

**RESTRICTED**

**ENCLOSURE (A)**

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

by

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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 ( $C_{26}H_{22}$ ), 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 aluminum 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 aluminum chloride at  $60^{\circ}\text{C}$ - $80^{\circ}\text{C}$ , 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  $(-140^{\circ}\text{C})$  with a cooling rate of  $1^{\circ}\text{C}$ - $5^{\circ}\text{C}$  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  $-20^{\circ}\text{C}$  for deasphalting and dewaxing and to extract the deasphalted and dewaxed oil with 3-4 volumes of furfural at  $80^{\circ}\text{C}$ - $100^{\circ}\text{C}$ . 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 8% by weight of the crude oil.

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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 Mizu, Selia or Mill 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)

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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

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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 457.8 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 80 parts of toluene in the presence of aluminium chloride at 90°C for 8 hours and then distilling under 5mm Hg of vacuum to out 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 separation 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

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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'-dicydiphenylamine, 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<sub>2</sub> 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 phenylsearate 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 3mm 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 Oba 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



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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 aluminum chloride at 50°C-100°C for 3 hours. The reaction was controlled by the addition 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 aluminum soap, and the extreme load carrying 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 caustic 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 133.4 S.U.S. and a viscosity index of 88, 6.48% of aluminum stearate, 0.72% of aluminum 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 130°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 clarinic 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 81.9 S.U.S., a viscosity index of 85 and a pour point of (-)36°C with 7% of aluminum stearate and 0.21% of calcium stearate at 160°C. The product obtained proved to be satisfactory in engine tests and had a consistency at (-)40°C of 234, 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, aluminum 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.)

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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	

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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