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

by

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LIST OF TABLES AND ILLUSTRATIONS

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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 naphtnalene 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 1.3.

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.

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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. at 100°F	Vis. in S.U.S. at 210°F	Vis. index	Conradson's carbon (%)	Acid Value	Saponification Value	Iodine Value	Pour pt. (°C)	Viscosity Ratio
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	1.68	
2.0	5	50	10	933.2	106.0	122	1.61	
0.2	5	80	10	120.4	116.9	106.2	1.52	
0.05	5	80	18	134.5	126.9	118.8	1.77	

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

Amount of submaterial added (wt.%)	Condition of Polymerisation			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	108	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/in^2	Time (min)	Width of wear test metal (mm)	Load carrying capacity (kg/cm^2)
0 120 B	85	25	3	0.89	180
0 120 3	85	30	4	0.95	220

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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 Miisu 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 Miisu crude oil	10	123	107	1.54
20% of acid treated residue over 200°C of Miisu 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.

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

Samples	Crude Barisol-wax	Pure Paraffin Wax
Density (d_4^{60})	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_4^{15})	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