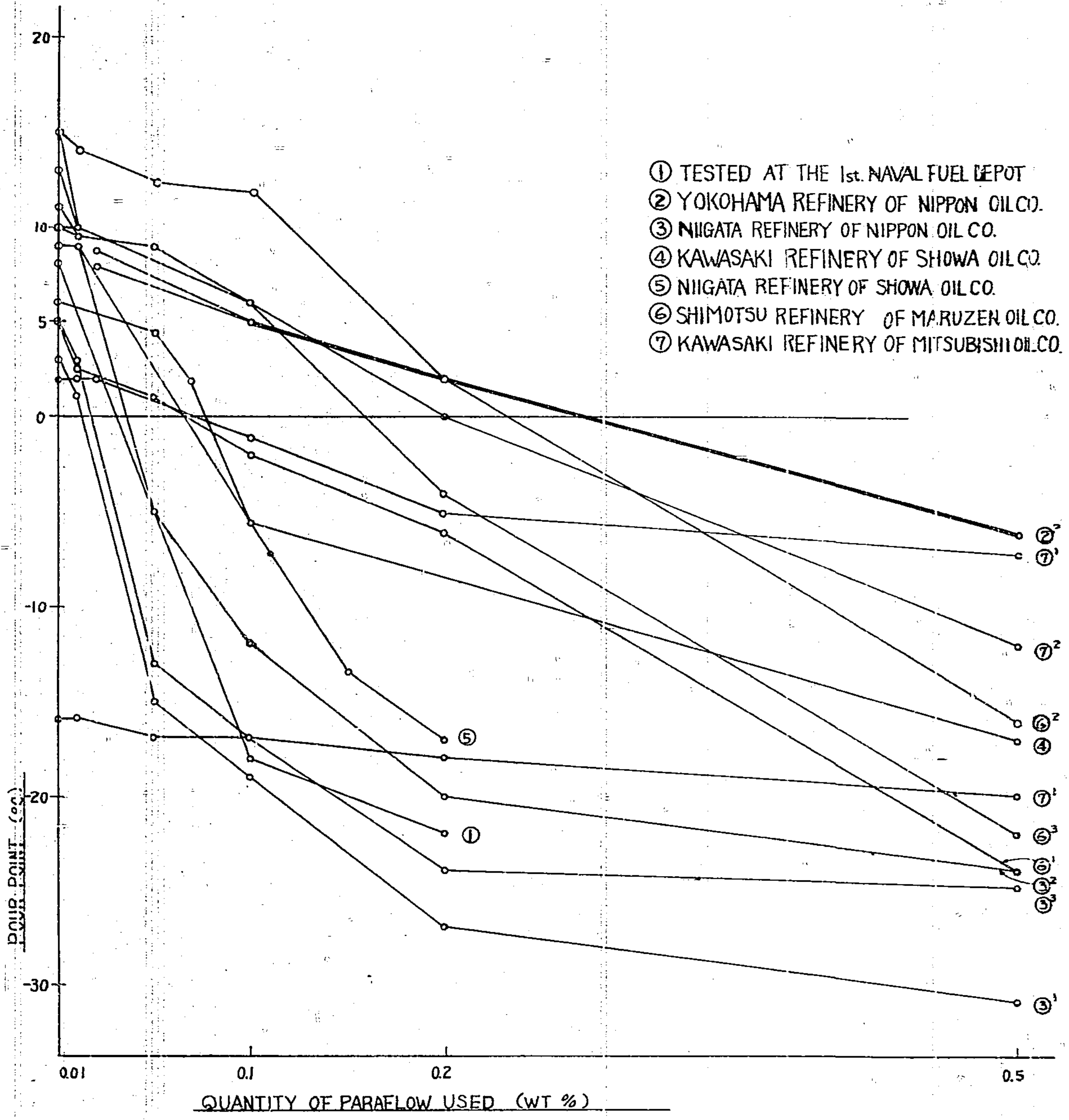

Figure 2(B)35
TEST OF PARAFLOW IN TURBINE OILS

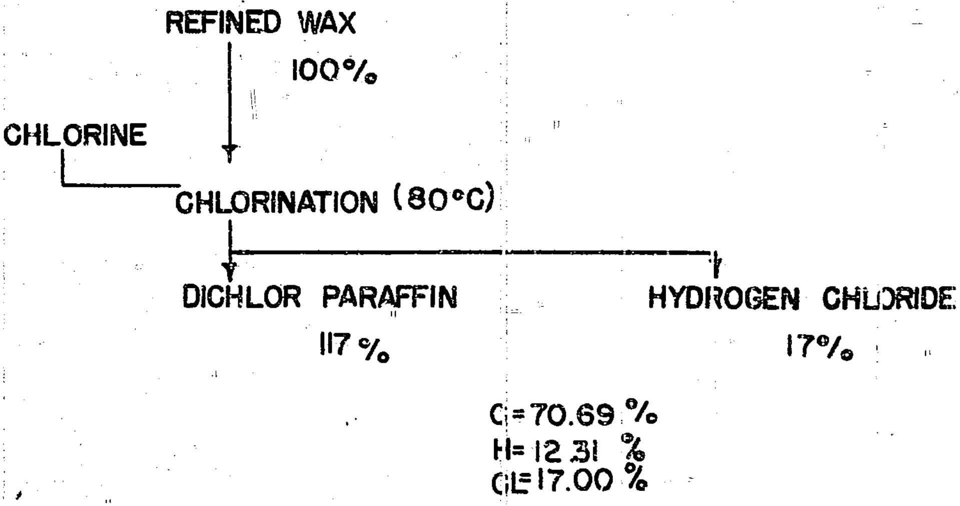

Figure 3(B)35
CHLORINATION OF PARAFFIN WAX

ENCLOSURE (B)35

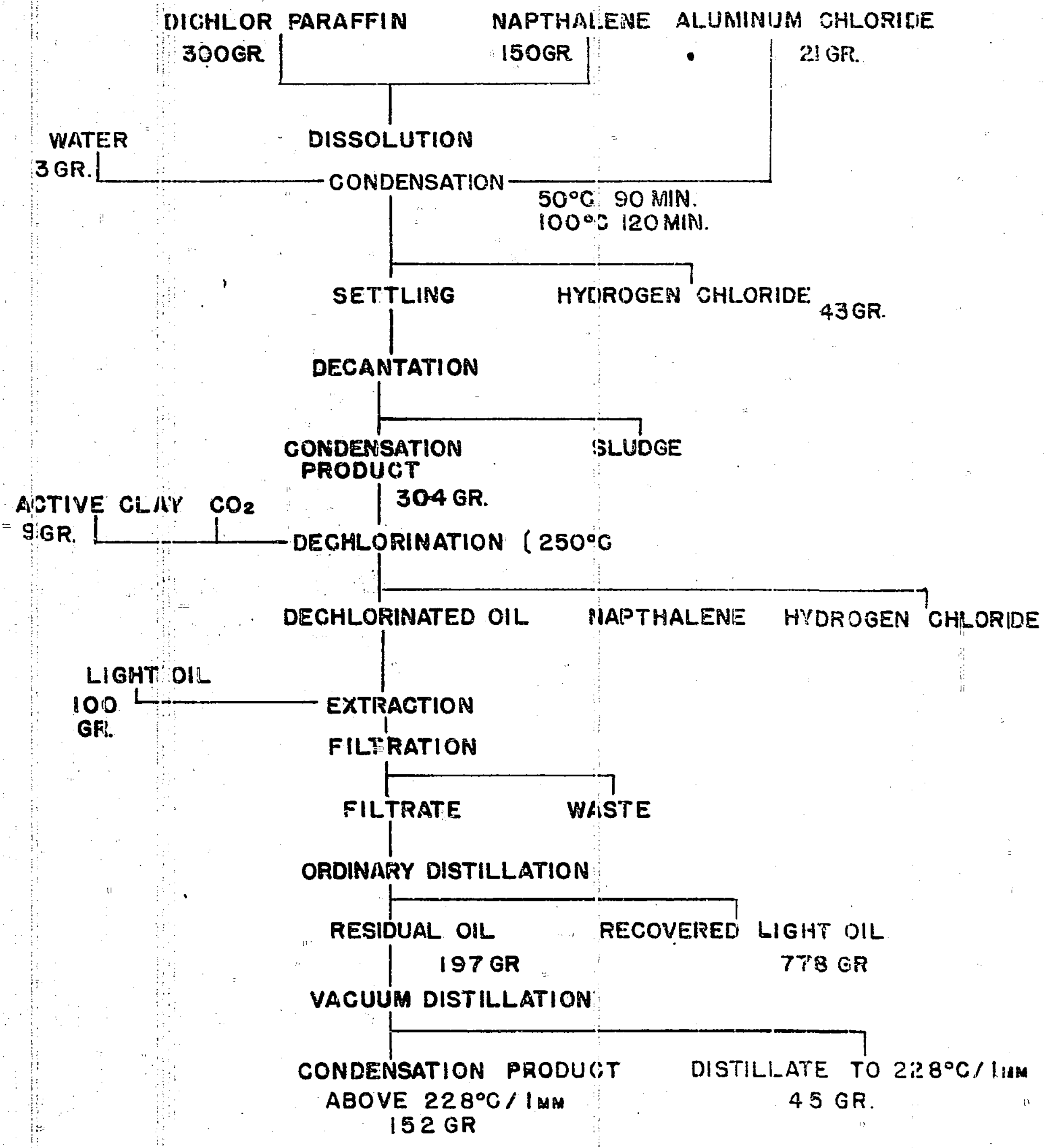

Figure 4(B)35

THE SYNTHETIC METHOD FOR PREPARING POUR POINT DEPRESSANT

ENCLOSURE (B)35

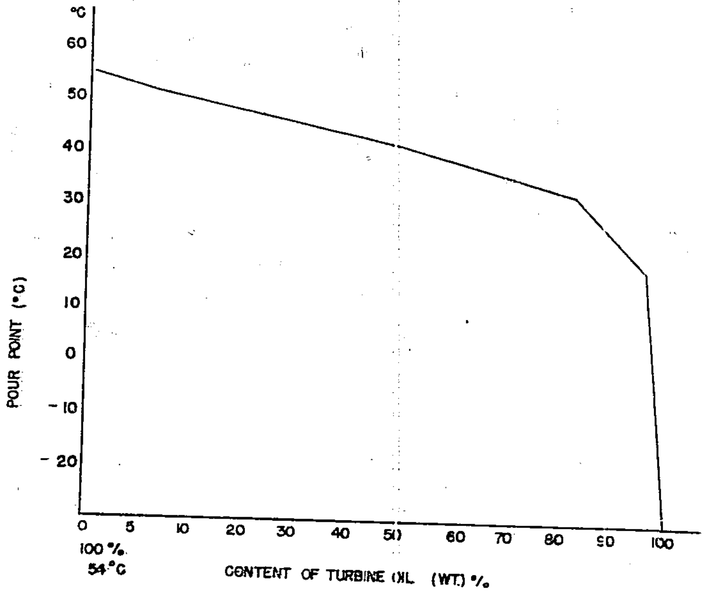

Figure 5(B)35
EFFECT OF WAX IN POUR POINT OF TURBINE OIL

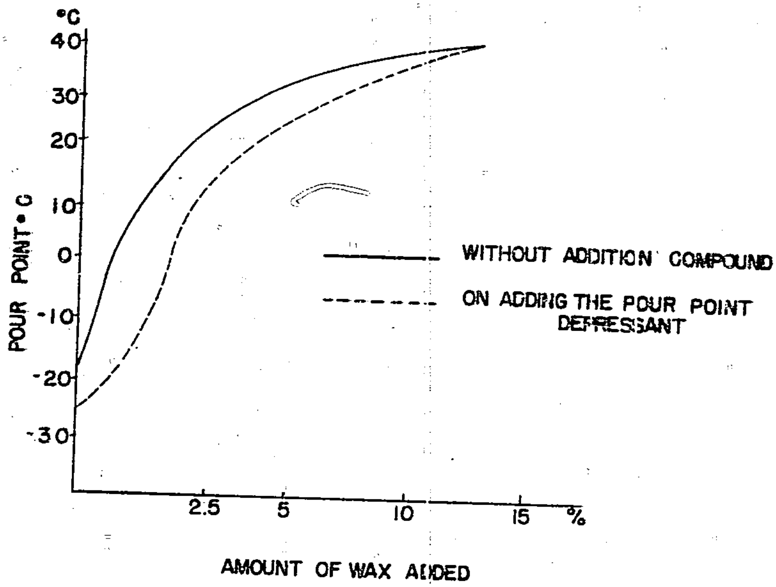

Figure 6(B)35
EFFECT OF THE POUR POINT DEPRESSANT IN TURBINE OIL
(Made at OFUNA)

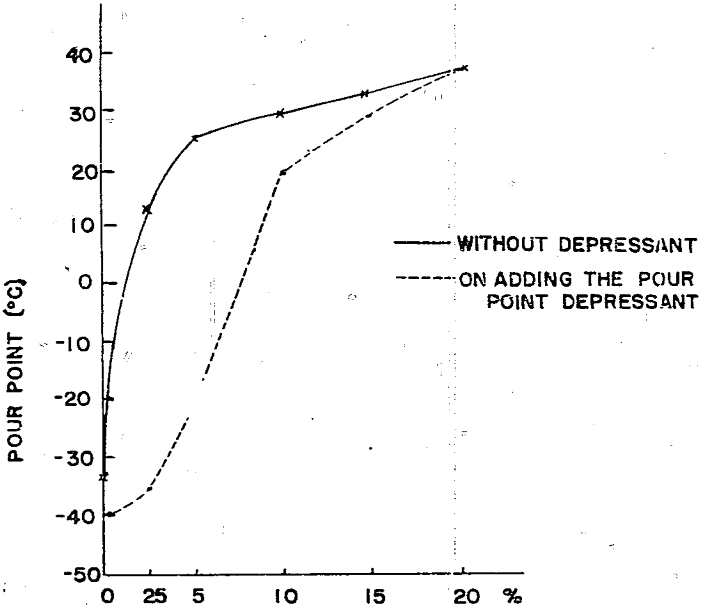

Figure 7(B)35

EFFECT OF POUR POINT DEPRESSANT FOR SPINDLE OIL

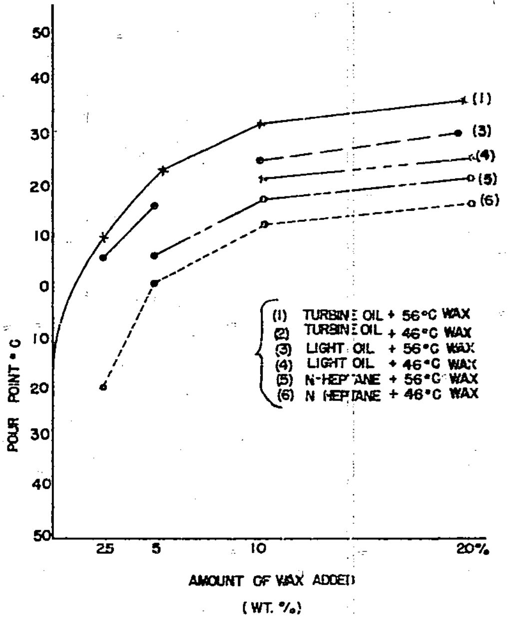

Figure 8(B)35

THE EFFECT OF WAX ON POUR POINT TEST

ENCLOSURE (B) 36

RESEARCH ON LUBRICATING SPECIAL GREASES

(In Three Parts)

by

CHEM. ENG. CAPT. DR. I. KAGEHIRA
CHEM. ENG. LT. COMDR. T. DAN

Research Period: 1938-1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

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PART I

SPECIAL GREASES

by

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Dr. I. KAGEHIRA

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Research Period: 1938 - 1945

SUMMARY

The results of researches on manufacturing imported special greases and other greases for special uses led to the conclusion that these special greases could be made by using the proper metallic soaps and heating them together with suitable refined mineral lubricating oils.

I. INTRODUCTION

Special high class lubricating greases for aviation engines and its auxiliary parts, i.e. magneto grease, controllable-pitch propeller grease and rocker arm grease, were chiefly imported from U.S.A., and in Japan, there was practically no research on these greases. The authors, therefore, carried on researches on the components and methods of manufacture for these greases from 1938 to 1943 and obtained various ones.

In 1943 a special rust-proof grease was needed for the framework of the aero-torpedo engine, and another grease was needed as a better anticorrosive material for the interior of the compressed air chambers of the aero-torpedo because of the lack of satisfactory ones at that time. Research led to success in establishing a suitable method of manufacture.

In 1944 a sea water-proof grease for submarines was investigated and a superior one was developed and found very satisfactory by practical test, particularly in regard to resistance to removal by water washing.

In 1944 the authors carried these researches to the pilot plant stage and manufactured these greases which had been studied in the laboratory.

II. DETAILED DESCRIPTION

A. Analytical Methods and Tests

Chemical laboratory tests are classified under two headings and were carried out in the following manner.

1. Control Test.

   a. Percent water...............A. S. T. M. D95 - 30

b. **Corrosion test.** Place a clean strip of polished pure sheet copper about 1/2 inch wide and 3 inch long in a clean test tube. Add enough of the sample to cover the strip completely. Maintain for 3 hours at 100°C. Rinse the copper strip with sulfur-free benzene and compare it with a similar strip of freshly polished copper. Discoloration or pitting indicates corrosion.

c. Saponification value........A. S. T. M. D94 -28

d. Percent free alkali and free acid...............A. S. T. M. D128-27

2. Quality Test

a. Grease analysis.............A. S. T. M. D128-27

b. Percent fillers.............A. S. T. M. D128-27

c. Percent mineral oil.........A. S. T. M. D128-27

d. Mineral oil tests...........A. S. T. M. D128-27

e. Percent soap................A. S. T. M. D128-27

f. Kind of soap................A. S. T. M. D128-27

g. Total mixed fatty acids.....A. S. T. M. D128-27

Physical laboratory tests may be similarly classified.

1. Control Test

a. Consistency test at 25°C...A. S. T. M. D217-33T

b. Dropping point................Ubbelohde method

c. Saybolt viscosity

2. Quality Test

Stability to heat: 20 to 25 gm of grease were heated to 100 to 105°C and held at that temperature for 3 hours. The specification is that after 24 hours standing no oil should separate.

B. Experimental Results

1. **Magneto Grease.** For an aero-motor magneto grease, "Bosch Magneto grease" imported from U.S.A. was generally used. Analysis of this grease showed the main composition was 26.8% of stearic and oleic acid sodium soap and 68.9% of low viscosity refined lubricating oil having a vis. of 43.2 S. U. S. at 210°F, vis. index, 109.

As a result of the experiments for manufacturing grease of the same property as the "Bosch Magneto grease", two trial samples were made.

One was composed of 20% of the sodium soap of castor oil (whole oil and not ricinoleic acid alone) heated together with 80% of turbine oil (sample No. 1, Table II(B)36), the other was heated with phenol refined oil (sample No. 2 Table II(B)36) at the temperature of 170°C to 180°C. After milling, with a roller type mill, these greases were comparable in general properties to "Bosch grease" and they were found very suitable for magnetos by engine tests at the First Naval Aeronautical Depot.

In this study, it was recognized that greases made from sodium stearate and sodium oleate soaps heated together with turbine oil are of fibrous texture. Therefore, they are not suitable for high speed ball-bearing greases.

The use of the sodium soap of castor oil plus milling led to success in obtaining a suitable smooth texture as possessed by "Bosch grease".

Next, sample No. 3, Table II(B)36 was made from 22.3% of the soda soap of castor oil with an excess of soda (1.33 times the theoretical saponification value) heated together with 68.7% of refrigerating machine oil at the temperature of 230°C. This grease was quickly cooled to prevent the grease from crystallizing out soap.

This sample possessed a higher dropping point and a better heat stability than any other sample. The data for "Bosch grease" and three samples are shown in the Table II(B)36.

2. <u>Controllable-Pitch Propeller Grease</u>. Up to 1940 "Mobile Grease" No. 2, produced by Standard Vacuum Oil Co., was used for controllable-pitch propeller. Analysis of this grease indicated a composition of 7.57% of aluminum soaps of palmitic, stearic and oleic acid, and 89.73% of high viscosity refined mineral oil (vis. of 131.5 S. U. S. at 210°F, vis. index 69). As the result of experiments on manufacturing a grease equal to this "Mobile Grease" No. 2, the grease sample was made by mixing 6.48% of aluminum stearate, 0.72% of aluminum oleate, 0.80% of lead oleate, 0.40% of glycerine and 91.6% of mineral lubricating oil (vis. S. U. S. at 210°F 133.4, vis. index 87.5) at the temperature of 150°C. It was confirmed by tests on coefficient of friction, and engine tests at the First Naval Aeronautical Depot that this sample of grease was as applicable to controllable-pitch propellers as "Mobile Grease" No 2. The data for Standard Vacuum Oil Co. Mobile Grease No. 2 and experimental grease are shown in Table III(B)36. Determination of Coefficient of Friction.

The Kinetic coefficients of friction of sample greases were determinted at various temperatures by means of a Bearing Type Testing apparatus described in detail in the report. "Studies on the Additives of the Submarine Diesel Engine Lubricant" by Eng. Capt. Dr. I. KAGEHIRA and Chem. Eng. Lt. Comdr. N. HIRATA.

The schematic view of the test apparatus is shown in Figure 1(B)36. The diameter of the test shaft was 3cm, and the length of the line of contact was 2cm.

The test piece and the test shaft were polished with 04 emery paper and washed with well refined gasoline.

The sample grease is charged in the oil cup (C) and then maintained at constant temperature by electric heating. A constant weight (F) is loaded on the test piece (A) and then the test shaft (B) is rotated under various rubbing speeds. Frictional resistance at various rubbing speeds is determined by the weight of balance (E) and frictional resistance divided by load (F) gives a value from which the coefficient of friction of motion may be calculated. The plots of the data are shown in Figure 2(B)36-a to Figure 2(B)36-b.

From these data it was shown that experimental grease No. 1 containing lead oleate matched Standard Vacuum Mobile grease No. 2 in lubricating value.

Experimental greases tested for determination of coefficient of friction had compositions and properties shown in Table I(B)36.

3. Rocker Arm Grease. Up to 1941 "Super Gear Lubricant" made in U.S.A. by the Vacuum Oil Co. was used as aviation rocker arm greases. Analysis of this grease showed the following composition: 4.4% of calcium soap of stearic and oleic acid, 95.7% of heavy lubricating oil (vis. S. U. S. at 210°F, 108, vis. index 89.2).

As the result of experiments, sample No. 1, Table IV(B)36, was prepared by the following treatment. Sodium oleate (4.55%), 2.45% of sodium stearate, 0.70% of glycerine and 92.30% of heavy refined lubricating oil (vis. S. U. S. at 210°F. 100.8, vis. index 77) were heated together at the temperature of 150°C. This experimental grease was analogous in general properties and was indicated to be as serviceable as "Super Gear Lubricant" by the engine tests at the First Naval Aeronautical Depot.

Sample No. 2, Table IV(B)36, consisted of 3.0% of sodium stearate, 3.0% of sodium oleate, 1.0% of calcium stearate, 1.0% of calcium oleate, 0.4% of glycerine and 91.2% of heavy refined lubricating oil (vis. S. U. S. at 210°F, 95, vis. index 67), was made to possess a good water-proof character and by engine test it was proved to give good service.

Compositions and properties of "Super Gear Lubricant" and two experimental greases are shown in Table IV(B)36.

4. Special Grease for the Framework of the Aero-Torpedo. For the framework grease of the main engine of the aero-torpedo, the experimental grease was prepared as follows: 7% of aluminum stearate, 0.21% of calcium stearate and 92.7% of cylinder oil for aero-torpedo (vis. S. U. S. at 210°F, 61.9, vis. index 85.3, Setting point (-)36°C) were heated together at a temperature of 150°C. The role of calcium stearate in the oil was to liquify and semi-plastify the aluminum stearate.

By engine test this experimental grease was proved to be excellent for the prevention of the corrosion of engine parts. Its composition and general properties are shown in Table V(B)36.

ENCLOSURE (B)36

5. Special Grease for Preventing Corrosion of the Interior of Compressed Air Chamber of Aero-Torpedoes. Up to 1943, as an anticorrosive for the interior of the compressed air chamber of the aero-torpedo, a heavy cylinder oil was used. However, it was unsatisfactory as an anticorrosive compound from the standpoint of adhesiveness and antifreezing character.

To improve these points the following grease was prepared, applied to practical tests and proved to be excellent, having very good adhesive and anticorrosive properties.

Aluminum stearate (12%), 0.36% of calcium stearate, and 87.64% of cylinder lubricating oil were heated together at a temperature of 150°C.

In each case the grease was milled three to four times in a roll type mill. Composition and general properties of this grease are shown in Table VI(B)36.

6. Sea Water Proof Greases (Anti-Corrosive and Anti-Wash). Sea Water Proof Greases to be used for the machine-gun mounted on submarines were studied and the following experimental greases No. 1 to No. 6 were prepared and subjected to practical tests at the Yokosuka Naval Arsenal.

Their compositions are shown in Table VII(B)36, sample No. 5, which consisted of 13% of aluminum stearate and 87% of heavy lubricating oil, was most suitable by the laboratory and practical tests. The composition and general properties of the grease are shown in Table VIII(B)36.

7. Summary of Laboratory Data. The results of researches are summarized in Table IX(B)36 and X(B)36, which show the best conditions for the preparation of each grease.

C. Detailed Description of Pilot Plant

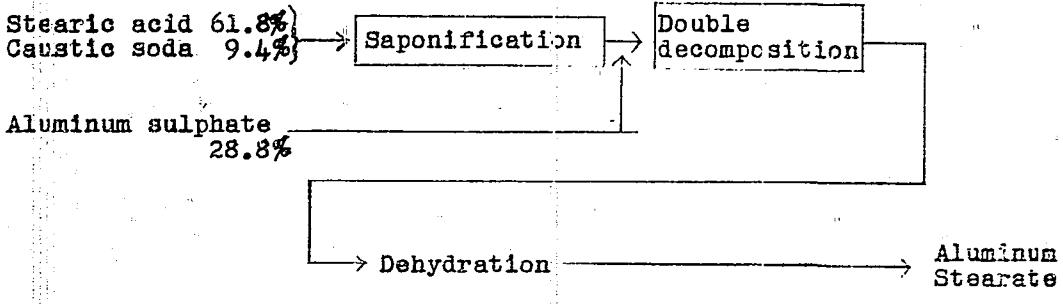
1. Description of Pilot Plant (erected February 1944)

a. Main equipment. This is shown in Table XI(B)36.

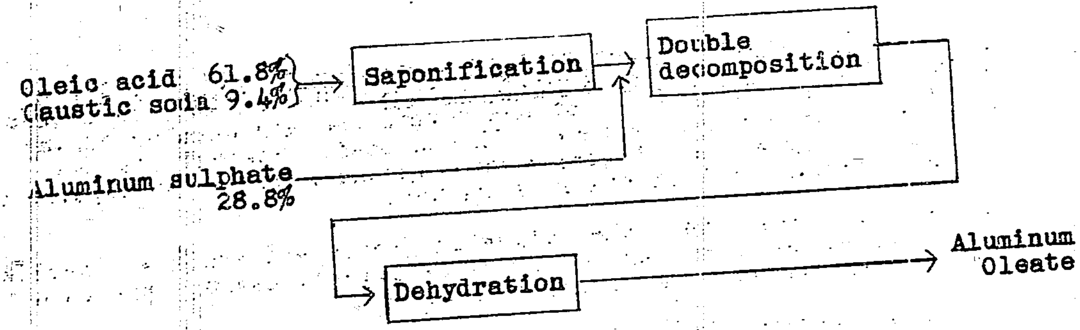
b. Flow sheets of pilot plant. These are shown in Plate I(B)36.

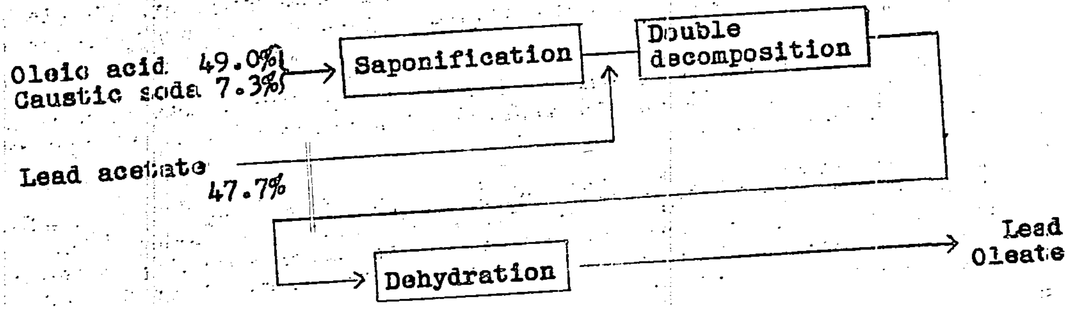
c. Process flow sheets of pilot units

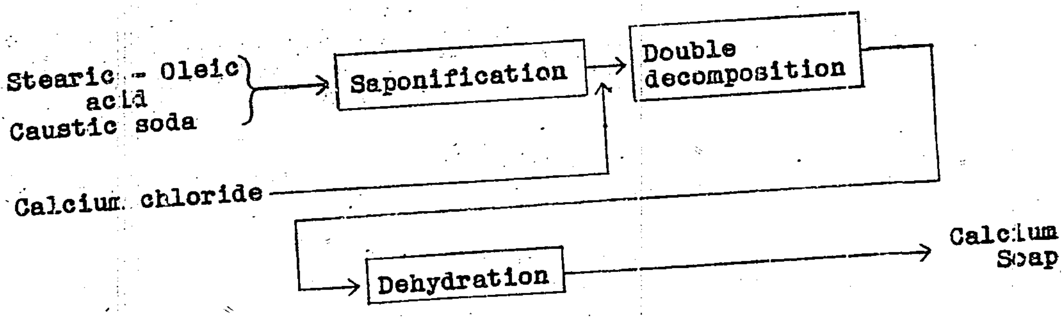
Preparation of Metallic Soaps



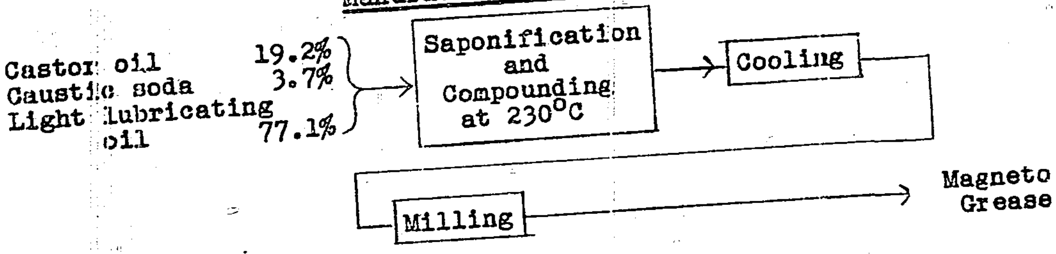
ENCLOSURE (B)36







Manufacture of Greases



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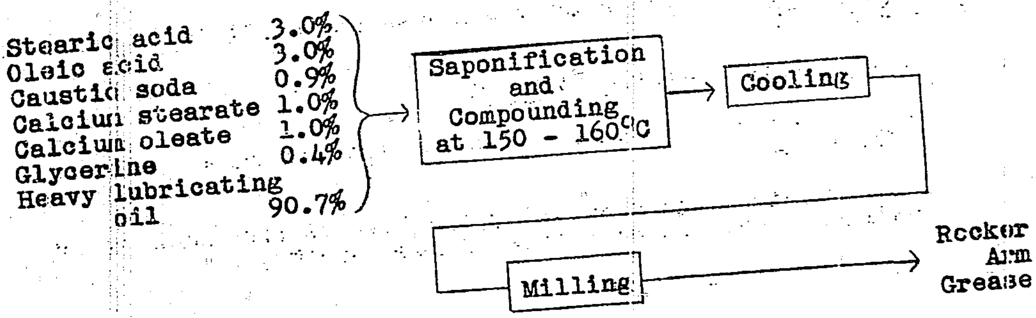

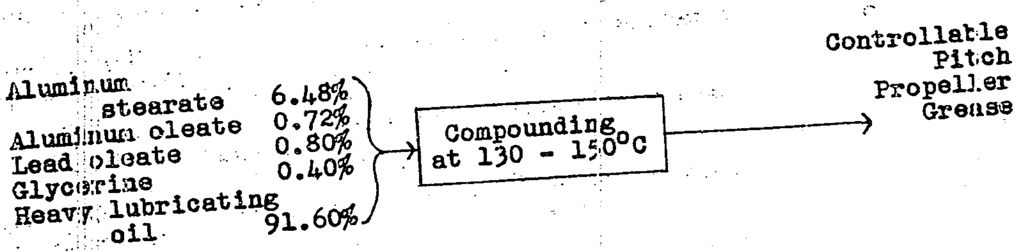

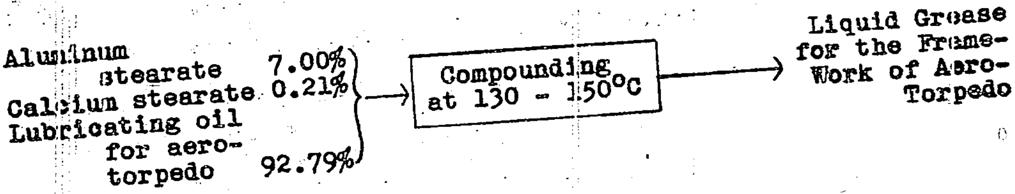

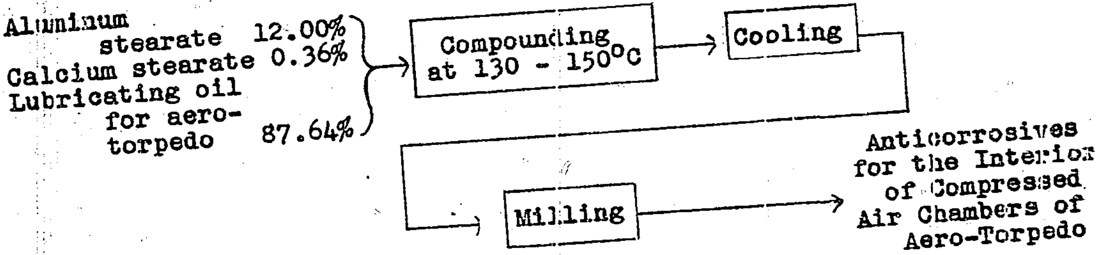

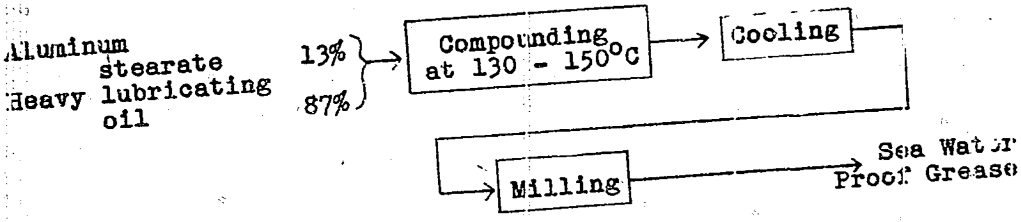

2. Procedures. Details of procedures and conditions are shown in Table XII(B)36.

3. Experimental Results in Pilot

a. Yield and material balance. This is shown in Table XIII(B)36.

b. Physical and chemical properties of products, intermediates, and raw materials of feed stocks.

(1) Chemicals

Caustic soda................................solid

Aluminum sulphate................$Al_2(SO_4)_3 \cdot 24H_2O$, Chemically pure

Lead acetate....................$Pb(C_2H_3O_2)_2 \cdot H_2O$, Chemically extra pure

Calcium chloride.......................$CaCl_2 \cdot 2H_2O$, Chemically pure

Glycerine.............................98% pure

(2) Lubricating oils: see Table XIV(B)36.

(3) Soap stocks: see Table XV(B)36.

(4) Intermediates: see Table XVI(B)36.

(5) Products: see Table XVII(B)36.

D. Summary of Data in Pilot Plant. Summary of data in pilot plant and comparison of general properties of greases obtained in pilot plant and laboratory are shown in Table XVIII(B)36.

These data proved that the greases manufactured in the pilot plant have very nearly the same properties as those prepared in laboratory.

III. CONCLUSIONS

The results of research on the manufacture of special greases, i.e. Magneto grease, Controllable-Pitch Propeller grease, Rocker Arm grease and other special grease for the Framework of Aero-Torpedo, Anticorrosives for the Interior of Compressed Air Chamber of Aero-Torpedo and Sea Water Proof grease, were successful in establishing a suitable method for the preparation of each grease.

Table I(B)36
COMPOSITIONS AND PROPERTIES OF GREASES
APPLIED TO THE FRICTION TEST

		Experimental Greases	
		No. 1	No. 2
Composition	Aluminum Stearate	6.1	6.56
	Aluminum Oleate	0.7	0.94
	Lead Oleate	0.7	absence
	Glycerine	0.38	0.38
	Mineral Oil	92.12	92.12
Properties of mineral oil	Flash Point 9C	268	
	Viscosity S. U. S. (at 210°F)	133.4	
	Viscosity Index	87.5	
	Carbon Residue (%)	0.4	
General properties	Appearance	Viscous, stringy	Viscous, stringy
	Dropping Point (°C)	86	84
	Consistency at 25°C	385	390
	Free Fatty Acid (%)	0.5	0.2
	Free Fatty Oil (%)	none	none
	Ash (%)	0.44	0.50
	Water (%)	trace	trace
	Corrosion	O. K.	O. K.
	Stability (100°C 3 hrs)	no oil bleeding	no oil bleeding

Table II(B)36
COMPARISON OF SAMPLE GREASES WITH BOSCH MAGNETO GREASE

	Compositions						
	Mineral Oil (%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid (%)	Free Fatty Oil (%)
Bosch magneto grease	68.9	26.8	0.5	5.76	0	5.5	
Sample grease No. 1	79.4	20.5	trace		0.05	0	0.11
Sample grease No. 2	79.4	20.5	trace	2.5	0.095	0	0.34
Sample grease No. 3	68.7	22.3	0.5	3.44	0.12	0	

	Properties of Mineral Oil						
	F.P.(°C)**	Viscosity 210°F	Viscosity 100°F	Vis. Index	Viscosity# (Redwood Sec.)	Setting Pt. (°C)	C.R.(%)##
Bosch magneto grease		43.2	144	109.2	176	-39	0.75
Sample grease No. 1	199	51.8	407.8	38	578	- 6	0.015
Sample grease No. 2	173	50.5	270.0	96	350	-14	0.010
Sample grease No. 3	155				130.8	-30	0.020

	General Properties					
	Appearance	Consistency* (-) 20°C	Consistency* (+) 25°C	Dropping Pt.	Corrosion	Stability (100°C 3 hrs.)
Bosch magneto grease	Smooth Texture		256	165	O.K.	no oil bleeding
Sample grease No. 1	Smooth Texture		200	165	O.K.	no oil bleeding
Sample grease No. 2	Smooth Texture		255	165	O.K.	no oil bleeding
Sample grease No. 3	Smooth Texture	180	254	175	O.K.	no oil bleeding

	Soap Fatty Acid		
	Acid Value	Sap. Value	Iodine Value
Bosch magneto grease	188.9	187.0	59.6
Sample grease No. 1		184.4	63.2
Sample grease No. 2		184.4	63.2
Sample grease No. 3	182.6	192.9	64.6

*Worked Penetration
**Flash Point

#Conradson Carbon Residue
##At 30°C

Table III(B)36
COMPARISON OF EXPERIMENTAL GREASE WITH STANDARD OIL CO. GREASE

	Compositions						
	Mineral Oil %	Soap %	Water %	Ash %	Free Alkali %	Free Fatty Acid %	Free Fatty Oil %
Standard Vacuum Oil Co. Mobile Grease No. 2	89.73	7.57	0.13	0.92	0	1.03	0.10
Experimental Grease	91.60	8.00	trace	1.08	0	0.67	0

	Properties				
	Appearance	Consistency* at 10°C	Dropping Pt. °C	Corrosion	Stability (100°C 3 hrs.)
Standard Vacuum Oil Co. Mobile Grease No. 2	Stringy Viscous Mobile	360	63.	O.K.	no oil bleeding
Experimental Grease	Stringy Viscous Mobile	347	40.	O.K.	no oil bleeding

	Mineral Oil				
	F.P.(°C)	Viscosity (S.U.S.)	V. I.	S. P. (°C)**	C. R. (%)***
Standard Vacuum Oil Co. Mobile Grease No. 2		131.5	69.	2.5	1.2
Experimental Grease	268	133.4	87.5	(-)15.5	0.4

	Soap Fatty Acid			
	M. P. (°C)	Acid Value	Sap. Value	Iod. Value
Standard Vacuum Oil Co. Mobile Grease No. 2	52.5	175.2	206.9	10.4
Experimental Grease	Mixture of Stearic and Oleic Acid			

*Worked Penetration A.S.T.M.

**Solidification Point

***Conradson Carbon Residue

Table IV(B)36
COMPARISON OF EXPERIMENTAL GREASES WITH SUPER GEAR LUBRICANT

	Compositions						
	Mineral Oil(%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid (%)	Free Fatty Oil (%)
Super Gear Lubricant	95.7	4.4	0.30	0.60	none	0.25	0.37
Experimental grease No. 1	92.3	7.0	0.02	1.24	0.006	none	none
Experimental grease No. 2	91.2	7.49	0.20	1.50	none	0.31	none

	General Properties				
	Appearance	Consistency* at 25°C	Dropping Pt. (°C)	Corrosion	Stability (100°C, 3 hrs)
Super Gear Lubricant	Semi Fluid Smooth	363	85	O. K.	Oil Bleeding, Soap-Separate
Experimental grease No. 1	Semi Fluid Smooth	370	65	O. K.	No Oil Bleeding
Experimental grease No. 2	Semi Fluid Smooth	360	119	O. K.	No Oil Bleeding

	Mineral Oil					Soap Fatty Acid			
	F. P. (°C)	Viscosity** S.U.S.	V. I.	C. R. (%)	S. P. (°C)	M. Pt. (°C)	Acid Value	Sap. Value	Iod. Value
Super Gear Lubricant		108	89.2	1.7	2.5	40-42.5	203.5	208	46.4
Experimental grease No. 1	230	100.8	77.1	0.86	(-)15	49-49.5	193.6	193.6	50.7
Experimental grease No. 2	218	95.0	67.3	2.01	(-)18	55	198	202.6	44

*Worked Penetration A.S.T.M.

**At 210°F.

ENCLOSURE (B)36

Table V(B)36
AERO-TORPEDO FRAMEWORK GREASE

	Compositions						
	Mineral Oil (%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid(%)	Free Fatty Oil(%)
Experimental grease for framework of aero-torpedo	92.79	7.21	0.05	0.50	none	0.50	none

	General Properties				
	Appearance	Consistency* (-) 40°C	Viscosity (S.U.S.)	Corrosion	Stability (100°C 3 hrs)
Experimental grease for framework of aero-torpedo	Liquid	284	1036	O. K.	no oil bleeding

	Mineral Oil (Base)					Soap Fatty Acid			
	F.Pt.(°C)	Viscosity** (S.U.S.)	V. I.	S. Pt. (°C)	C. R. (%)	M. Pt. (°C)	Acid Value	Sap. Value	Iod. Value
Experimental grease for framework of aero-torpedo	203	61.9	85.3	(-)36	0.36	65-67	202	206	0

*Worked Penetration A.S.T.M. **At 210°F

Table VI(B)36
COMPRESSED AIR CHAMBER GREASE

	Compositions						
	Mineral Oil (%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid (%)	Free Fatty Oil (%)
Experimental Grease for Interior of Compressed Air Chamber of Aero-Torpedo	87.64	12.36	0.04	0.80	none	0.50	none

	General Properties				
	Appearance	Consistency* at 25°C	Dropping Point (°C)	Corrosion	Stability (100°C, 3 hrs)
Experimental Grease for Interior of Compressed Air Chamber of Aero-Torpedo	Smooth	326	90	O. K.	No oil bleeding

	Mineral Oil					Soap Fatty Acid			
	F. P.(°C)	Viscosity** (S.U.S.)	V. I.	S. Pt. (°C)	C. R. (%)	M. Pt. (°C)	Acid Value	Sap. Value	Iod. Value
Experimental Grease for Interior of Compressed Air Chamber of Aero-Torpedo	203	61.9	85.3	(-)36	0.36	65-67	202	206	0

*Worked Penetration A.S.T.M. **At 210°F

Table VII(B)36
COMPOSITION OF EXPERIMENTAL GREASES

No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Calcium Stearate 10%	Calcium Stearate 9.7%	Calcium Stearate 9.7%	Calcium Stearate 11%	Aluminum Stearate 13%	Zinc Stearate 20%
Calcium Oleate 10%	Calcium Oleate 9.7%	Calcium Oleate 9.7%	Calcium Oleate 11%	Heavy Lubricating Oil 87%	Turbine Oil 80%
	Zinc Powder 2.0%	Zinc Stearate 1.0%	Heavy Lubricating Oil 28%		
Turbine Oil 80%	Turbine Oil 78.6%	Zinc Oleate 1.0%			
		Turbine Oil 78.6%			

Table VIII(B)36
SEA WATER-PROOF GREASE

	Compositions						
	Mineral Oil (%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid (%)	Free Fatty Oil (%)
Experimental Grease No. 5 for Sea Water-Proof	87	13	trace	0.94	none	0.5	none

	General Properties				
	Appearance	Consistency* at 25°C	Dropping Pt. (°C)	Corrosion	Stability (100°C 3 hrs.)
Experimental Grease No. 5 for Sea Water-Proof	Adhesive Smooth	310	88.3	O.K.	no oil bleeding

	Mineral Oil				Soap Fatty Acid		
	F. P. (°C)	Viscosity 210°F (S.U.S)	V. I.	C. R. (%)	M. P. (°C)	Sap. Value	Iod. Value
Experimental Grease No. 5 for Sea Water-Proof	270	141	15	5.0		193	3.1

*Worked Penetration, A.S.T.M.

Table IX(B)36
VARIOUS SPECIAL GREASES

Name of Greases	Components		Conditions of Mixing or Compounding	Milling	Uses
Experimental grease for magneto	Castor oil sodium soap Light lubricating oil	22.3% 68.7%	Saponification and Compounding at 230°C	Milling	(1) For magnetos, generators and motors etc. (2) For back sliding gear box of V.D.M. type Controllable-pitch propeller.
Experimental grease for controllable-pitch propeller	Aluminum stearate Aluminum oleate Lead oleate Glycerine Heavy lubricating oil	6.48% 0.72% 0.80% 0.40% 91.60%	Compounding at 150°C	No	(1) For controllable pitch propeller of Hamilton-Type.
Experimental grease for Rocker arms	Sodium stearate Sodium oleate Glycerine Calcium stearate Calcium oleate Heavy lubricating oil	3.0 % 3.0 % 0.4 % 1.0 % 1.0 % 91.2 %	Saponification and Compounding at 150-160°C	Milling	(1) For rocker box of aero-engine. (2) Will be useful for the lubrication of gears and valves which operate at high temperature.
Experimental grease for framework of aero-torpedo	Aluminum stearate Calcium stearate Cylinder lubricating oil for aero-torpedo	7.0 % 0.21% 92.79%	Compounding at 150°C	No	(1) For the anti-corrosives of engine parts.
Experimental anti-corrosive grease for interior of compressed air chamber of aero-torpedo	Aluminum stearate Calcium stearate Cylinder lubricating oil for aero-torpedo	12.0 % 0.36% 87.64%	Compounding at 150°C	Milling	(1) For the anti-corrosives of the interior of compressed air chamber of aero-torpedo.*
Experimental water-proof grease resistant sea water	Aluminum stearate Heavy lubricating oil	13.0 % 87.0 %	Compounding at 150°C	Milling	(1) For the lubrication and anti-corrosive of sliding parts of the machine gun mounted on submarines.

*For the lubricating of sliding parts of the periscope mounted on submarines.

Table X(B)36
COMPOSITIONS AND PROPERTIES OF SPECIAL GREASES

	Compositions							General Properties**				
	Mineral Oil(%)	Soap (%)	Water (%)	Ash (%)	Free Alkali (%)	Free Fatty Acid(%)	Free Fatty Oil(%)	Appearance	Consistency* At 25°C		Viscosity 210°F (S. U. S.)	Dropping Pt. (°C)
Experimental Grease for magneto	68.7	22.3	0.5	3.44	0.12	0.0		Smooth texture	(At-20°C) 180	254		175
for controllable-pitch propeller	91.6	8.0	trace	1.08	0.00	0.67	none	Stringy viscous mobile	(At 10°C) 347			40
for rocker arms	91.2	7.49	0.20		0.00	0.31		Semi Fluid smooth		360		119
for framework of aero-torpedo	92.79	7.21	0.05	0.50	none		none	Liquid	(At-40°C) 284	Too fluid	1,036	
as anticorrosive for interior aero-torpedo	87.64	12.36	0.04	0.80	none		none	Smooth		326		90
for water-proofing against sea water	87.00	13.00	trace	0.94	none		none	Adhesive smooth		310		88

	Properties of Mineral Oil						Characteristics of Soap Fatty Acid			
	Flash Point (°C)	Vis(S.U.S.) 210°F	Vis. Index	Vis(Red-wood sec.)	Setting Point (°C)	C. R. (%)	Melting Point (°C)	Acid Value	Sap. Value	Iod. Value
Experimental Grease for magneto	155			130.8	(-)30	0.02		182.6	192.9	84.6
for controllable-pitch propeller	263	133.4	87.5		(-)15.5	0.40				
for rocker arms	218	95.0	67.3		(-)18.0	2.01	55	198	202.6	44
for framework of aero-torpedo	203	61.9	85.3		(-)36	0.36	65~67	202	206	0
as anticorrosive for interior aero-torpedo	203	61.9	85.3		(-)36	0.36	65~67	202	206	0
for water proofing against sea water	270	141	15		(+)1	5.0		193	193	3.1

*Worked Penetration, A.S.T.M.

**All these greases were non-corrosive and in the stability test there was no oil bleeding (100°C, 3 hrs).

Table XI(B)36
EQUIPMENT FOR GREASE MANUFACTURE

Part I

	Name of Equipment	Set	Remarks	Capacity
For Metallic Soaps	Dissolving tank	2	Enameled ironware with stirring mechanism, steam coil heating	$1,000m^3$
	Saponification vessel	3	Enameled ironware with stirring mechanism, jacket steam heating	$1,000m^3$
	Double-decomposition vessel	4	Enameled ironware with stirring mechanism, steam jacket heating	$1,500m^3$
	Double-decomposition vessel	2	Enameled ironware with stirring mechanism, steam jacket heating	
	Centrifuge	5		
	Steam heated drier	4		
	Alkali tank	1		
	Oleic acid tank	1		

Part II

	Name of Equipment	Set	Remarks	Capacity
Grease Kettles	Indirect-steam heated kettle	3	Steel with double-motion agitator	$1,500m^3$
	Indirect-electrically heated kettle	3	Steel with double-motion agitator	$500m^3$
	Measuring tank	3	Enameled ironware	$1,000m^3$

Part III

	Name of Equipment	Set	Remarks	Capacity
Grease Milling	Three roller mixing machine	3		

Part IV

	Name of Equipment	Set	Remarks	Capacity
Others	Transformer	3		
	Mineral oil storage tank	2		$10,000m^3$
	Mineral oil storage tank	1		$5,000m^3$
	Pump	6		

		Raw Materials	Procedures	Conditions	Used Plant
Greases	Controllable-pitch propeller grease	Aluminum stearate Aluminum Oleate Lead oleate Glycerine Mineral oil	Compounding: Aluminum stearate, aluminum oleate, lead oleate, glycerine and mineral oil is thoroughly mixed in the cold and then the mixture is compounded by heating. After the mixture is perfectly dissolved, the grease is then slowly cooled under slow agitation and then poured into product tank.	Temp. of compounding at 130~150°C Time of heating at comp. temp: 3~4 hrs. Cooling to room temp: by cooling water jacket. Time for cooling: 12 hrs. Total time from charge to products: 24 hrs.	Indirect steam heated steel kettle
	Special grease for framework of aero-torpedo	Aluminum stearate Calcium stearate Cylinder oil for aero-torpedo	Compounding: Aluminum stearate, calcium stearate and oil are thoroughly mixed in the cold and then the mixture is compounded by heating, comp. & after treatments are same as case of controllable-pitch propeller grease.	Temp. of compounding at 130~150°C	Indirect steam heated steel kettle
	Special grease as the anticorrosives for the interior of compressed air chamber of aero-torpedo	Aluminum stearate Calcium stearate Cylinder oil for aero-torpedo	Compounding: Aluminum stearate, calcium stearate and oil are thoroughly mixed in the cold and then compounded by heating. After the mixture is perfectly dissolved, the grease is then poured into cooling pans & placed in ordinary temp. The grease is then milled.	Temp. of compounding at 130~150°C Time of heating at comp. temp: 3~4 hrs.	Indirect steam heated steel kettle Three roller mixer
	Sea water-proof grease	Aluminum stearate Heavy lubricating oil	Compounding: Same as anticorrosive grease. After the compounding and cooling, the grease is milled.	Temp. of compounding at 130~150°C Time of heating at comp. temp: 3~4 hrs.	Indirect steam heated steel kettle Three roller mixer

Table XII(B)36 (Cont)
GREASE MANUFACTURING PROCEDURES

Table XII(B)36 (Cont'd)
GREASE MANUFACTURING PROCEDURES

		Raw Materials	Procedures	Conditions	Used Plant
Metallic Soaps	Aluminum stearate	Stearic acid Caustic soda Aluminum sulphate	Saponification: Stearic acid is saponified by heating with caustic soda and water. Double decomposition: 5% of sol'n. of sodium stearate is converted to metallic soap by treatment with 25% sol'n. of aluminum sulphate.	Temp. of saponification, at 95~98°C Temp. of double decomposition at 60°C	Saponification vessel Double decomposition vessel
	Aluminum oleate	Oleic acid Caustic soda Aluminum sulphate	Saponification: Oleic acid is saponified by heating with caustic soda and water. Double decomposition: Same as aluminum stearate.	Temp. of saponification, at 95~98°C Temp. of double decomposition at 30°C	Saponification vessel Double decomposition vessel
	Lead oleate	Oleic acid Caustic soda Lead acetate	Saponification: Same as aluminum oleate Double decomposition: 5% sol'n. of sodium oleate is converted to metallic soap by treatment with a 5% sol'n. of lead acetate.	Temp. of saponification, at 95~98°C Temp. of double decomposition at 30°C	Saponification vessel Double decomposition vessel
	Calcium stearate	Stearic acid Caustic soda Calcium chloride	Saponification: Same as aluminum stearate. Double decomposition: 5% sol'n. of sodium stearate is converted to metallic soap by treatment with a 5% sol'n. of calcium chloride.	Temp. of double decomposition at 60°C	Saponification & Double decomposition vessel
	Calcium oleate	Oleic acid Caustic soda Calcium chloride	Saponification: Same as aluminum oleate Double decomposition: Same as calcium stearate.	Temp. of double decomposition at 30°C	Saponification & Double decomposition vessel
Greases	Magneto grease	Castor oil Caustic soda Lubricating oil	Saponification and Compounding: Castor oil and mineral oil are saponified by heating with 40% sol'n. of caustic soda & then compounded. The grease is then poured into cooling pans & may be cooled, is milled.	Temp. of saponification, at 100°C Temp. of compounding, at 230°C	Electrically heated steel kettle Three roller mixer
	Rocker arm grease	Stearic acid Oleic acid Caustic soda Glycerine Mineral oil Calcium stearate Calcium oleate	Saponification and Compounding: Fatty acids and mineral oil are saponified by heating with 30% sol'n. of caustic soda, and then calcium soaps are added to mixture and is compounded by heating. The grease is poured into cooling pans, after cooling, is milled.	Temp. of saponification, at 100°C Temp. of compounding at 150~160°C	Electrically heated steel kettle Three roller mixer

ENCLOSURE (B)36

Table XIII(B)36
FLOWSHEET OF GREASE MANUFACTURE

Raw Materials	Charge (kgs)	Balance			Intermediates & Products
Stearic acid	40	100	Saponification	Double Decomposition Washing & Drying	Aluminum-stearate 34 kgs, 85% per stearic acid
Caustic soda	6	15			
Aluminum sulphate	18.8	47			
Oleic acid	25	100	Saponification	Double Decomposition Washing & Drying	Aluminum-oleate 22.5% kgs, 90% per oleic acid
Caustic soda	3.8	15			
Aluminum sulphate	12.0	47			
Oleic acid	25	100	Saponification	Double Decomposition Washing & Drying	Lead-oleate 22.5 kgs, 90% per oleic acid
Caustic soda	3.8	15			
Lead acetate	22.5	90			
Fatty acid	40	100	Saponification	Double Decomposition Washing & Drying	Calcium soap 32 kgs, 80% per fatty acid
Caustic soda	6	15			
Calcium chloride	14	35			
	(kgs)	(%)			(Product)
Castor oil	56	79.2	Saponification & Compounding	Cooling & Milling	Magneto grease 245 kgs Yield: 94%
Caustic soda	11	3.7			
Light lub. oil	250 lit	77.1			
Total	292	100			
	(kgs)	(%)			
Stearic acid	10.5	3.0	Saponification & Compounding	Cooling & Milling	Rocker arm grease 336 kgs Yield: 96%
Oleic acid	10.5	3.0			
Caustic soda	3.15	0.9			
Glycerine	1.40	0.4			
Calcium stearate	3.5	1.0			
Calcium oleate	3.5	1.0			
Heavy lub. oil	317.5	90.7			
Total	350	100			
	(kgs)	(%)			
Aluminum stearate	64.8	6.48	Compounding		Controllable pitch propeller grease 980 kgs Yield: 98%
Aluminum oleate	7.2	0.72			
Lead oleate	8.0	0.80			
Glycerine	4.0	0.40			
Lubricating oil	916.0	91.60			
Total	1000	100			
	(kgs)	(%)			
Aluminum stearate	70.0	7.00	Compounding		Anticorrosive liquid grease for aero-torpedo 990 kgs Yield: 99%
Calcium stearate	2.1	0.21			
Lub. oil for aero-torpedo	927.9	92.79			
Total	1000	100			
	(kgs)	(%)			
Aluminum stearate	120	12.00	Compounding	Cooling & Milling	Anticorrosive grease for the interior of compressed air chamber 960 kgs of aero-torpedo Yield: 96%
Calcium stearate	3.6	0.36			
Lub. oil for aero-torpedo	876.4	87.64			
Total	1000	100			
	(kgs)	(%)			
Aluminum stearate	130	13.0	Compounding	Cooling & Milling	Sea water proof grease 960 kgs, Yield: 96%
Heavy lub. oil	870	87.0			
Total	1000	100			

ENCLOSURE (B)36

Table XIV(B)36
LUBRICATING OILS

Base oils for	Flash point (°C)	Viscosity		Vis. Index	Setting point (°C)	Carbon Residue (%)
		(S.U.S.) (210°F)	(Redwood) (sec.) at 30°C			
Magneto grease	155		130.8		30	0.02
Rocker arm grease	218	95.0		67.3	18	2.01
Controllable-pitch propeller grease	268	133.4		87.5	15.5	0.40
Aero-torpedo grease	203	61.9		85.3	36	0.36
Sea water-proof grease	270	141.0		15.0	1	5.0

Table XV(B)36
SOAP STOCKS

	M.P. (°C)	Acid Value	Sap. Value	Iod. Value	Remarks
Castor oil		0.5	192.9	84.6	
Stearic acid	63.0	189	193	3.1	Hydrogenated tea-seed fatty acid
Oleic acid					Tubaki-seed fatty acid
Stearic acid	65~67	202	206	0	Market, pure

Table XVI(B)36
INTERMEDIATES

	Moisture (%)	Residue after burning (%)	
		Total	Water Soluble
Aluminum stearate	0.5	8.16	.8
Aluminum oleate	1.0	10.5	1.6
Lead oleate	1.0		
Calcium soap (stearic 50%, oleic 50%)	0.3	12.3	.5

Table XVII(B)36
PRODUCTS*

	Appearance	Consistency (at 25°C)		Dropping Point (°C)	Free Alkali (%)	Free Fatty Acid (%)	Water (%)	Ash (%)
Magneto grease	Smooth texture	180 at -20°C	250	171	0.10	none	0.3	3.5
Rocker arm grease	Semi-fluid Smooth texture		350	130	none	0.4	0.5	1.5
Controllable-pitch propeller grease	Stringy viscous fluid		350 at 10°C	75	none	1.0	trace	1.2
Liquid grease for the framework of aero-torpedo	Fluid texture	290 at -40°C	Vis.(S.U.S.) 210°F 1,500 cal.		none		0.4	0.37
Anticorrosives for the interior of compressed air chamber	Smooth texture		310	92	none	0.5	0.1	0.90
Sea water-proof grease	Adhesive smooth		330	86	none	0.5	0.1	1.0

*All these greases were non-corrosive and possessed satisfactory stability (100°C, 3 hr).

Table XVIII(B)36
COMPOUNDING AND PROPERTIES OF SPECIAL GREASES

	Products (Remarks)	Yield (%) per charge	Appearance	General Properties **							
				Consistency* at 0°C	Consistency* at 25°C	Dropping Pt. (°C)	Mineral Oil (%)	Free Alkali (%)	Free Fatty Acid (%)	Water (%)	Ash (%)
Magneto grease	In pilot plant	94	Smooth texture	(-)20 189	250	171		0.10	none	0.3	3.5
	In laboratory		Smooth texture	180	254	175	68.7	0.12	none	0.5	3.44
Rocker arm grease	In pilot plant	96	Semi-fluid Smooth		350	130	90.7	none	0.40	0.50	1.5
	In laboratory		Semi-fluid Smooth		360	119	91.2	0.0	0.31	0.20	1.5
Controllable-pitch propeller grease	In pilot plant	98	Stringy Viscous Fluid	(+)10 350		75	91.6	none	1.0	trace	1.2
	In laboratory		Stringy Viscous Fluid	350		40	91.6	none	0.67	trace	1.08
Anti-corrosive liquid grease for the framework of aero-torpedo	In pilot plant	99	Fluid	(-)40 290		Viscosity (S.U.S.) 210°F 1500	92.79			0.4	0.37
	In laboratory		Fluid	284		1036	92.79		0.5	0.05	0.50
Anti-corrosive grease for the interior of compressed air chamber of aero-torpedo	In pilot plant	96	Smooth texture		310	92	87.6		0.5	0.10	0.9
	In laboratory		Smooth texture		330	89	87.6		0.5	0.04	0.8
Sea Water-proof grease	In pilot plant	96	Adhesive smooth		330	86	87	none	0.5	0.1	1.0
	In laboratory		Adhesive smooth		310	88	87	none	0.5	trace	0.94

*Worked Penetration, A.S.T.M.

**All these greases were non-corrosive and in the stability test there was no oil bleeding (100°C 3 hrs).

Table XVIII(B)36 (Cont'd)
COMPOUNDING AND PROPERTIES OF SPECIAL GREASES

Name of Greases	Formula		Charge	Type of Grease Kettle Used	Performance Treatments
Magneto grease	Castor oil Caustic soda Water Light lubricating oil	19.2% 3.7% 77.1%	56 kgs 11 kgs 250 lit Total 300 kgs	Electrically heated kettle 500 liter capacity	Cooking and compounding at 230°C Cooling without agitation in cooling pan Milling by three roller mill
Rocker arm grease	Stearic acid Oleic acid Caustic soda Calcium stearate Calcium oleate Glycerine Heavy lubricating oil	3.0% 3.0% 0.9% 1.0% 1.0% 0.4% 90.7%	Total charge 350 kgs	Electrically heated kettle 500 liter capacity	Cooking and compounding at 150-160°C Cooling without agitation in cooling pan Milling by three roller mill
Controllable-pitch propeller grease	Aluminum stearate Aluminum oleate Lead oleate Glycerine Lubricating oil	6.48% 0.72% 0.80% 0.40% 91.60	Total charge 1000 kgs	Indirect steam heated kettle 1500 liter capacity	Compounding at 130-150°C Slow cooling with agitation
Anti-corrosive liquid grease for the framework of aero-torpedo	Aluminum stearate Calcium stearate Lubricating oil for aero-torpedo	7.0% 0.21% 92.79%	Total charge 1000 kgs	Indirect steam heated kettle 1500 liters capacity	Compounding at 130-150°C Slow cooling with agitation
Anti-corrosive grease for the interior of compressed air chamber of aero-torpedo	Aluminum stearate Calcium stearate Lubricating oil for aero-torpedo	12.0% 0.36% 87.64%	Total charge 1000 kgs	Indirect steam heated kettle 1500 liter capacity	Compounding at 130-150°C Cooling without agitation in cooling pan Milling by three roller mill
Sea water-proof grease	Aluminum stearate Heavy lubricating oil	13.0% 87.0%	Total charge 1000 kgs	Indirect steam heated kettle 1500 liter capacity	Compounding at 130-150 C Cooling without agitation in cooling pan Milling by three roller mill

ENCLOSURE (B)36

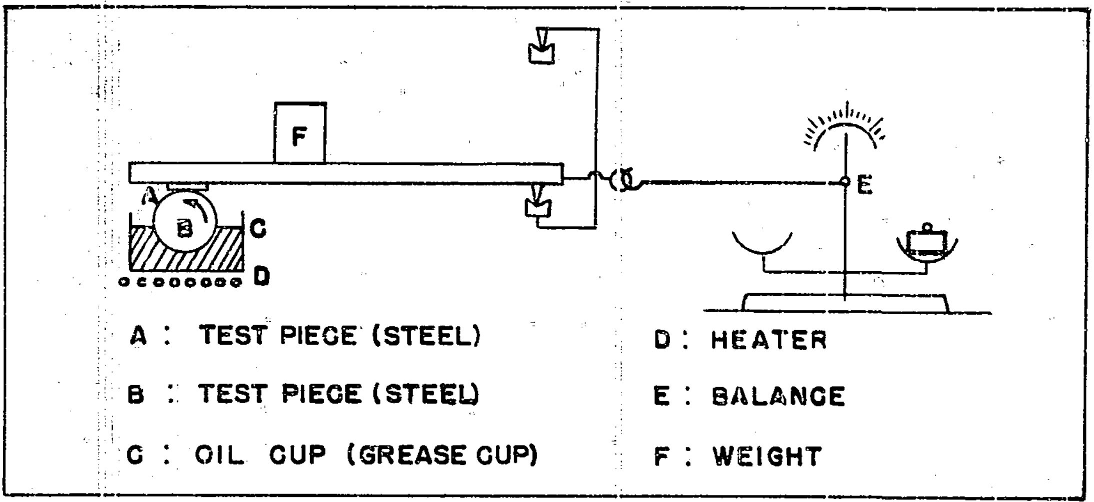

Figure 1(B)36
SKETCH OF MECHANISM OF BEARING TYPE TESTING APPARATUS

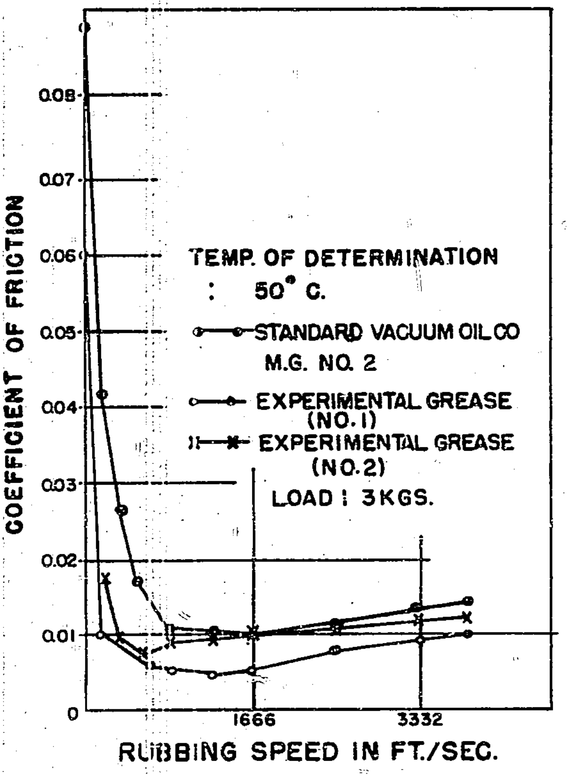

Figure 2(B)36-a
CHART OF COEFFICIENT OF FRICTION
BEARING TYPE TESTING MACHINE

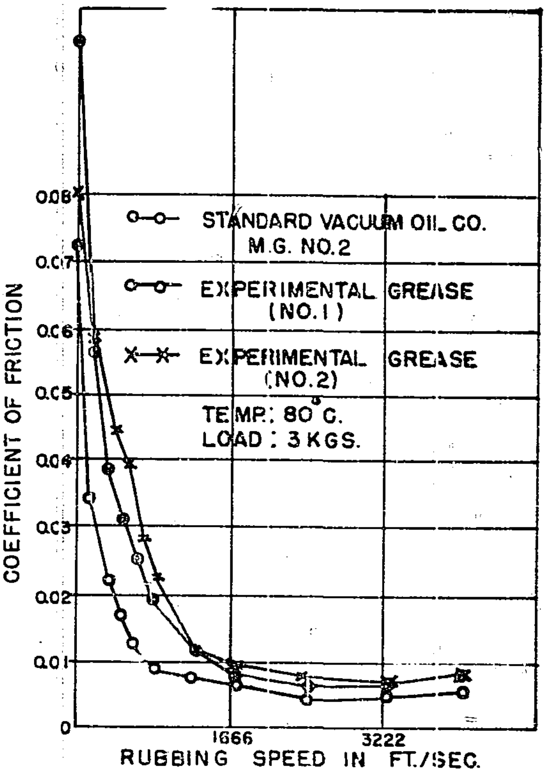

Figure 2(B)36-b
CHART OF COEFFICIENT OF FRICTION
BEARING TYPE TESTING MACHINE

ENCLOSURE (B)36

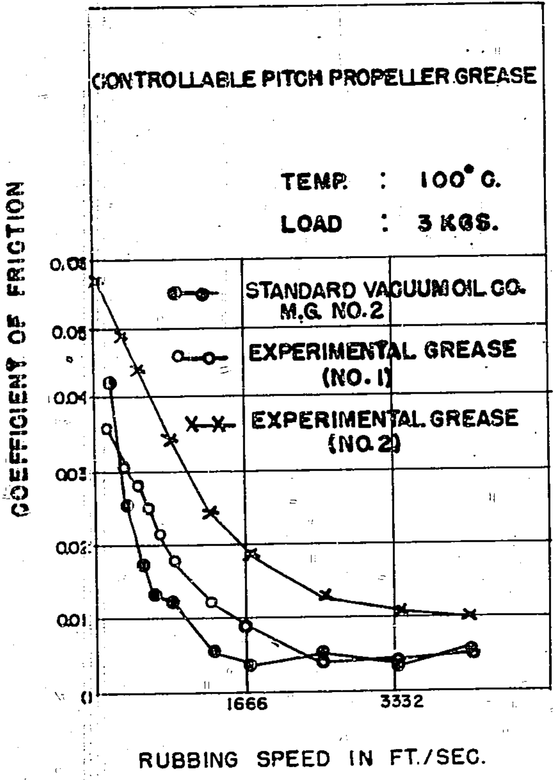

Figure 2(B)36-c

CHART OF COEFFICIENT OF FRICTION

BEARING TYPE TESTING MACHINE

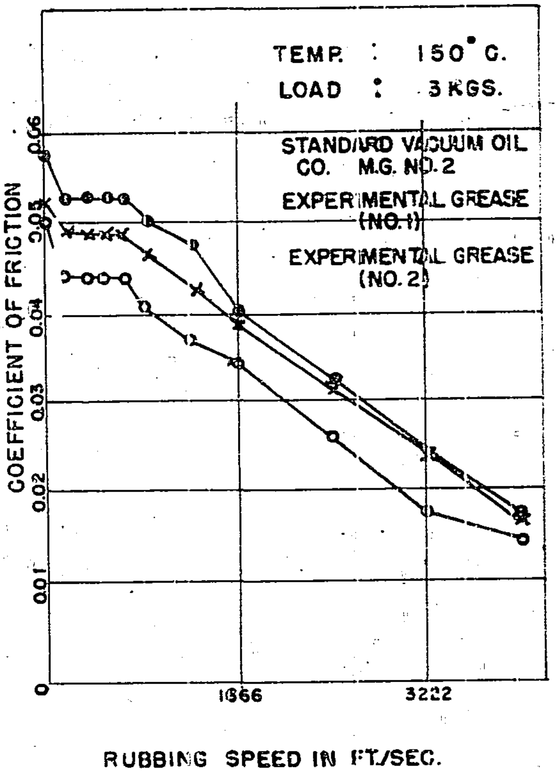

Figure 2(B)36-d

CHART OF COEFFICIENT OF FRICTION

CONTROLLABLE PITCH PROPELLER GREASE

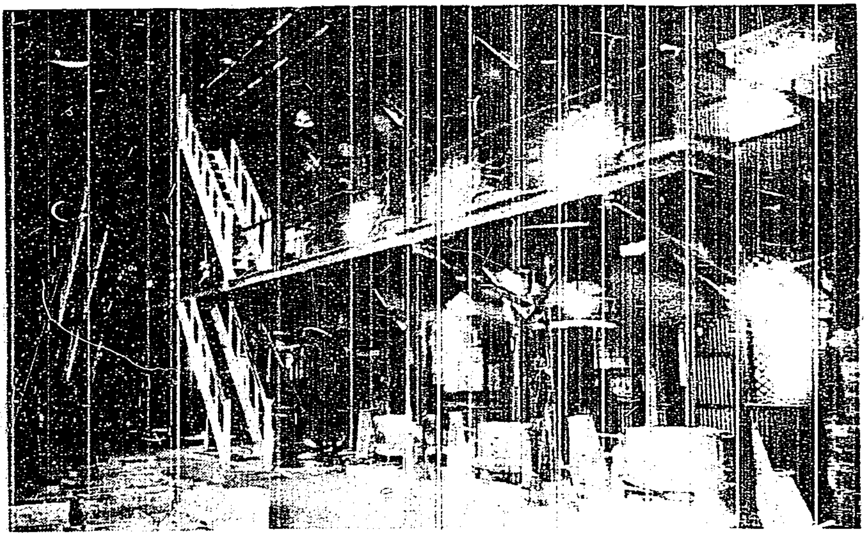

Figure 3(B)36

PILOT PLANT FOR MANUFACTURING GREASES

ENCLOSURE (B)36

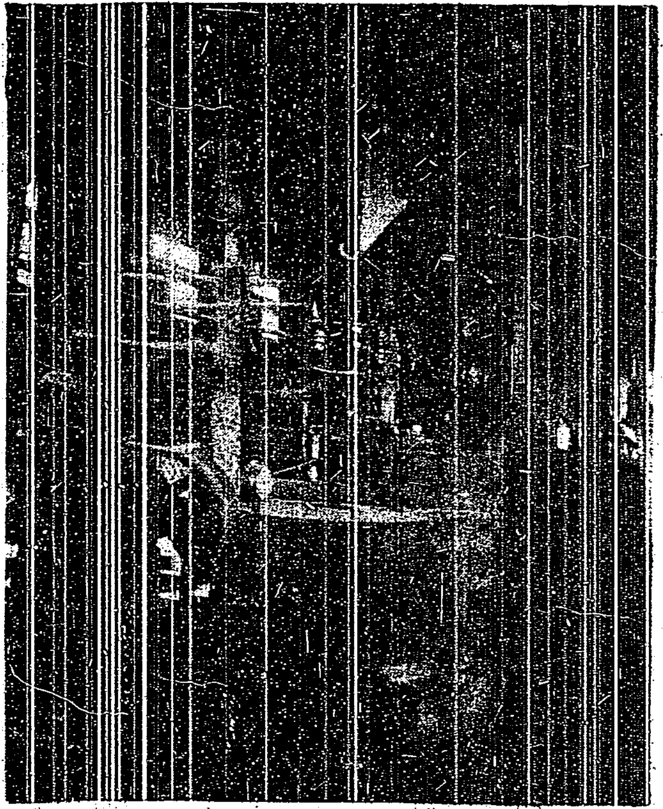

Figure 4(B)36
DOUBLE DECOMPOSITION VESSELS

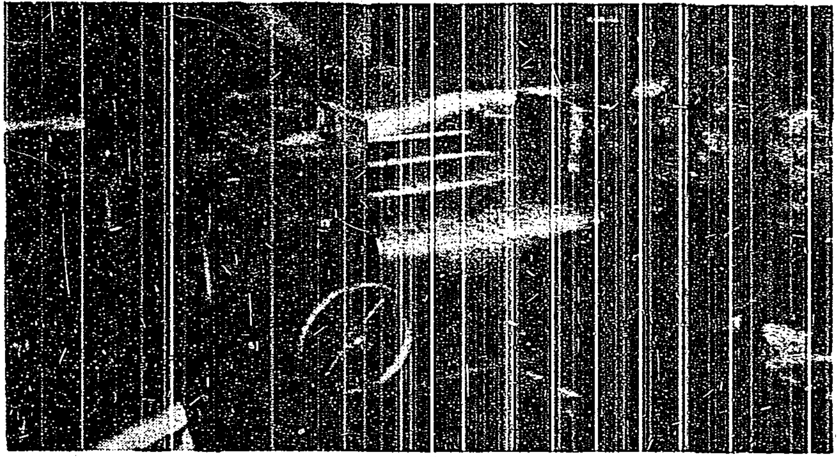

Figure 5(B)36
THREE ROLLER TYPE MILLING MACHINE

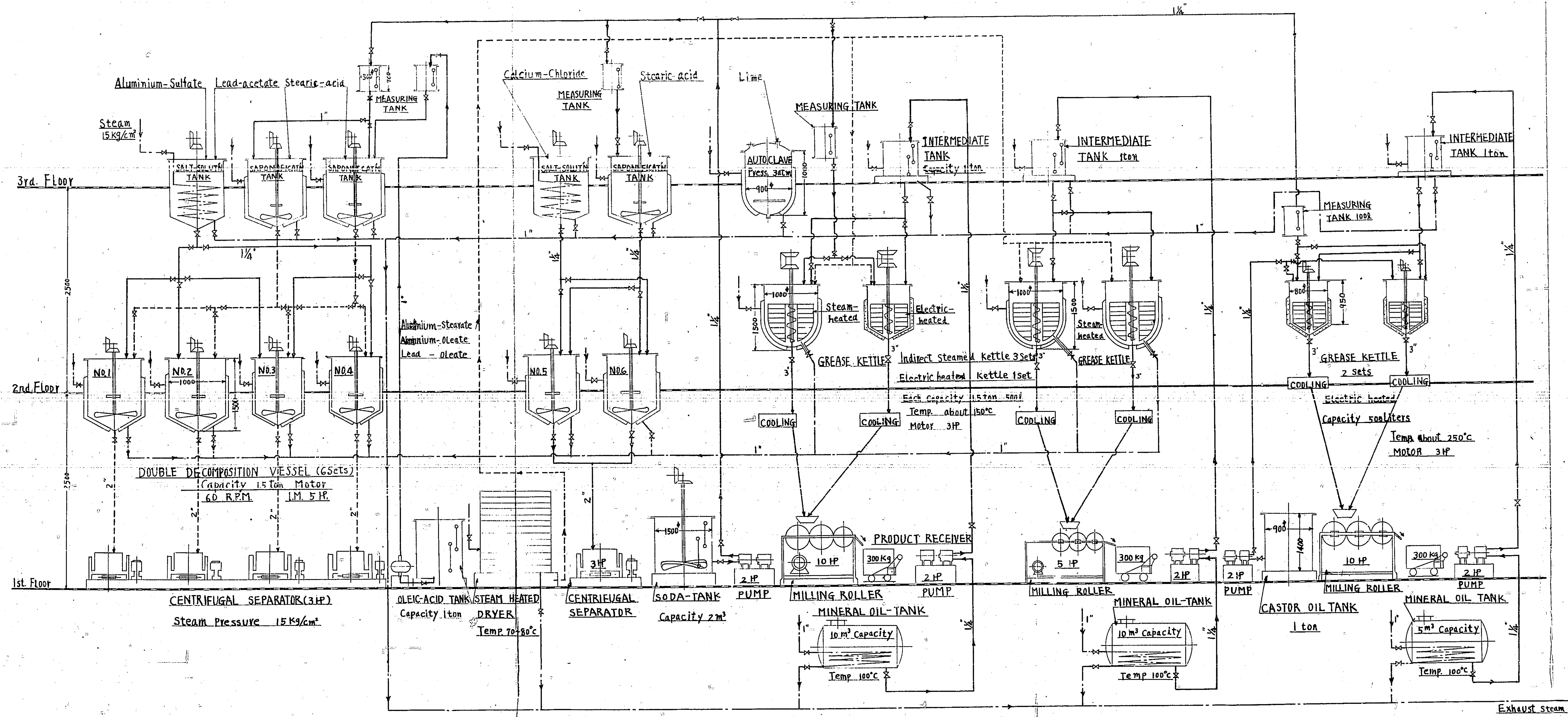

PLATE I(B)36

FLOW SHEET OF PILOT PLANT FOR GREASE MANUFACTURE

ENCLOSURE (B)36

PART II

MANUFACTURE OF LUBRICATING GREASE FROM SYNTHETIC LUBRICATING OIL IN PLACE OF NATURAL OIL

by

CHEM. ENG. CAPT. DR., I KAGEHIRA
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CHEM. ENG. LT. M. ABE

Research Period: 1943-1944

SUMMARY

In studying various synthetic lubricating oils as base oils for the manufacture of various greases, it was observed that for the calcium or sodium soap greases, condensation products of olefinic and aromatic hydrocarbons were suitable.

I. INTRODUCTION

When soaps are mixed in mineral oil with agitation and this mixture is heated, gradually the soap dissolves in the mineral oil. On cooling, dissolved soaps are crystallized out. The mineral oils as the dispersion medium are enveloped by the crystal structure, and it is assumed that a special structure such as a honey comb form is produced. Then, there are protective colloidal matters to guard the arrangement of this crystal structure. The protective matters in the case of calcium soap are hydroxide compounds such as water, alcohol, glycerine sugars, etc. When synthetic oil was used in place of natural mineral lubricant investigations were made to determine whether paraffinic or aromatic synthetic types of oils were more suitable for the manufacture of greases. Generally the natural lubricant from crude oil consists of aromatic hydrocarbons, which have good solubility and affinity for soaps compared to paraffinic hydrocarbons.

It was concluded that the condensation product of olefinic hydrocarbons and aromatic hydrocarbons (naphthalene, benzene, etc.) would be suitable. Low viscosity oils, in general, have the property of good solubility in soap, so that, even paraffinic polymerization oils of low viscosity would also be suitable to make several types of greases.

These studies were carried on during 1944.

II. DETAILED DESCRIPTION

A. Calcium Soap Base Grease:

In the manufactures of "Cup Grease," containing calcium soaps, two methods are generally used:

1. Calcium soaps (calcium-stearate and oleate) are added to mineral oil, well mixed by stirring and heated to 80°C. Then water (alkaline water solution which contains NaOH below 0.2% for total oil) is added, and heated quickly to 105°C with agitation, until the water content is below 2% as judged by consistency. Then the grease is cooled to 80°C.

2. Fatty acids (stearic-and oleic-acid) are added and dissolved in mineral oil by heating. At below 70°C a slight excess of the theoretical value of calcium hydroxide solution, calculated from the saponification value of the fatty acids, are added. The mixture is heated with agitation, keeping below 105°C, and the excess water is evaporated gradually. When the plasticity increases suddenly, heating is stopped and the temperature is decreased to 80°C.

But in either method, if the calcium soap base grease retains a trace of alkali, it is difficult for the grease to have the desired consistency.

The first method of preparation has the defect that the distribution of water is not uniform, and it is difficult to make grease of uniform composition.

On the contrary, the second method is very easy and provides grease of uniform composition. Generally, the consistency of calcium soap base grease is affected by water content to some extent, the more water, the harder.

B. No. 1 and No. 2 Cup Greases

These greases are mixtures of the calcium soaps and a mineral oil which has a viscosity over 50 Redwood No. 1 sec. at 30°C. and a flash point above 130°C. Natural mineral oil (viscosity about 130 sec. at 30°C in Redwood No. 1 sec.) made from Niizu crude oil, has an aniline point of about 80 and grease of good stability is easily manufactured using this oil.

Polymerization oil made from cracked distilled waxes, which has the same viscosity as the above-mentioned oil, has an aniline point of about 116. In manufacturing the cup grease from the polymerization oil, the soap is mixed in with difficulty and the soap is inclined to separate from the oil. Therefore, with such polymerization oils more than 50% of calcium soap of an unsaturated fatty acid, such as oleic acid, must be added in order to produce good stability grease of higher consistency. However the grease thus obtained does not meet the Naval Specifications in regard to soap content.

When oil prepared by the simultaneous condensation of olefines and aromatic compounds (benzene and naphthalene) is used, a grease can be made which is as stable as natural mineral oil. The synthesis of such oil was carried on as follows: The c acked distillate was polymerized alone or with benzene or naphthalene in the presence of 5% of $AlCl_3$, at 80-100°C for 10 hrs. This product was distilled in a vacuum of 5mm Hg and the fraction boiling below 300°C. is used as the raw material for making greases. Table XIX(B)36 shows their properties.

Naphthalene-benzene condensation oil, topped to 280°C, has a low aniline point as shown in Table XX(B)36 and is the suitable material for this grease. This method has the advantage of utilizing the by-product (light end) in the synthesis of aero engine oil.

ENCLOSURE (B)36

C. Cup Grease for Cold-Proof (low temperature) Grease (so called "No. 4 Grease"

Since the greases of synthetic oil have a lower freezing point than those of natural mineral oil, they should be good for low temperature.

The natural mineral oil (class No. 3 precise oil) had about an 80 aniline point, and so synthetic oils which had aniline points of the same order were prepared from the condensation of the cracked distillate of paraffin wax with benzene, toluene, cyclohexane, naphthalene and benzene, or naphthalene and toluene.

The synthetic oils had pour points below (-) 60°C., so it was possible to prepare good cold proof greases from them. It was found that naphthalene and benzene, and, naphthalene and toluene condensation oils were the most suitable. In order to obtain the lowest pour point of the naphthalene and benzene condensation oil, it was found that a ratio of 15 parts naphthalene to 85 parts of benzene by volume was required, as shown in Figure 6(B)36.

2% of anhydrous aluminum chloride was added and after the catalyst was completely dissolved by heating at about 80°C, four parts of cracked distillate from waxes (boiling from 150°C to 230°C.) to one part of aromatic compound, were dropped in and kept at a high temperature.

Then the aromatic compounds were completely condensed with the cracked distillate and a 50% yield of oil having a pour point below -60°C, was obtained. (When 1.5% of anhydrous $AlCl_3$ and 0.5% of anhydrous $ZnCl_2$ were used, dechlorination of polymer was very easy.)

The properties of "No. 4 Cup Grease" made from this synthetic oil are shown in Table XXI(B)36

D. "Mobile Grease" for Controllable-Pitch Propellers (Known in Japanese Navy as "No. 5 Grease")

It is necessary that the base oil of this grease have a high viscosity (115 S. U. S. at 210°F). Using polymerization oil cracked distillate or its condensation with naphthalene or naphthalene and benzene, good results were obtained as seen in Table XXII(B)36.

Aluminium stearate, aluminium oleate, lead oleate and glycerine are added to about one third of the synthetic oil to be used, heated to about 130°C, with attendant stirring. After the water present is evaporated and the mixing of the soaps in the oil is complete, the remaining two thirds of the oil are added. Keeping at about 130°C, the mixture is well agitated for 3-5 hours, then the grease is cooled to 80°C.

E. Grease for Rocker Arms. (So called "No. 6 Grease")

The base oil used in this study was a condensation oil of cracked distillate of wax with naphthalene and benzene. Table XXIII(B)36 shows its properties.

Fatty acids were added to about one third of the synthetic oil to be used and the mixture was heated while stirring continuously. After adding approximately 20% water solution which contained the calculated amount of sodium hydroxide at about 40°C, the temperature was gradually raised and the water evaporated. Calcium soaps were added at about 130°C and then cooled to 120°C. Next the residual two thirds of oil and glycerine were put in and well mixed for 1.5 hours at 120°C and then taken out at 100°C.

In manufacturing this grease, one of the most important factors was that the oil be weakly acid when mixed and when free fatty acids were 0.4-0.5%, good results were obtained. But, when the amounts of free acid were below 0.2%, their stability was not only bad, but their consistency was inclined to increase. Although glycerine was effective in providing heat stability, excess glycerine had a tendency to increase the consistency. Consequently the quantity of glycerine is a very significant factor.

F. <u>Magneto Grease (So-called "No. 7 Grease")</u>

Generally, the manufacturing method for this grease was as follows:

About 20% of sodium soaps of castor oil were added to the mineral oil and mixed at more than 200°C. The properties of the base oil were:

Flash point	above 170°C
Viscosity in Redwood No.1 sec.	over 200 sec at 30°C
Pour point	-30°C.(below)

Mineral oil used was a refined distillate of NIIZU crude oil, of which the properties are as follows:

Viscosity in Redwood No.1 sec.	about 208 at 30°C
Aniline point (°C)	81.5
Flash point (°C)	183
Pour point (°C)	-47

This grease also contained the sodium soap of sebatic acid which formed from the cracking of some ricinoleic acid.

In another case the mixed sodium and calcium soaps were used and heated to 170°C. Then studies were carried on to determine whether oils of either paraffinic or naphthenic structure were suitable for preparing this grease. This work showed that the polymers of cracked wax distillate were not suitable for preparing magneto grease, because the castor oil soap separated.

Table XXIV(B)36 presents the details of the grease preparation from the condensation oil.

Although this is an excellent cold-proof grease, as the table shows, it will be noticed that some soap separates from the oil at the dropping point. However, the stability is improved if the calcium oleate (1%) and glycerine (0.2%) are added Table XXV(B)36 shows the results:

Thus, when the viscosity of oil is about 200 Redwood No. 1 sec. at 30°C and its aniline point is below 90, the naphthenic oil is excellent as the base oil, but oil with an aniline point above 90, however, is not suitable. Therefore, this method was tried using other soaps. In this study, the synthetic oils, aniline points of which are 90-105, were used with mixed sodium and calcium soaps of fatty acids, (stearic and oleic). The results show that these were suitable materials, as seen in Table XXVI(B)32.

Whether castor oil or other fatty acids are to be used, depends upon the aniline point of the base oil. In the case of using sodium soap, castor oil or fatty acids were generally added in ratio of one third of the mineral oil used, and saponified by adding a 20% solution of the calculated amount of NaOH at 40-70°C. The water present is gradually evaporated by heating to 130°C. In the case of castor oil, after the oil was heated for 30-60 minutes at 200°C (with agitation), the residual two-thirds of mineral oil was added. After agitation, the grease was drawn at 170°C, and cooled quickly.

In the case of mixed-base soaps prepared from fatty acids, the sodium soap was first added to one third of the oil and the mixture heated to 130°C.

Then the calcium soap and glycerine were added and heated to 150°C after which the remaining oil was added. After heating for 1.5 hours, the grease was cooled quickly.

III. CONCLUSIONS

The methods of A - B for "Cup Grease" manufacture are very satisfactory, and one of the most suitable synthetic lubricants is the condensation oil of olefines with naphthalene and benzene.

For cold-proof grease ("No. 4 Cup Grease"), the best base oil is the one which is made by condensation of cracked wax distillate (boiling from 150°C to 230°C) with naphthalene and benzene.

For "Mobile Grease" (No. 5 Grease), a polymerization product of olefines is unsuitable due to soap separation. It is necessary that the properties of condensed oil be as follows:

Viscosity in S. U. S. at 210°F.........	..125
Aniline point (°C)	below 15

For "Rocker Arm Grease" ("No. 6 Grease"), polymerization oil is unsuitable, but condensation oil of naphthenic character is suitable.

For "Magneto Grease" ("No. 7 Grease") using the soap of castor oil, the properties of suitable synthetic oil are as follows:

Viscosity in Redwood No. 1 sec...........	about 200
Aniline point (°C)	below 90

However, if sodium stearate and sodium oleate are used, the condensation oil which has an aniline point above 90 is suitable.

ENCLOSURE (B)35

Table XIX(B)36
PROPERTIES OF SYNTHETIC OILS

	Materials	Temp(°C)	Time (hr.)	$AlCl_3$ (%)
Polymerization oil of paraffin cracked oil	Cracked distillate of wax	80 - 100	8	5
Condensation oil of paraffin cracked oil and benzene	Fraction boiling from 100°C to 250°C of distillate of wax 80	80 - 100	8	5
Condensation oil of paraffin cracked oil and naphthalene	benzol ...... 20 Fraction boiling from 100°C-250°C of distillate wax .... 80 naphthalene .. 20	80 - 100	8	5

Viscosity (Redwood 1, sec.)			Aniline point (°C)	Pour point (°C)
10°C	30°C	50°C	118	-15
640	785	150	65	-25
527.8	155.8	88.1	95.4	-25
565.8	200.2	95.4		

ENCLOSURE (B)36

Table XX(B)36
COMPOSITION AND PROPERTIES OF SYNTHETIC GREASES
(NO.1 AND NO. 2 CUP GREASE)

Conditions of synthesis	Materials	Naphthalene and benzene condensation	
Time (hrs) .... 10 Temperature (°C) .... 80-120 $AlCl_3$ (%) 5		Cracked distillate boiling from 100°C to 250°C of waxes ...... 80 Naphthalene .... 10 Benzol 10	
Properties of Product			
Viscosity in Redwood no. 1, sec.	at 30°C	93.8	
	at 50°C	42.6	
Aniline point (°C)		56	
Flash point (°C)		58	
Pour point (°C)		-12	
Acid value		0.1	
Saponification value		0.01	
Evaporation loss at 100°C for 5 hrs. (%)		0.08	
Composition of Grease		Order	
		No. 1	No. 2
Synthetic oil		70	73.1
Calcium stearate		21	22.7
Calcium stearate		9	4.2
Properties of Greases		Order	
		No. 1	No. 2
Dropping point (°C)		120	105
Worked consistency at 250°C *		201	230
Free alkali (%)		0.18	0.14
Water (%)		1.41	1.2
Ash (%)		3.0	2.8
Stability		O.K	O.K
Corrosion		O.K	O.K

* Work penetration, A.S.T.M.

ENCLOSURE (B)36

Table XXI(B)36
COMPOSITION AND PROPERTIES OF SYNTHETIC GREASES
(NO. 4 CUP GREASE)

Properties of Materials		Naphthalene and benzene condensation (A)	Naphthalene condensation (B)
Conditions of Synthesis*	Materials	Cracked distillate boiling from 100°C to 250°C of waxes .... 80 Naphthalene ... 10 Benzene 10	Cracked distillate boiling from 100°C to 250°C of waxes .... 85 Naphthalene .. 15
Properties of Product			
Vis. in S.U.S. at 210°F		110.0	150
Viscosity index		110.0	113.1
Specific gravity D_4^{20}		0.8539	0.8856
Aniline point (°C)		107.5	109.0
Pour point (°C)		-30	-30
Saponification value		0.16	0.10
Acid value		0.02	0.02
Composition of Grease		(A)	(B)
Synthetic oil		89	89
Aluminium stearate		7.6	7.6
Aluminium oleate		1.2	1.2
Lead oleate		1.2	1.2
Glycerin		1	1
Properties of Grease		(A)	(B)
Appearance		Fibroid, viscous semi-fluid	Fibroid, viscous semi-fluid
Dropping point (°C)		84	88
Worked consistency at 10 C		374	362
Free alkali (%)		-	0.16
Free fatty acid (%)		0.22	-
Corrosion		None	None
Stability		O.K	O.K
Ash (%)		0.73	0.81

* For both condensations, time was 10 hr, temperature was 80°C, and 5% of $AlCl_3$ was used

ENCLOSURE (B)36

Table XXII(B)36
COMPOSITION AND PROPERTIES
(CONTROLLABLE PITCH PROPELLER)

Conditions of Synthesis*	Materials		Naphthalene and toluene condensation (A)	Naphthalene and benzene condensation (B)
			Cracked distillate boiling from 150°C to 230°C of waxes .... 80 Naphthalene .... 3 Toluene 17	Cracked distillate boiling from 150°C to 230°C of waxes .... 80 Naphthalene .... 3 Benzene 17
	Catalyst		$AlCl_3$: 1.5% $ZnCl_2$: 0.5%	$AlCl_3$: 1.5% $ZnCl_2$: 0.5%
Properties of Products				
Viscosity in Redwood no. 1, sec.	at 30°C		168	132.4
	at 50°C		70	64
Aniline point (°C)			69	93
Flash point (°C)			162	154
Pour point (°C)			-60	-63
Composition of Greases				
			(A)	(B)
	Synthetic oil (%)		82.4	82
	Calcium stearate (%)		8.8	9
	Calcium oleate (%)		8.8	9
Properties of Greases			(A)	(B)
	Dropping point (°C)		101.5	107
	Worked consistency	at 25°C	270	269
		at 5°C	220	225 (at 0°C)
		at 25°C	210	210 (at 20°C)
		at 40°C	188	186
	Solidifying point (°C)		-63	-60
	Free alkali (%)		0.17	0.57
	Water (%)		1.8	0.26
	Ash (%)		1.6	1.78
	Stability		O.K.	O.K.
	Corrosion		O.K.	O.K.

*For both condensations, time was 6 hrs, temperature was 80-120°C

ENCLOSURE (B)36

Table XXIII(B)36
COMPOSITION AND PROPERTIES
(ROCKER AND GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials $AlCl_3$ (%) .... 5 Temp (°C) ..... 80-30 Time (hrs) 6	Cracked distillate of wax .... 80 Naphthalene .... 3 Benzene 17
Viscosity in S.U.S. at 210°F		110
Viscosity index		109
Aniline point (°C)		100
Flash point (°C)		220
Pour point (°C)		-38
Acid value		0.03
Saponification value		0.11
Composition of Grease		
Synthetic oil, (%)		91.11
Calcium stearate (%)		1.82
Calcium oleate (%)		1.82
Sodium stearate (%)		2.00
Sodium oleate (%)		2.00
Glycerin (%)		1.25
Properties of Grease		
Appearance		fluolescent, semi-fluid smooth texture
Dropping point (°C)		92
Worked consistency at 25°C		355
Free fatty acid (%)		0.68
Ash (%)		1.12
Stability		O.K
Corrosion		O.K

* For both condensations, time was 6 hr, temperature was 80-130°C, and 5% of $AlCl_3$ was used

ENCLOSURE (B)36

Table XXIV(B)36
COMPOSITION AND PROPERTIES
(MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials $AlCl_3$ (%) .... 4 Temp (°C) ..... 80-140 Time (hrs) 6	Cracked distillate of wax from 150°C-230°C .... 80 Naphthalene .... 3 Benzene 17
Viscosity in	at 10°C	631
Redwood No. 1 sec.	" 30°C	214
Aniline point	(°C)	69
Pour point	(°C)	-60
Flash point	(°C)	165
Composition of Grease		
Synthetic oil	(%)	80
Sodium soap of castor oil	(%)	20
Note: mixed well at 200°C, and then quickly cool		
Properties of Grease		
Appearance Dropping point (°C)		light brown color smooth texture 176.5
	at 25°C	260
Worked consistency	" 0°C	207
	" -40°C	168

* For both condensations, time was 6 hr, temperature was 80-140°C and 4% of $AlCl_3$ was used

ENCLOSURE (B)36

Table XXV(B)36
COMPOSITION AND PROPERTIES
(IMPROVED MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials	Cracked distillate of wax from 150°C-230°C .... 80 Naphthalene .... 3 Benzene 17
Viscosity in	at 10°C	631
Redwood No. 1 sec.	" 30°C	214
Aniline point	(°C)	69
Pour point	(°C)	-60
Flash point	(°C)	165
Composition of Grease		
Synthetic oil	(%)	80
Sodium soap of castor oil	(%)	18.8
Calcium oleate	(%)	1.0
Glycerine	(%)	0.2
Properties of Grease		
Appearance		light brown color and unguent type
Dropping point	(°C)	165
Worked consistency	at 250°C	259.5
	" 0°C	211
	" -40°C	191
Solidifying point	(°C)	-55
Free alkali	(%)	0.226
Ash	(%)	1.2
Stability		O.K
Corrosion		O.K

* For both condensations, time was 6 hr, temperature was 80-140°C and 4% of $AlCl_3$ was used

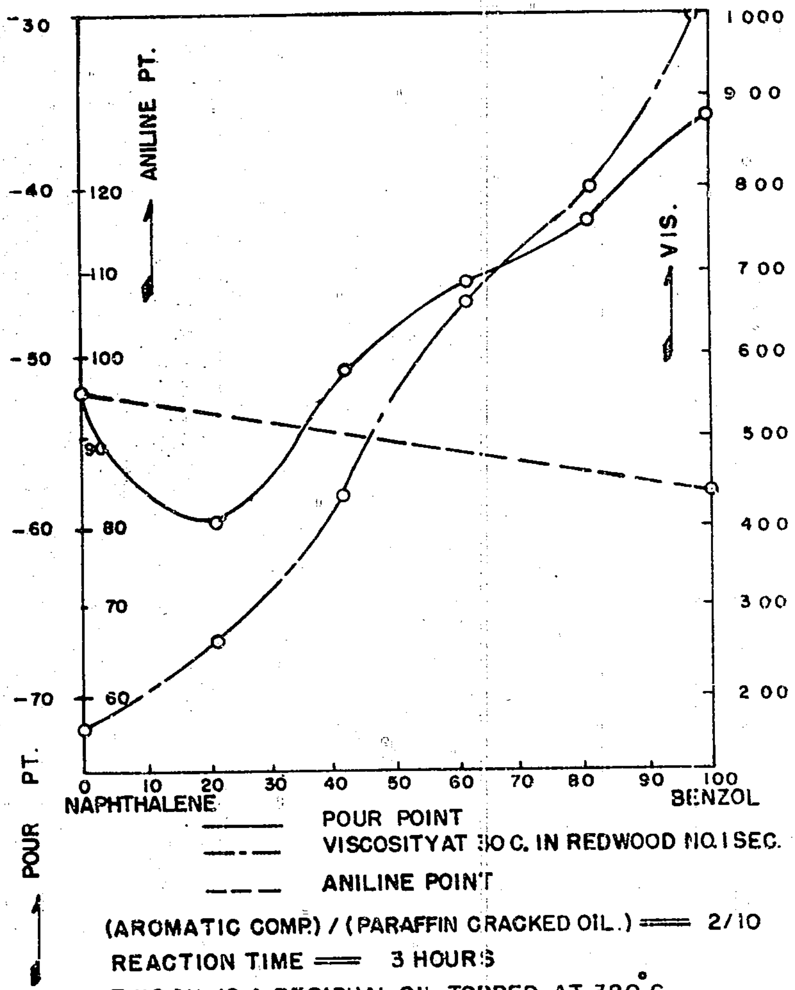
ENCLOSURE (B)36

Table XXVI(B)36
COMPOSITION AND PROPERTIES
(MIXED BASE MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Material	Cracked distillate boiling from 150°C to 230°C of wax .... 90 Naphthalene .... 5 Benzene 5
Viscosity in	at 30°C	206
Redwood No. 1 sec.	10°C	602.1
Aniline point	(°C)	94
Flash point	(°C)	163
Pour point	(°C)	-58
Composition of Grease		
Synthetic oil	(%)	77
Sodium-stearate	(%)	7.5
Sodium- oleate	(%)	7.5
Calcium-stearate	(%)	4.93
Calcium- oleate	(%)	4.93
Glycerine	(%)	0.89
Properties of Grease		
Appearance		light brown color and smooth textures
Dropping point	(°C)	649
Worked consistency	at 25°C	230
	at 20°C	179
Free fatty acid	(%)	0.35
Ash	(%)	2.0
Stability		O.K.
Corrosion		O.K.

* For both condensations, time was 6 hr, temperature was 80-130°C and 3% of $AlCl_3$ was used

ENCLOSURE (B)36



(AROMATIC COMP.) / (PARAFFIN CRACKED OIL.) ═══ 2/10
REACTION TIME ═══ 3 HOURS
THIS OIL IS A RESIDUAL OIL TOPPED AT 320° C.

Figure 6(B)36
VISCOSITY POUR POINT AND ANILINE POINT
FOR NAPHTHALENE-BENZENE CONDENSATION OIL

ENCLOSURE (B)36

PART III

RESEARCH ON LUBRICATING GREASES

by

ENGINEERING LT. COMDR.
T. DAN

Research Period: 1945

SUMMARY

Research on special greases having the following characteristics was carried on.

1. A grease having high dropping point and water-proof characteristics.

2. A grease having alcohol-proof characteristics.

3. A grease having concentrated nitric acid proof characteristics.

Up to the time of this report, conclusive results were not obtained. However, the summary of the experimental data as a progress report is given as follows:

1. A grease having high dropping point and water-proof characteristics.

This grease was prepared by several methods, but results were all negative in regard to objectives sought.

According to the literature,* barium soap base grease made from petroleum acids obtained by oxidation of paraffin wax, but this was not tried.

2. A grease having an alcohol proof nature.

A grease consisting of aluminium stearate and mineral oil, refined by alcohol extraction, may be suitable.

3. A grease having an acid-proof nature.

A mixture of petrolatum and paraffin wax may be suitable.

I. INTRODUCTION

Ordinary cup greases have water-proof characteristics, but their dropping points are generally below 100°C.

Magneto grease is of high dropping point nature, but this grease is water soluble. Therefore, a grease which satisfies both conditions was needed for lubricating conditions of very high temperature and for contact with cooling water.

Moreover, special greases for lubricating conditions involving contact with alcohol or concentrated nitric acid, were required. Therefore, the researches on these special lubricating greases were carried on during 1945.

II. DETAILED DESCRIPTION

A. Research for Manufacturing Water-Proof Grease having High Dropping Point

1. Since calcium soap base grease is water-proof, the question of what kind of fatty acids in combination with calcium soap influenced the dropping point was studied.

The prepared greases had the properties shown in Table XXVII(B)36.

From these results, calcium soap greases prepared with calcium stearate had the highest dropping point, but these dropping points were too low.

2. Calcium and Other Mixed Base Greases. Calcium and sodium soap greases were prepared in order to add the high dropping point nature of sodium soap base grease to the water-proof nature of calcium base grease. Their properties were as shown in Table XIX(B)36.

From these results, it is evident that generally the dropping point of mixed base grease is lower than that of mono-base grease, and the water-proof characteristic becomes poorer by adding sodium soap, so that this method is also unsatisfactory.

3. Several Metallic Soap Base Greases. Since the stearates of aluminum, cobalt, barium, and nickel are insoluble in water, we prepared greases, by mixing a constant amount of mineral turbine oil and 20% of these soaps.

From the results, it can be seen that aluminum, cobalt, nickel, and magnesium soap greases are very water-proof but that their dropping points vary from 60° to 120°C and, do not reach the desired 150°C.

4. Resin Acid-Calcium Soap Base Grease. Calcium resinate, which was prepared by double decomposition of calcium chloride and potassium resinate, has a higher melting point than the other calcium fatty acid soaps.

Calcium Soaps	Melting Point (°C)
Calcium Stearate	113
Calcium Oleate	93
Calcium Resinate	212-241

So, when this calcium resinate (20%) was mixed with mineral oil (80%), a grease was obtained whose dropping point was 98°C and its general characteristics were as follows:

Consistency at 25°C	170
Dropping Point (°C)	98
Water-proof Characteristics	Good

5. Conclusions. Greases were prepared by several methods, but a grease of the desired characteristics was not successfully made.

According to the literature, 0.1% of potassium permanganate and 1% of stearic acid, as the catalyst were added to paraffin wax. This was heated to about 130°C passing air into it, and oxidized petroleum acid was prepared.

The preparation of a grease composed of the barium soap of petroleum acid and mineral oil was not tried.

B. Alcohol-Proof Grease

As the preliminary test, several greases were extracted by alcohol in a Soxlet's apparatus. The results were as follows:

Samples of Greases	Amount of Extracted (%)
Experimental grease for magneto	26.7
Ordinary cup grease	17.7
Mixture of petrolatum and 10% of aluminum stearate	3.0

These results showed that the grease mixture of petrolatum and aluminum stearate is best for alcohol proof grease.

The example of composition and general characteristics were as follows:

Composition (%):

Petrolatum	54.5%
Mineral oil (residue extracted from alcohol)	36.4%
Aluminum Stearate	9.1%

General Characteristics:

Consistency at 25°C (Worked Penetration)	216
Extracted amount by alcohol (%)	3.0

C. Concentrated Nitric Acid-Proof Grease

According to the investigations in the laboratory, among the calcium, sodium and aluminum soap base greases and petrolatum, petrolatum was most inactive for concentrated nitric acid at the ordinary temperature.

And then to make petrolatum possible to use at higher temperatures than 50°C, powdered graphite or talc was added as an inorganic solid lubricant. However, the results were unsatisfactory as shown in Tables XXXI(B)36 and XXXII(B)36.

III. CONCLUSIONS

A. Water-Proof Grease Having High Dropping Point

This grease was prepared by several methods using calcium soap base, calcium and sodium mixed soap base, several metallic soaps as a base, and calcium resinate base, but none had the desired dropping point of 150°C or above.

According to the literature, barium soap base grease of petroleum acid is preferable and its trial is intended.

B. Alcohol-Proof Grease

The following grease which consisted of aluminum stearate and refined mineral oil may be suitable.

Composition (%):

Petrolatum	54.5%
Refined mineral oil (by alcohol)	36.4%
Aluminum Stearate	9.1%

General Properties:

Consistency at $25^{\circ}C$	216
Amount extracted by alcohol (%)	3.0

C. Concentrated Nitric Acid Proof Grease

The following two examples were prepared but were not subjected to practical tests.

Example Grease No. 1

Petrolatum	80%
Paraffin wax	20%
Fine powdered graphite	1%

Example Grease No. 2

Petrolatum	48%
Paraffin wax	12%
Talc	40%

Table XXVII(B)36
CALCIUM SOAP GREASE PROPERTIES

Stearic acid(gm)	Oleic acid(gm)	CaO (gm)	Mineral oil(gm)	Consistency $(25^{\circ}C)$*	Dropping pt. ($^{\circ}C$)	Water-proof characteristics
25	25	6.58	232	250	103	Good
60	—	7.85	232	280	119	Good
—	50	6.58	232	235	82	Good

*Worked Penetration

ENCLOSURE (B)36

Table XXIX(B)36
CALCIUM AND SODIUM MIXED-BASE GREASES

Sample No.	Mixing Ratio		Consistency (25°C)*	Dropping pt. (°C)	Water-proof characteristics
	Sodium soap base grease (soap cont. 20%)	Carusume soap base grease (soap cont. 20%)			
1	0	1	263	113	Good
2	1	10	207	103	Good
3	1	5	260	120	Emulsify
4	1	2	-	98	Emulsify
5	1	1	-	96	Emulsify
6	1	0	250	150	Emulsify

*Worked Penetration

Table XXX(B)36
VARIOUS METALLIC-BASE GREASES

Name of soap base	Consistency (25°C)*	Dropping point (°C)	Water-proof characteristics
Calcium stearate	150	100	Good
Cobalt stearate	230	110	Good
Nickel stearate	250	120	Good
Magnesium stearate	180	60	Good
Aluminium stearate	170	90	Good

*Worked Penetration

ENCLOSURE (B)36

Table XXXI(B)36
TEST GREASE NO. 1

	Percent	Consistency (25°C)*	General Properties	
			Dropping pt.(°C)	Ash(%)
Petrolatum	80			
Paraffin wax	20	260	46	0.2
Fine powdered graphite	1.0			

*Worked Penetration

Table XXXII(B)36
TEST GREASE NO. 2

	Percent	Consistency (25°C)*	General Properties	
			Dropping pt.(°C)	Ash(%)
Petrolatum	48			
Paraffin wax	12	185	47.5	37.4
Talc	40			

*Worked Penetration

ENCLOSURE (B) 37

STUDIES ON THE PREPARATION OF ANTICORROSIVE CYLINDER OIL

by
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Research Period: 1940-1943

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)37

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)37

SUMMARY

An anticorrosive cylinder oil having the following composition was found to be satisfactory for practical use, and has been manufactured and used since 1941.

Refined rape seed oil	75% wt.
Aluminium stearate	10-12% wt.
Triethanol amine	5% wt.
n-Butanol	10-8% wt.

I. INTRODUCTION

A. History

In 1935, it was known from the literature and from the results of the analysis of imported samples that anticorrosive cylinder oils were composed of a fatty oil of comparatively low iodine value, aluminium stearate, triethanol amine and butanol, and a product which had the following composition was brought to practical use.

Lard Oil	75% wt.
Aluminium stearate	10-12% wt.
Triethanol amine	5% wt.
n-Butanol	10-8% wt.

Since 1940 lard oil had become difficultly obtainable, and refined rape seed oil was substituted for it. It was found to be satisfactory and has been practically used ever since.

II. DETAILED DESCRIPTION

Refined rape seed oil (75% wt.) is charged in the chamber, and heated to about 125°C while being stirred. Aluminium stearate (12% wt.) is then added to it in small increments. Satisfactory stirring is necessary in this step of the process. It is then cooled to 100°C and triethanol amine (5% by wt.) is then gradually added with stirring. The solution is cooled to 50-60°C. Butanol (5-8% wt.) is added finally and stirring is continued. See Figure 1(B)37 and Figure 2(B)37. The resulting product is filtered at 50-60°C using a calico filter. The specifications and properties of a sample product are shown in Table I(B)37. With the object of reducing the use of triethanol amine, a sample having the following composition was prepared:

Refined rape seed oil	77.5% wt.
Aluminium stearate	10-12% wt.
Triethanol amine	2% wt.
Cyclohexyl amine	0.5% wt.
n-Butanol	10-8% wt.

The above mixture was satisfactory in laboratory tests, but practical engine tests have not yet been carried out.

III. CONCLUSION

An anticorrosive cylinder oil, having the following composition, was very satisfactory for practical use in aero engine cylinders and was produced on a commercial scale.

ENCLOSURE (B)37

Table I(B)37
SPECIFICATIONS AND PROPERTIES OF ANTICORROSIVE CYLINDER OIL

		Specification	Properties of a Sample Oil
Reaction		Slightly basic	Slightly basic
Viscosity(R.I.)	at 30°C	below 1000	976
	at 50°C	350-420	415
Pour Point °C		below 5	0

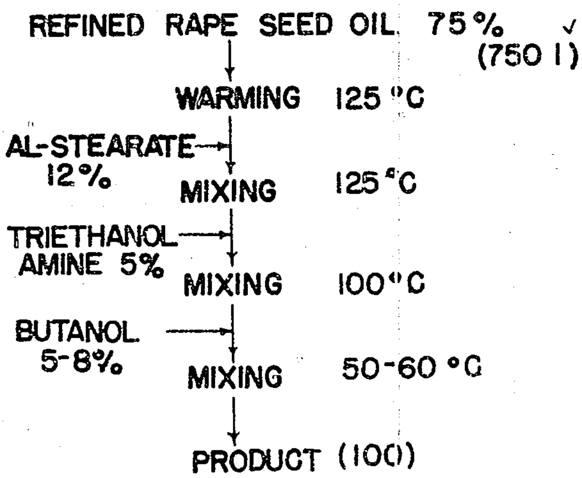


Figure 1(B)37
SCHEMATIC DIAGRAM FOR PREPARING ANTICORROSIVE CYLINDER OIL

ENCLOSURE (B)37

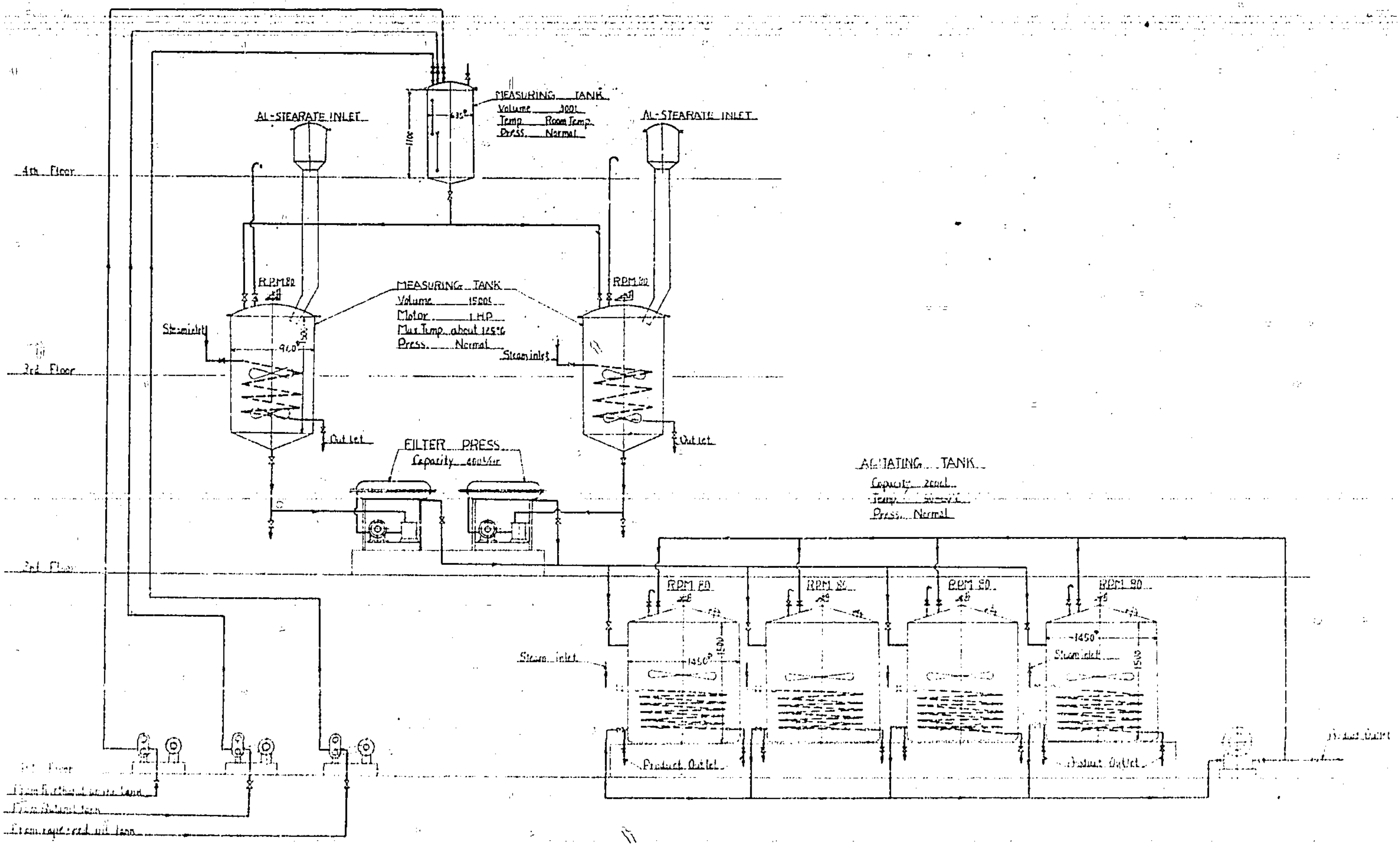


Figure 2(B)37
FLOW SHEET OF PILOT PLANT OF
ANTICORROSIVE CYLINDER OIL

ENCLOSURE (B)37

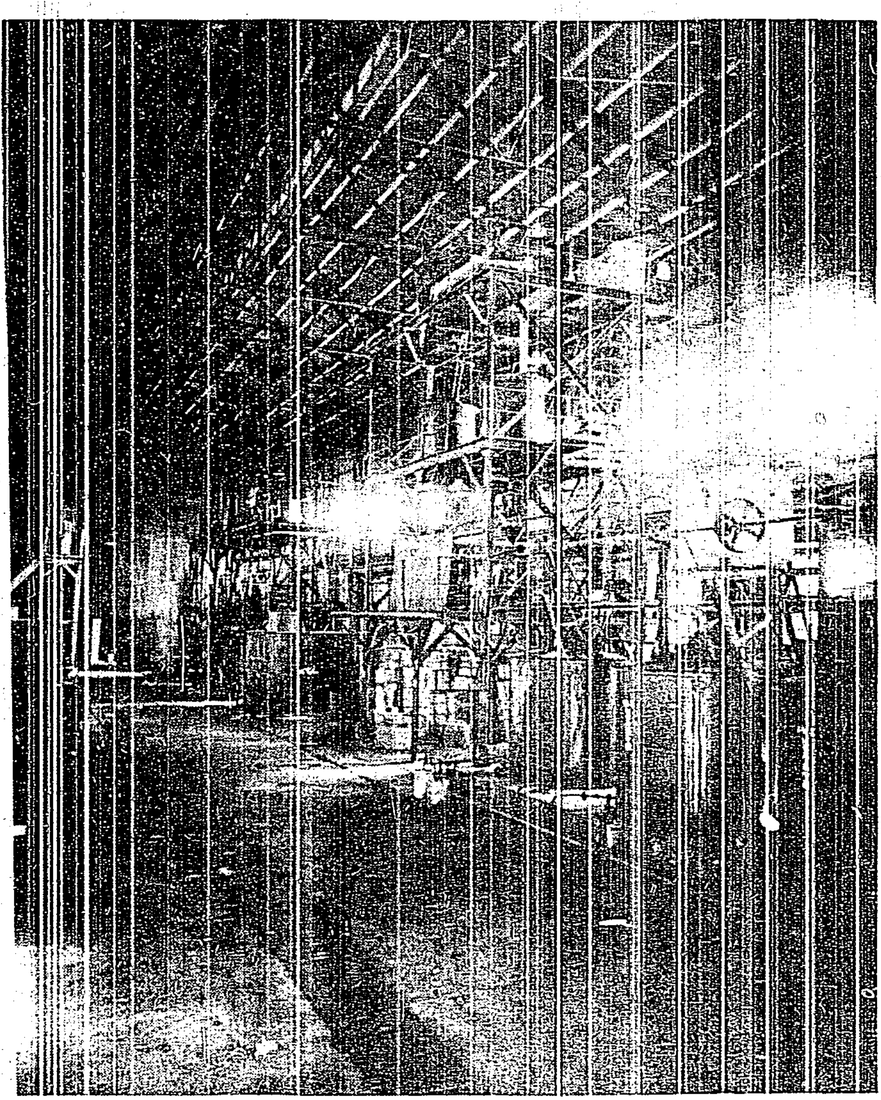


Figure 3(B)37
PILOT PLANT FOR MANUFACTURING
ANTICORROSIVE CYLINDER OIL

ENCLOSURE (C)

LIST OF JAPANESE DOCUMENTS PERTAINING TO LUBRICATING OIL RESEARCH

(Forwarded through ATIS to the Washington Document Center)

I. OBTAINED FROM THE FIRST NAVAL FUEL DEPOT, OFUNA. (ATIS No. for All Documents Listed Below is 4580.)

NavTechJap No.	Title	Author	Year
ND26-0009.1	Experiments on the Determination of the Conversion Table for Viscosity.	K. SHIMODA	10-26
ND26-0009.2	Manufacture of Transformer Oil from Residual Oil in Cracking Plant.	R. BEPPU Y. MIYATA	4-27
ND26-0009.3	On the Testing Method of the Deemulsibility of Lubricating Oils.	K. SHIMODA G. AKASHI	9-27
ND26-0009.4	On the Change of Turbine Oil Heated to 150°C.	K. SHIMODA G. AKASHI	2-28
ND26-0009.5	On the Rust Caused by Lubricating Oils.	K. SHIMODA	12-28
ND26-0009.6	Studies on Lubricating Oils, Part I, Synthesis of Cyclic Hydrocarbons.	I. KAGEHIRA	12-29
ND26-0009.7	Production of Turbine Oil from Oha Crude Oil.	I. KAGEHIRA S. SAKAMOTO	10-31
ND26-0009.8	Studies on Lubricating Oils, Part II, Physical Properties of Cyclic Compound.	I. KAGEHIRA	4-33
ND26-0009.9	Studies on the Manufacture of Aero Engine Oil.	I. KAGEHIRA	8-33
ND26-0009.10	Deterioration of Turbine Oil and the Limit of its Use.	I. KAGEHIRA S. SAKAMOTO H. FUJIMOTO	11-34
ND26-0009.11	Studies on the Manufacture of Aero Engine Oil, Part II, Utilization of Fish Oil.	I. KAGEHIRA S. SAKAMOTO	6-35
ND26-0009.12	Studies on Lubricating Oils, Part III, Viscosity of Cyclic Hydrocarbons.	I. KAGEHIRA	8-35
ND26-0009.13	Studies on the Lubricating Oils. IV. Synthesis of Hydrodiphenylbenzene and its Viscosity.	I. KAGEHIRA	4-38
ND26-0009.14	Synthesis of Lubricating Oil.	I. KAGEHIRA	6-38

ND26-0009.15	Corrosion of the Piston-ring of Gas Compressor.	S. MIYAZAKI I. TAKAHASHI K. HIRAI	7-38
ND26-0009.16	Literature on Fish Oils.	I. KAGEHIRA	2-45

II. OBTAINED FROM THE MIIKE SYNTHETIC OIL COMPANY, OMUTA. (ATIS No. for All Documents Listed Below is 4587.)

NavTechJap No.	Title	Year
ND26-0016.1	Report concerning Synthetic Oil Produced from GISHIN coal.	9-11-39
ND26-0016.2	Description of Lubricating Oil Plant Including Flow Chart.	no date
ND26-0016.3	The Process of Manufacturing Grease from Oxidation on Products of Paraffin Hydrocarbons.	24- 7-43
ND26-0016.4	Copy of above.	
ND26-0016.5	Stability of Lubricating Oils Produced by Polymerization of Olefins.	15-11-43
ND26-0016.6	Report on Attempt to Improve the Synthetic Polymerized Oil whose Index of Viscosity is too Low for Use in Aircraft Engines by Making a Cut at the Lower Boiling Point.	3- 8-44
ND26-0016.7	Comparison of Properties of Various Lubricating Oils.	4-37
ND26-0016.8	Research on Polymerization of Synthetic Lube Oils Using $AlCl_3$ Catalyst.	no date
ND26-0016.9	Research on the Manufacture of Olefins by Normal Pressure Cracking.	15-10-43
ND26-0016.10	Translation into Japanese of Final Fischer Method Contract.	no date

ENCLOSURE (D)

ENCLOSURE (D)

REPORT ON
THE JAPANESE MOTOR OIL COMPANY
(NIHON HATSUJKOKIYU K.K.)
UBE, YAMAGUCHI PREFECTURE

ENCLOSURE (D)

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (D)

I. INTRODUCTION

This report records and summarizes the technical information pertaining to the Ube plant of the Japanese Motor Oil Company (NIHON HATSUDOKIYU K. K.) obtained by the Petroleum Section of the U.S. Naval Technical Mission to Japan on 29 October 1945. The following Japanese personnel were interviewed and assisted in gathering the information presented herewith:

Mr. S. KORA, President
Mr. S. NAGATA, Managing Director
Mr. T. YOSHII, Head of Manufacturing Department

II. HISTORY AND ORGANIZATION

The Japanese Motor Oil Company was established in 1928 as a refinery for automobile lubricants. During the war, however, production of mineral oil lubricants was stopped and the entire production capacity was transferred to the manufacture of special oils such as hydraulic brake fluids and ester-type lubricants obtained from vegetable products. The capitalization of the plant is two million yen, and the entire stock is owned by individuals. The company also owns a grease manufacturing plant in nearby MISAKI and a plant manufacturing cutting oil in TOKYO.

There were 111 men employed at the UBE plant at the end of the war.

III. DESCRIPTION OF PRODUCTS AND PRODUCTION DATA

The principal products prepared by the Japanese Motor Oil Company are discussed below. The physical and chemical properties of these products are tabulated in Table I(D) and production data for each is given in Table II(D).

A. Hydraulic Brake Fluid

The hydraulic brake fluid prepared by subject company consisted of a mixture of butyl ricinoleate (45% by volume) in n-butanol (55% by volume). A schematic flow diagram showing the various steps in the manufacture of this fluid is given in Figure 1(D). This product was prepared specifically for the Japanese Army and was utilized by them throughout the war.

B. Low Temperature Lubricating Oil

A special low temperature lubricating oil was manufactured for the use of the Army in Manchurian operations. Production of this oil was stopped early in 1944 since there was no appreciable military activity in that area. The oil was composed of a blend of butyl ricinoleate (87% volume) and polymerized soya bean oil (13% by volume). A schematic flow diagram showing the steps in the manufacture of the oil is given in Figure 1(D). The product was satisfactory in most respects but was found to be subject to deterioration during prolonged storage.

C. "Mixed" Automobile Oil

A lubricating oil similar to the low temperature lubricant described above was prepared in much the same manner using a mixture of ethyl ricinoleate (90% by volume) and polymerized soya bean oil (10% by volume). This lubricant was first prepared in February 1945, and production was discontinued in April 1945 because of poor performance characteristics. When this lubricant was used in engines many failures were encountered due to evaporation of the ester and subsequent sticking of pistons in the presence of high concentrations of polymerized oil.

ENCLOSURE (D)

D. "Sulfurized" Automobile Oil

A new product which had been in production for only a month at the end of the war was the so-called "sulfurized" automobile oil. This lubricant was prepared by adding 0.5% sulfur to rape seed oil which had first been neutralized and treated with Japanese acid clay. The sulfur-oil mixture was churned for 6 hours at 150°C and then filtered. No performance data for this oil were available.

IV. RESEARCH

During the war the chemists employed by the Japanese Motor Oil Company were primarily concerned with control work. However, in 1945 some research was undertaken relative to improving the storage stability of the low temperature lubricating oil. Diphenyl amine or hydroquinone inhibitors were found to be effective. Lubricating oils prepared from pine root oil, tar, or pitch and soya bean oil, were also investigated. As would be expected, both of these lubricants had poor oxidation stability.

Research pertaining to post-war activities is now underway and includes a study of processes for reclaiming lubricating oils, the manufacture of insecticides and water proof paints, and various substitute food studies.

ENCLOSURE (D)

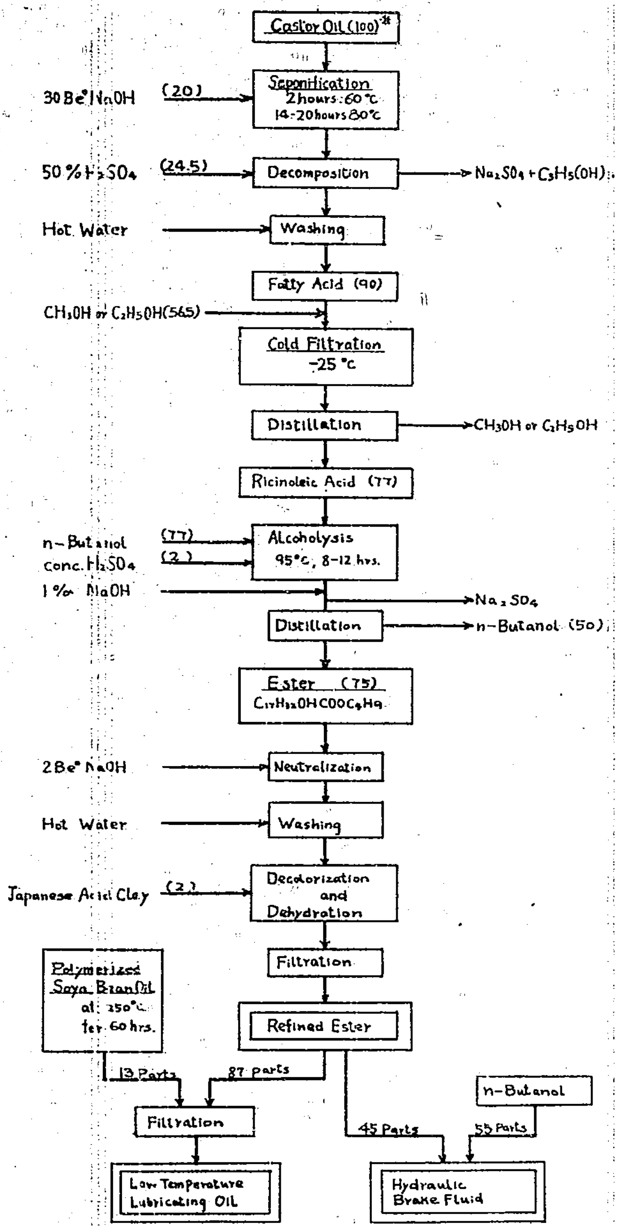
Table I(D)
PROPERTIES OF LUBRICANTS PREPARED BY THE JAPANESE MOTOR OIL CO.

		Oil			
		Hydraulic Brake	Low Temperature Lubricating	"Mixed" Automobile	"Sulfurized" Automobile
Specific Gravity, 15/4°C.		0.86	-	0.93	0.92
Reaction		Neutral	Neutral	Neutral	Neutral
Flash Point (°C)		34	183	185	190
Pour Point (°C)		-60	-52	-28	0
Neutralization Number		0.15	2.2	2.0	2.2
Corrosion, Cu Strip, 3hrs.		None	None	None	None
Ash (%)		-	-	-	0.02
Conradson Carbon (%)		-	-	-	1.2
Viscosity, Redwood Seconds	at 50°C.	-	198	190	-
	at 100°C.	-	65.2	65	55
Viscosity, Stokes	at -30°C.	-	80	-	-
	at -40°C.	20	-	-	-
Viscosity Index		-	-	-	140

Table II(D)
PRODUCTION DATA OF THE JAPANESE MOTOR OIL COMPANY

Oil	Period	Production (kl)
Hydraulic Brake	May 1941 - July 1945	600
Low Temperature Lubricating	May 1941 - Jan. 1944	2800
"Mixed" Automobile	Feb. 1945 - April 1945	248
"Sulfurized" Automobile	July 1945	178

ENCLOSURE (D)



Properties

Reaction		Neutral
Flash Point °C		183
Viscosity, Red. sec.		
	at 100°C	65.2
	at 50°C	198
Viscosity, Stokes		
	at -30°C	80
Pour Point °C		-52
Neut, No.		2.2
Corrosion		None

Properties

Reaction		Neutral
Sp. Gr.		0.86
Viscosity, Storkes		
	at -40°C	200
Flash Point, °C		34
Pour Point, °C		-60
Neut. No.		0.15
Corrosion		None

Figure 1(D)
PREPARATION OF
LOW TEMPERATURE
LUBRICATING OIL AND
HYDRAULIC BRAKE FLUID

* Note: Figures in parentheses represent parts by weight based on initial charge of castor oil as 100