ENCLOSURE (B) 32

STUDIES ON ADDITIVES FOR SUBMARINE DIESEL ENGINE LUBRICANTS

by

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Research Period: 1942-1943

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

December 1945

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LIST OF TABLES AND ILLUSTRATIONS

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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

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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/in² 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 [illegible] effective.

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3. <u>Stability Test</u>: 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. <u>Detergency Test</u>: 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. <u>Dispersion Test</u>: 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.

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Table I(B)32
PROPERTIES AND METHODS OF PREPARATION OF COMPOUNDS

Name	M.P. (°C)	B.P. (°C)	Elemental Analysis C %	Elemental Analysis H %	Method of Preparation
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	1.	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		233-242/1mm	obs. 68.42 cal. 68.48	obs. 5.74 cal. 5.72	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	U.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	c.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	C.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	C.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	U.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

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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	C.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
		0.008	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	0.042	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

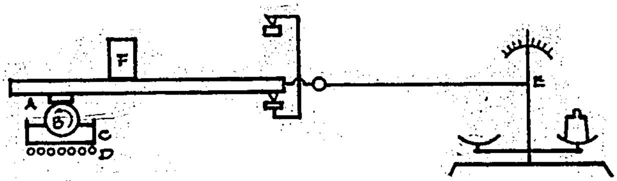

Figure 1(B)32
KINETIC FRICTION TESTING MACHINE

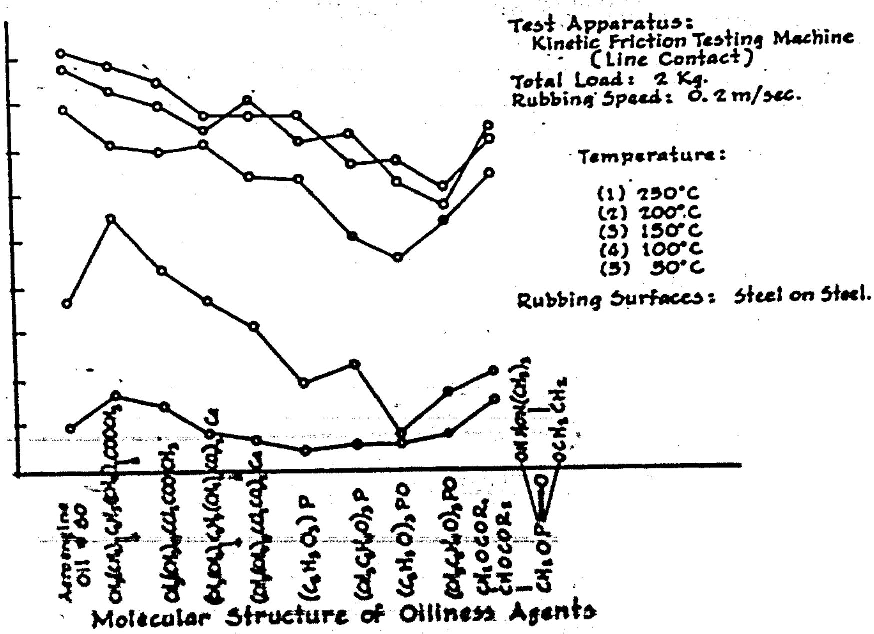

Figure 2(B)32
KINETIC COEFFICIENTS OF FRICTION OF STRAIGHT AEROENGINE OIL #80 AND THAT WHICH CONTAINS 1% WT. OF VARIOUS OILINESS AGENTS

ENCLOSURE (B)32

TEST APPARATUS
KINETIC FRICTION TESTING MACHINE (LINE CONTACT)
FRICTION SURFACES: STEEL ON STEEL
TOTAL LOAD: 2 KG.

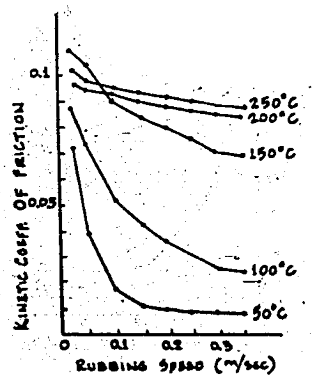

Figure 3(B)32
AEROENGINE OIL #80

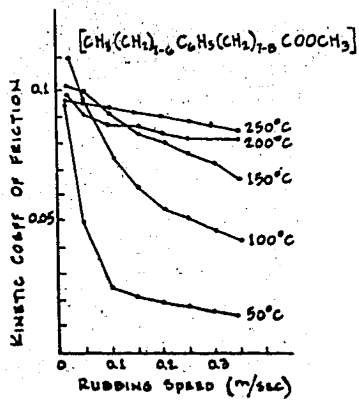

Figure 4(B)32
AEROENGINE OIL #80
METHYL PHENYL STEARATE

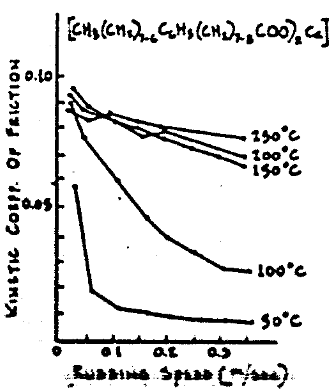

Figure 5(B)32
AEROENGINE OIL #80
METHYL DICHLOROSTEARATE

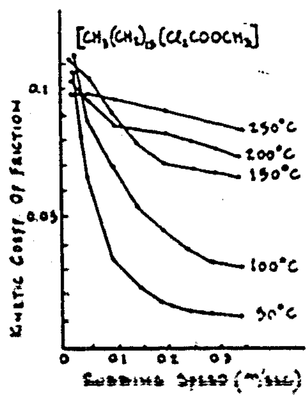

Figure 6(B)32
AEROENGINE OIL #80
CALCIUM PHENYL STEARATE

ENCLOSURE (B)32

Test Apparatus

Kinetic Friction Testing Machine (Line Contact)
Friction Surfaces: Steel on Steel
Total Load: 2 Kg.

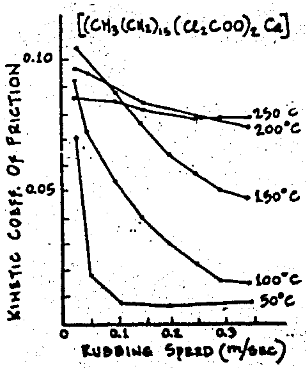

Figure 7(B)32
AEROENGINE OIL #80
CALCIUM DICHLOROSTEARATE

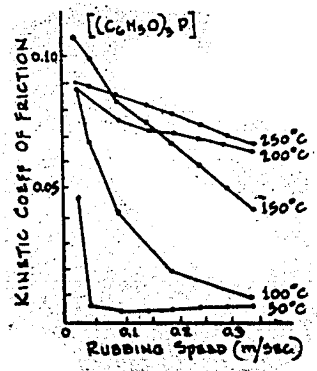

Figure 8(B)32
AEROENGINE OIL #80
TRIPHENYL PHOSPHITE

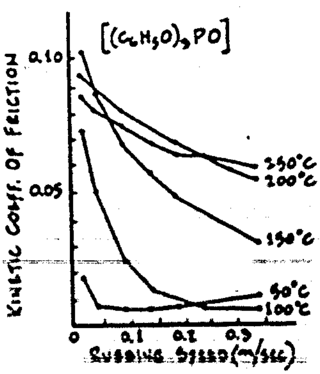

Figure 9(B)32
AEROENGINE OIL #80
TRIPHENYL PHOSPHATE

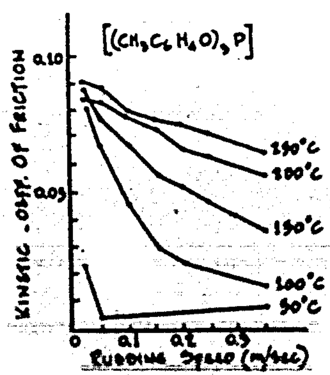

Figure 10(B)32
AEROENGINE OIL #80
TRICRESYL PHOSPHITE

ENCLOSURE (B)32

TEST APPARATUS
KINETIC FRICTION TESTING MACHINE (LINE CONTACT)
FRICTION SURFACES: STEEL ON STEEL
TOTAL LOAD: 2 KG.

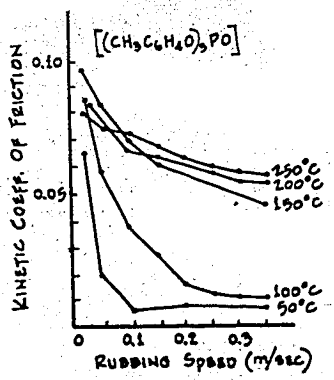

Figure 11(B)32
AEROENGINE OIL #80
TRICRESYL PHOSPHATE

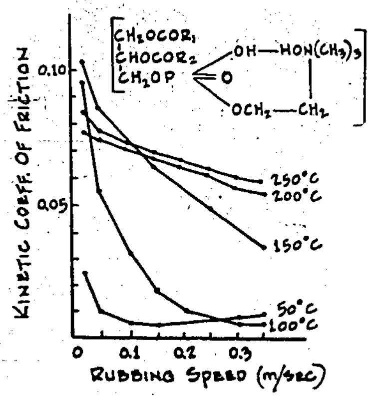

Figure 12(B)32
AEROENGINE OIL #80
LECITHIN

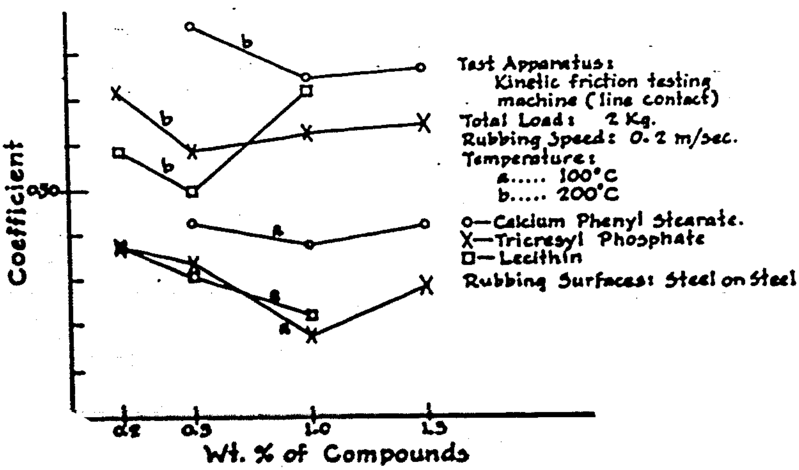

Figure 13(B)32
KINETIC COEFFICIENTS OF FRICTION OF AEROENGINE OIL #80
CONTAINING DIFFERENT WT.% OF OILINESS AGENTS

ENCLOSURE (B)32

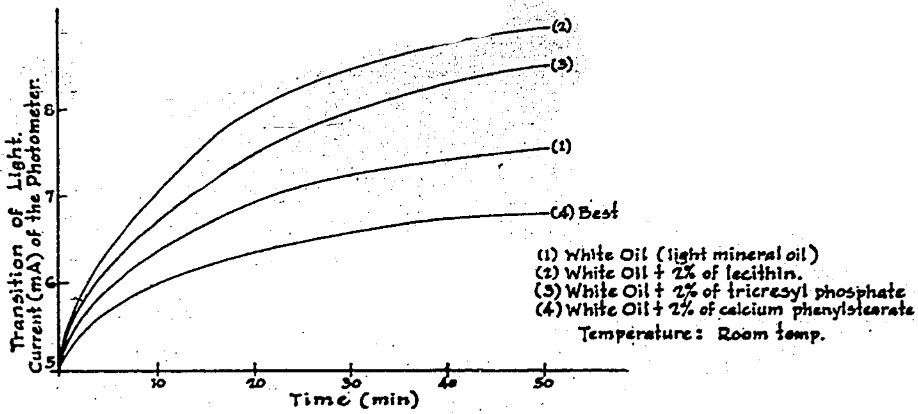

Figure 14(B)32
SEDIMENTATION VELOCITY OF SLUDGE IN OILS