ENCLOSURE (B) 23

S T U D I E S   O N   A N T I O X I D A N T S

F O R   T H E   A E R O - E N G I N E   O I L S

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LIST OF TABLES AND ILLUSTRATIONS

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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

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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.

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 Ministry 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 (°C)	200
Time (hr)	12
Rate of air blowing (liter/hr)	15
Material of test tube	glass

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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)

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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	-

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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	—

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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	—	—	—	—	—	—	—	—

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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	0.68	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

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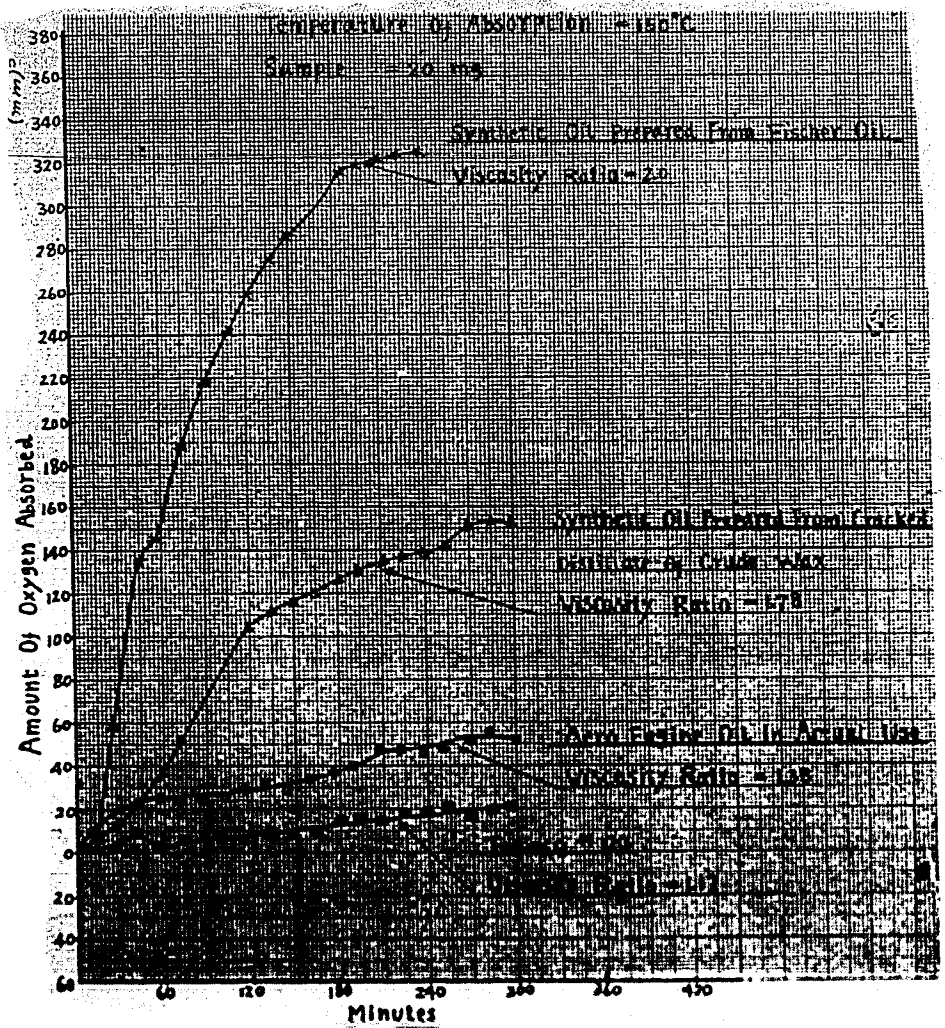

Figure 1(B)23
OXYGEN ABSORPTION TEST ON THE AIRPLANE OIL

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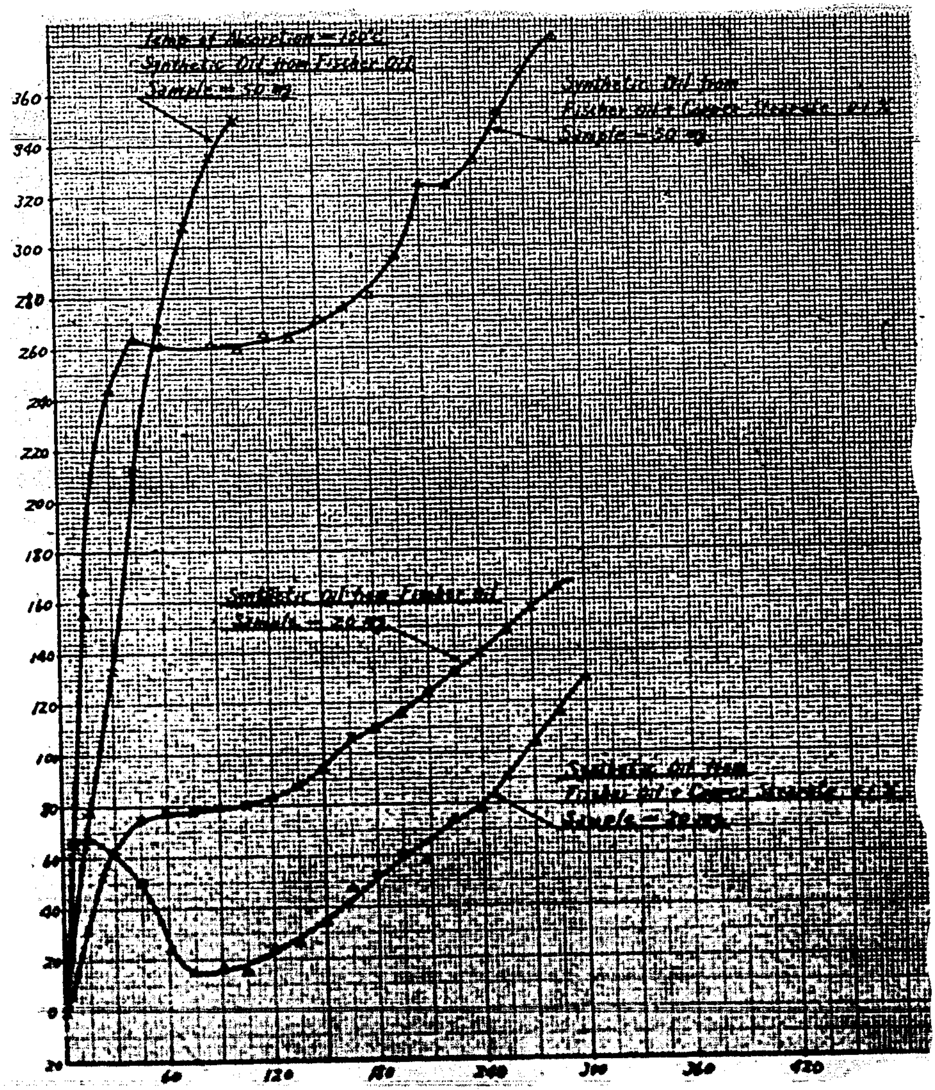

Figure 2(B)2.
INFLUENCE OF COPPER STEARATE ON THE ABSORPTION OF OXYGEN IN AEROENGINE OIL