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# STORAGE STABILITY OF SYNTHETIC LUBRICANTS

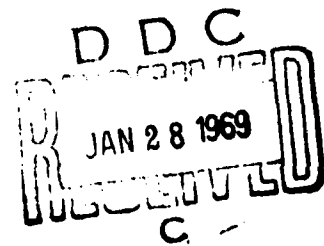
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**TECHNICAL REPORT AFAPL-TR-68-133**

January 1969

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**Air Force Aero Propulsion Laboratory  
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AFAPL-TR-68-133

# STORAGE STABILITY OF SYNTHETIC LUBRICANTS

J. P. Cuellar  
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## FOREWORD

This report was prepared by Southwest Research Institute, 8500 Culebra Road, San Antonio, Texas, under Contract F33615-68-C-1264. The contract was initiated under Project No. 3048. The work was administered by the Fuels, Lubrication, and Hazards Branch, Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The project engineers were Messrs. G. A. Beane, L. J. DeBrohun, and H. A. Smith (APFL).

This report covers one phase of work performed under the subject contract. This report was submitted by the authors October 1968.

This technical report has been reviewed and is approved.

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## ABSTRACT

Lubricant storage stability data are presented for two separate programs, each of 2 years' duration, using controlled storage conditions. One study dealt solely with the stability characteristics of an MIL-L-7808 lubricant. The second program involved five lubricant types including one MIL-L-9236B lubricant, one MIL-L-23699 type fluid, one MIL-L-27502 fluid, a 5P4E polyphenyl ether, and one experimental lubricant formulation related to polyphenyl ether. On the basis of lead corrosion test results, the presence of dissolved moisture is shown to be the controlling factor in the deterioration of the MIL-L-7808 lubricant, and the presence or absence of oxygen (air) had essentially no effect. Similarly, in the second study, three fluids of the ester class showed degradation, as evidenced by lead corrosion, in the case of the moisture-containing samples. The presence of an oxidative atmosphere had no measurable effect on fluid stability. The polyphenyl ether and the modified polyphenyl ether formulation did not indicate measurable storage deterioration over the 2-year period under any of the storage conditions investigated.

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## SECTION I

### INTRODUCTION

This report summarizes a selected portion of continuing work performed at Southwest Research Institute and being reported under Contract F33615-68-C-1264, entitled "Lubrication Research for Aero Propulsion Systems." The objectives of this broad program are the development or refinement of lubricant evaluation techniques for aero propulsion systems and the evaluation of candidate lubricants and lubrication techniques. This report is concerned with only one phase of the overall effort: the storage stability characteristics of aircraft turbine engine lubricants.

The objective of the lubricant storage stability phase of this program is to provide results and information relative to lubricant storage life under controlled conditions. Data are presented herein from two separate studies on the storage stability characteristics of various lubricant types. A 2-year program was conducted to determine the effects of oxygen, moisture, and the presence of Ethyl 703 antioxidant on the storage stability of a MIL-L-7808 lubricant.

A second test series was conducted on the storage stability characteristics of more advanced lubricant types. Data are presented on samples after storage for 6, 12, and 24 months. This program, which was also designed to evaluate the effects of moisture and oxygen on storage stability, was conducted on five oils. Lubricant types represented include a MIL-L 9236B fluid, one MIL-L-23699 oil, one MIL-L-27502 type fluid, a 5P4E polyphenyl ether, and one experimental lubricant related to polyphenyl ether. The fluid types involved in this study were selected in order that the investigation cover lubricant classes of possible interest for advanced aircraft application. The individual lubricants selected are not necessarily of direct interest, but are considered typical of their respective chemical classes.

## SECTION II

### TEST LUBRICANTS

Table 1 presents a listing of the test lubricants employed in this study, along with initial viscosity and neutralization number data and available information on lubricant type.

TABLE 1. DESCRIPTION OF TEST LUBRICANTS

Oil Code	Viscosity, cs		Neut. No., mg KOH/g	Description
	100°F	210°F		
GTO-880	13.4	3.4	0.08	Bis (2-ethylhexyl) sebacate (MIL-L 7808C)
O-62-25	15.6	3.5	0.06	MIL-L-9236B
O-64-2	27.5	5.1	0.07	MIL-L-23699
O-64-20	24.2	4.1	0.00	Experimental
ATL-401	26.3	5.1	0.11	MIL-L-27502 type
F-1041	354.5	12.9	0.00	Polyphenyl ether, 5P4E mixed isomers

## SECTION III

### MIL-L-7808 LUBRICANT STORAGE

#### 1. General

The test lubricant used in this program was GTO-880, which is a conventional MIL-L-7808 diester lubricant containing standard types of antioxidant and load-carrying additive. Three sample groups, each of which consisted of three 1-gallon samples, were prepared in this study. For one group, the base lubricant (GTO-880) was stored under a nitrogen atmosphere. A second sample group was stored under an oxidizing (air) atmosphere. For another group of samples using an oxidizing atmosphere, 0.1 percent by weight of Ethyl 703 (2,6-di-tert-butyl- $\alpha$ -dimethylamino-4-methyl-phenol) was added to the base lubricant. The Ethyl 703 is used in some MIL-L-7808 lubricant formulations to improve storage stability, and had been thought to function as a low-temperature antioxidant. One container within each sample group was equilibrated, using the appropriate atmosphere, at a nominal relative humidity of zero percent. A second sample from each group was similarly equilibrated at 75-percent RH, and a third sample at 100-percent RH.

The test samples were stored in 1-gallon glass containers, sealed with Teflon liners. At the time of placing in storage, each sample was equilibrated by bubbling air or nitrogen of controlled humidity through the sample for 24 hours, and sealing immediately. The sealed containers were stored in semidarkness in an outdoor cabinet with forced air circulation; thus the entire group of samples was exposed to identical cycling temperatures which followed the outdoor ambient temperature quite closely. The storage containers were sampled 2 months after the initial preparation. The container caps were removed and sealed caps, fitted with pressurizing and siphoning tubes, were attached. Approximately 550 ml were withdrawn from each container by pressurizing with the corresponding gas of the required humidity. The containers were then resealed with permanent caps for a 2-year period.

#### 2. Test Results and Discussion

The results of the storage tests are summarized in Table 2. Following normal practice, storage deterioration was evaluated by an assessment of the lubricant's tendency to corrode lead in the S.O.D. corrosion test. The most important points to be noted from data given in Table 2 are that: (1) keeping the samples dry prevented deterioration completely, (2) keeping air out (by using nitrogen) did not prevent deterioration of the humidified samples, and (3) the use of Ethyl 703 did substantially prevent deterioration.

TABLE 2. RESULTS OF 2-YEAR STORAGE STABILITY TEST ON A MIL-L-7808 TYPE LUBRICANT (GTO-880)

Relative Humidity at Time of Storage, %	S. O. D. Lead Loss, mg/in <sup>2</sup> (a)	Lubricant Properties after 26-Month Storage		Appearance
		Neut. No., mg KOH/g	Water Content, ppm(b)	
<u>GTO-880, nitrogen</u>				
0	0	0	44	Clear and bright
75	8	260	121	Very slight haze; some white precipitate
100	28	78	276	Very slight haze; considerable white precipitate
<u>GTO-880, air</u>				
0	0	1	41	Clear and bright
75	24	175	205	Very slight haze; some white precipitate
100	49	63	325	Very slight haze; some white precipitate
<u>GTO-880 + 0.1% Ethyl 703, air</u>				
0	0	0	78	Clear and bright, trace precipitate
75	0	6	1536	Very slight haze, some white precipitate, brown gum
100	0	4	1937	Very slight haze, some white precipitate, brown gum (darker than in 75% RH sample)

(a) Federal Test Method 5321.

(b) ASTM Method D 1744.

The 26-month data agree directionally with the 2-month data, except that the relative ratings of the 75- and 100-percent RH samples are reversed between the two periods. It is possible that the corrosivity of the 100-percent RH samples went through a maximum at some intermediate period and then decreased. Changes in the relative balance between acid ester and sebacic acid could be responsible for such behavior.

The water contents, determined by Karl Fischer reagent titration, are very interesting in that they indicate the extent to which water was consumed by ester hydrolysis reactions during storage. Water solubility in this oil (with or without Ethyl 703) has been determined to be about 2100 ppm (0.21 percent), using a static saturation method.\* Thus, it may be assumed that the initial samples at the time of storing contained 2100 ppm water in the case of the 100-percent RH samples, and 1575 ppm water in the case of the 75-percent RH samples. On this basis, the samples containing Ethyl 703 have shown essentially no consumption of water during storage, whereas the samples without Ethyl 703 have shown consumption of most of their original water. Thus, the Ethyl 703 would appear to function as an antihydrolysis agent rather than as an antioxidant in this particular system. Such a function is readily explained if it is assumed that the ester hydrolysis is acid-catalyzed, since the Ethyl 703 can act as an acid acceptor.

The lesser role of oxidation in the deterioration process is demonstrated by the lack of any significant effect when air was excluded. Another interesting comparison may be made on the basis of the amount of oxygen available for forming acidic compounds. In each sample which was air-bubbled at the time of sealing, 0.33 gram of oxygen was present.\*\* If this were all used in forming carboxyl groups, the resulting neutralization number of the 2760 grams of oil in the container would be only 0.21 mg KOH/g. Since in fact two of the samples developed neutralization numbers above 6.0, it is almost impossible that oxidation could have been responsible.

On the other hand, the decrease in water contents shows a striking correlation with neutralization number. Assuming that all samples started at the theoretical water content (0, 1575, and 2100 ppm for 0-, 75-, and 100-percent RH, respectively), the following are the theoretical neutralization numbers based on simple hydrolysis reactions, in comparison with the values actually obtained:

\*The accuracy of this value is probably about  $\pm 10$  percent. The static saturation required about 7 days to reach equilibrium, and during this time there was some evidence of reaction at the interface (scum formation).

\*\*Total in free space and dissolved in oil, taking solubility at 30°C =  $4.4 \times 10^{-3}$  wt percent. (1)†

†Superscript numbers in parentheses refer to the List of References.

<u>Sample Condition</u>	<u>Decrease in Water Content, ppm</u>	<u>Neut. No., mg KOH/g</u>	
		<u>Theoret.</u>	<u>Actual</u>
<u>GTO-880, N<sub>2</sub></u>			
0% RH	*	0.0	0.1
75% RH	1454	4.5	4.6
100% RH	1824	5.7	6.5
<u>GTO-880, air</u>			
0% RH	*	0.0	0.1
75% RH	1370	4.3	3.5
100% RH	1775	5.5	6.0
<u>GTO-880 + Ethyl 703, air</u>			
0% RH	*	0.0	0.1
75% RH	39	0.1	0.2
100% RH	163	0.5	0.2

It should be noted that although the neutralization numbers were associated very closely with water disappearance, the lead corrosion values showed only a broad qualitative relationship with neutralization number:

<u>Lead Loss</u>	<u>Neut. No.</u>
0 - 6	0.0 - 0.2
60 - 260	3.5 - 6.2

Visual observation of the samples after storage showed relatively small amounts of white precipitate in all of the moist samples. No attempt was made to identify this material. It should be noted that the dissolved water contents were far below equilibrium. One possibility is that it represented free acid, the final hydrolysis product, in excess of the amount soluble in the ester. The moist samples containing Ethyl 703 showed a gummy brown precipitate, similar to that which often appears in aliphatic amines during storage.

From the results of this study, it appears that reduction of dissolved water content at the time of packaging would be the most effective means of eliminating storage deterioration problems. It also appears that control of water content is extremely important in accelerated testing of storage stability.

\*These samples showed small apparent net increases in water content, if zero water is assumed as the starting value. These apparent increases may be caused by incomplete dehydration at starting conditions, or they may merely reflect moisture pickup in handling the samples after storage.

## SECTION IV

### ADDITIONAL CANDIDATE LUBRICANT STORAGE

#### 1. General

Samples for this program were stored in 1-quart tin-plated metal containers, sealed with aluminum foil liners. In addition, one sample for each lubricant-condition combination was stored in clear Pyrex bottles. These latter samples were removed from storage at the end of the 24-month period to provide additional information on the possible effect of container material. Individual samples for each time period (6, 12, and 24 months) were prepared for the lubricants in metal containers. Thus, intermediate sampling did not disturb other containers.

The storage facility was that described in the previous section on MIL-L-7808 lubricant storage. Table 3 identifies the sample atmospheres investigated in this program. Sample analysis upon removal from storage consisted of viscosity (100°F) and neutralization number determination, and a visual evaluation of lubricant appearance. In addition, storage deterioration was characterized by a suitable oxidation-corrosion test. For MIL-L-7808 lubricants, storage deterioration is normally evidenced by an increase in the oil's lead corrosion properties, as indicated by the standard 1-hr S. O. D. lead test at 325°F. In the program on advanced lubricant types, however, lead corrosion tendency was considered a secondary criterion. There was no prior experience concerning the lead corrosion properties of the lubricants, and it was suspected that the fluids might be of a chemical type which would not exhibit lead attack even after storage deterioration. Thus, lead corrosion tests were performed only with the 24-month metal-container samples, whereas oxidation-corrosion testing was conducted on all samples.

There was a slight disadvantage in evaluation by means of an oxidation-corrosion test in that, due to varying lubricant capabilities, all oils could not be tested under identical conditions. Oxidation-corrosion test conditions were selected on the basis of previously available results. The oxidation-corrosion test apparatus was described in connection with other studies. (2, 3) Test conditions are summarized here for individual lubricants:

<u>Lubricant Code</u>	<u>Test Temp, °F</u>	<u>Duration, hr</u>	<u>Air Rate, liters/hr</u>	<u>Sample Vol., ml</u>
O-62-25	415	18	130	200
O-64-2	425	18	130	200
O-64-20	500	18	130	200
ATL-401	425	18	130	200
F-1041	600	48	75	250

**TABLE 3. ADVANCED LUBRICANT STORAGE CONDITIONS**

<u>Sample Code</u>	<u>Sample Treatment</u>
A	24-hour flush with dry air
B	24-hour flush with 50% RH air
C	24-hour flush with dry nitrogen
D	24-hour flush with 50% RH nitrogen
E	As-is sample from cold storage

All tests employed a nonreflux glassware configuration and a metal specimen set of aluminum, titanium, silver, steel, and stainless steel. Test conditions were selected with the intention that severe deterioration would be avoided so that lubricant breakdown in storage would not be obscured by test data variability at high degradation levels.

## 2. Test Results and Discussion

### a. Water Content Data

In view of the significant influence observed for moisture in the MIL-L-7808 tests, water content was closely monitored in the current program. Table 4 presents saturation data on the lubricants and water contents on the test samples just prior to storage. It should be noted that, upon initiation of the storage program, water analysis was performed for each group of samples after equilibration with dry or moist gas. This analysis, however, was not made on each individual container but for one sample from each group of the same type. Thus, some variation in results may be expected among like samples.

Table 5 lists water content data for all storage periods. The E sample is from the normal working supply of lubricant which is kept in cold storage except for periods of various laboratory testing. When not in use, the containers are maintained at a temperature of approximately 40°F. There is no record available as to the number of times the E containers may have been opened and portions withdrawn over the 24-month storage period. No clearcut trend is apparent from the data of Table 5 with respect to water consumption by the storage samples. The moist-gas samples (B and D) of O-62-25 showed some decrease in water at 6 months and little change thereafter except for the moist-air sample in glass which further decreased at 24 months. O-64-2 moist-gas samples also indicated some water consumption between 12 and 24 months, as did O-64-20. The latter fluid, however, did not show a similar decrease for the B sample in the metal container.

Analysis for the presence of water in the dry-gas samples (A and C) showed unexpected increases for several of the 24-month samples. The increase was noted to some extent for all such samples in glass and for the O-64-2-A sample in metal. Of the glass containers, the effect was most pronounced for lubricants O-64-2, O-64-20, F-1041, and the ATL-401-C sample. The cause of the phenomenon was initially attributed to possible container leakage. Certain water contents, however, were so high as to be beyond a level attained solely through leakage. Infrared analysis of the samples in question showed no unusual absorption peaks. Since many of the glass samples indicated a water increase, an evaluation of the effect of light was made. In addition, some darkening of the glass samples was noted with all lubricants in storage which suggested some sensitivity to light.

TABLE 4. WATER CONTENT OF LUBRICANT SAMPLES  
AT ZERO STORAGE TIME

Oil Code	Sat'n	Water Content, ppm(a)				Water Content, % of Sat'n			
		A	B	C	D	A	B	C	D
O-62-25	3150	57	1626	52	1590	1.8	52	1.7	50
O-64-2	3620	31	1790	68	1850	0.9	49	1.9	51
O-64-20	446	3	228	4	237	0.7	51	0.9	53
ATL-401	2240	20	1151	78	1170	0.9	51	3.5	52
F-1041	440	5	289	3	250	1.1	66	0.7	57

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Condition	Sample Treatment
A	24-hour flush with dry air
B	24-hour flush with 50% RH air
C	24-hour flush with dry nitrogen
D	24-hour flush with 50% RH nitrogen

(a) ASTM Method D 1744.

**TABLE 5. WATER CONTENT RESULTS ON LUBRICANT STORAGE STABILITY SAMPLES**

<u>Sample Condition</u>	<u>Water Content, ppm</u>				
	<u>0 Months</u>	<u>6 Months</u>	<u>12 Months</u>	<u>24 Months</u>	
				<u>Metal</u>	<u>Glass</u>
<u>O-62-25</u>					
A	57	40	24	38	68
B	1626	1443	1478	1394	1074
C	52	44	78	35	73
D	1590	1408	1377	1447	1450
E	--	178	307	322	--
<u>O-64-2</u>					
A	31	59	35	496	228
B	1790	1777	1842	1664	1663
C	68	32	29	28	360
D	1850	1723	1838	1670	1719
E	--	539	529	514	--
<u>O-64-20</u>					
A	3	13	27	10	59
B	228	213	188	193	118
C	4	16	11	10	176
D	237	224	216	114	118
E	--	92	70	66	--
<u>ATL-401</u>					
A	20	54	30	39	46
B	1151	1136	1241	1202	1100
C	78	29	27	30	174
D	1170	1136	1192	975	1088
E	--	394	247	241	--
<u>F-1041</u>					
A	5	13	7	23	184
B	289	276	269	294	284
C	3	14	28	19	134
D	250	260	228	281	246
E	--	108	64	84	--

Accordingly, duplicate samples of all lubricants, except O-62-25 which had been depleted, were placed in glass containers and subjected to a 45-hr flush with dry nitrogen. Each sample was analyzed for water. One set of samples was then placed in total darkness for 21 days, and one set exposed only to ultraviolet light (3660 Å) for a similar period. After UV exposure, considerable darkening of all lubricants was observed. In addition, O-64-20 emitted a distinct sulfurous odor. Further, considerable increases in "water" were found for all samples except the polyphenyl ether, F-1041, as shown by the data of Table 6. Because of the significant effect obtained with O-64-2, the investigation was repeated for that lubricant and a later batch of the fluid identified as O-67-12. These results, also shown in Table 6, indicated a lesser increase in apparent water content.

The study described in Table 6 appears to verify the existence of a photochemical reaction of some type. It is doubtful that the reaction actually yields water as such. It is believed more likely that the products are of a type, possibly associated with the formation of color bodies, which reacts with the Karl Fischer reagent used in water titration, thus giving false titer values not selective to water.

The phenomenon of photochemical reaction, however, does not clarify the results obtained for the dry-gas samples of F-1041 or the high value noted for O-64-2-A in metal. These cases are not explainable. It is possible that container leakage or improper handling may be contributing factors.

b. Viscosity and Acidity Data

Table 7 lists sample viscosity and neutralization number results obtained on all samples after storage termination. It will be noted that viscosity data for samples stored under dry gas (A and C) compare closely. These data are also in good agreement with values obtained on these fluids when originally received. In contrast, the 50-percent RH conditions (B and D) resulted in a noticeable decrease in viscosity for all lubricants except O-64-20, and a relatively significant increase in neutralization number, particularly for O-62-25 and O-64-2. To determine whether these differences reflected an actual chemical change or were merely caused by the presence of relatively large amounts of water, portions of the 12-month B samples, omitting O-64-20, were purged with dry air to remove dissolved water and retested for viscosity and acidity. Viscosity data at 100°F are shown here for the samples before and after drying:

**TABLE 6. EFFECT OF UV LIGHT ON SAMPLE WATER DETERMINATIONS**

Oil Code	Water Content, ppm <sup>(a)</sup>			
	Before Exposure <sup>(b)</sup>		After Exposure	
	Darkness	UV Light	Darkness <sup>(c)</sup>	UV Light <sup>(d)</sup>
O-64-2	32	32	35	235
	36	35	36	93
O-67-12 <sup>(e)</sup>	36	35	36	66
O-64-20	18	18	18	66
ATL-401	33	33	34	57
F-1041	23	26	27	23

**(a) ASTM Method D 1744.**

**(b) Samples flushed with dry nitrogen for 45 hr.**

**(c) Samples stored in total darkness for 21 days.**

**(d) Samples stored under ultraviolet light only for 21 days.**

**(e) Different batch of O-64-2.**

TABLE 7. VISCOSITY AND NEUTRALIZATION NUMBER DATA ON LUBRICANT STORAGE SAMPLES

Sample Condition	100° F Viscosity, cs					Neut. No., mg KOH/g								
	0 Months	6 Months	12 Months	24 Months		0 Months	6 Months	12 Months	24 Months					
				Metal	Glass				Metal	Glass				
<u>O-62-25</u>														
A	--	15.58	15.56	15.57	15.55	--	0.06	0.06	0.07	0.09	--	0.06	0.07	0.09
B	--	15.31	15.28	15.31	15.34	--	--	0.28	0.77	0.66	--	0.35	0.77	0.66
C	--	15.63	15.56	15.60	15.58	--	--	0.06	0.07	0.08	--	0.06	0.07	0.08
D	--	15.31	15.27	15.33	15.32	--	--	0.26	0.74	0.70	--	0.34	0.74	0.70
E	15.59	--	--	--	--	0.06	--	--	0.06	--	--	--	0.06	--
<u>O-64-2</u>														
A	--	27.88	27.91	27.48	27.69	--	--	0.09	0.14	0.12	--	0.10	0.14	0.12
B	--	27.18	27.11	26.97	26.94	--	--	0.15	0.29	0.36	--	0.17	0.29	0.36
C	--	27.88	27.73	27.93	27.65	--	--	0.09	0.09	0.13	--	0.09	0.09	0.13
D	--	27.19	26.83	27.19	26.93	--	--	0.16	0.29	0.40	--	0.16	0.29	0.40
E	27.50	--	--	--	--	0.07	--	--	--	--	--	--	--	--
<u>O-64-20</u>														
A	--	24.27	24.27	24.27	24.22	--	--	0.0	0.01	0.03	--	0.0	0.01	0.03
B	--	23.91	24.14	24.14	24.12	--	--	0.0	0.08	0.14	--	0.05	0.08	0.14
C	--	24.17	24.16	24.20	23.98	--	--	0.0	0.01	0.09	--	0.0	0.01	0.09
D	--	24.19	23.87	23.91	23.92	--	--	0.0	0.07	0.12	--	0.05	0.07	0.12
E	24.22	--	--	--	--	0.0	--	--	--	--	--	--	--	--
<u>ATL-401</u>														
A	--	26.29	26.16	26.33	26.34	--	--	0.11	0.10	0.12	--	0.10	0.10	0.12
B	--	25.87	25.61	25.65	25.89	--	--	0.13	0.19	0.20	--	0.14	0.19	0.20
C	--	26.32	26.27	26.06	26.30	--	--	0.10	0.11	0.12	--	0.10	0.11	0.12
D	--	25.83	25.83	25.92	25.78	--	--	0.13	0.18	0.12	--	0.13	0.18	0.12
E	26.30	--	--	--	--	0.11	--	--	--	--	--	--	--	--
<u>F-1041</u>														
A	--	354.3	353.8	352.4	346.7	--	--	0.0	0.0	0.0	--	0.0	0.0	0.0
B	--	346.2	345.4	344.1	343.5	--	--	0.0	0.0	0.0	--	0.0	0.0	0.0
C	--	354.1	352.8	353.0	347.6	--	--	0.0	0.0	0.0	--	0.0	0.0	0.0
D	--	346.3	346.4	343.8	345.0	--	--	0.0	0.0	0.0	--	0.0	0.0	0.0
E	354.5	--	--	--	--	0.0	--	--	--	--	--	--	--	--

<u>Sample Condition</u>	<u>100°F Viscosity, cs</u>			
	<u>O-62-25</u>	<u>O-64-2</u>	<u>ATL-401</u>	<u>F-1041</u>
B	15.31	27.18	25.87	346.2
B, after drying	15.59	27.98	26.27	352.4
Original value	15.59	27.50	26.30	354.5

Thus, it is seen that lubricant viscosity returned to its original value after drying. It is theorized that the presence of dissolved water exhibited a slight dilution effect upon lubricant viscosity in much the same manner as the addition of a low-viscosity fluid. This effect is not too astonishing in view of the fact that three of the oils contain water in excess of 1000 ppm (0.1 percent) for conditions B and D. In the case of F-1041, the moist samples contain less than 300 ppm; however, it must be recognized that the inherent viscosity of this material is very high. Therefore, it is expected that the fluid would be more sensitive to slight dilution effects.

Neutralization number data on the B samples after purging showed no change as a consequence of the drying process. Thus it appears that some increase in acidic components occurred with the moist samples in both the oxidizing and inert environments. Because this effect was quantitatively similar for both atmospheres, the phenomenon is attributed to a hydrolytic process rather than a low-temperature oxidation reaction. Only F-1041 gave no indication of the formation of acidic materials. The fluid did exhibit an unusual aspect by the reduced viscosity of the dry samples in glass--an effect not shown by the other lubricants.

#### c. Oxidation-Corrosion Test Results

Table 8 lists viscosity increase results obtained in oxidation-corrosion testing of the subject lubricants. Data for O-62-25 were erratic and inconclusive. Lubricant deterioration of the metal container samples was highest for the dry nitrogen atmosphere, which would normally be expected to prevent any storage degradation. The moist air sample likewise gave a relatively severe viscosity increase, whereas all other samples indicated little change from 12-month data. All of the glass-container O-62-25 samples underwent mild degradation in the oxidation-corrosion test; however, the dry nitrogen sample once again showed the largest viscosity increase.

Results given in Table 8 for O-64-2 indicated a more consistent pattern. The dry gas samples underwent less oxidative degradation than the moist gas fluids. The difference between these two categories was slight; however, the effect was consistent throughout. There was no significant effect apparent for container type with O-64-2. It will be noted that this lubricant experienced a measurable loss in oxidation-corrosion test

TABLE 8. OXIDATION-CORROSION TEST SUMMARY  
FOR VISCOSITY DATA

Sample Condition	100°F Vis Increase, %				
	0 Months	6 Months	12 Months	24 Months	
				Metal	Glass
<u>O-62-25</u>					
A	--	--	19	30	19
B	--	--	26	54	20
C	--	--	18	76	36
D	--	--	22	22	22
E	--	24(a)	19	21	--
<u>O-64-2</u>					
A	--	105	161	184	164
B	--	127	163	206	220
C	--	100	188(b)	188	182
D	--	122	127(b)	233	257
E	100	86	166	207	--
<u>O-64-20</u>					
A	--	52	61	41	46
B	--	54	56	45	44
C	--	59	57	47	46
D	--	50	60	54	50
E	53	54	65	52	--
<u>ATL-401</u>					
A	--	42	42	46	45
B	--	45	48	49	48
C	--	43	46	46	44
D	--	46	48	46	48
E	41	41	60	46	--
<u>F-1041</u>					
A	--	66	73	86	96
B	--	66	82	100	109
C	--	56	67	101	99
D	--	66	71	92	100
E	74(a)	64	65	82	--

(a) Average results for duplicate determinations.

(b) C and D samples suspected of being reversed for this determination.

performance capability over the 24-month period. Viscosity increase nearly doubled within this period for all sample types, including the cold storage supply.

Viscosity results for O-64-20 and ATL-401 indicate that the fluids underwent no significant change for any storage condition throughout the 24-month period. The data of Table 8 also show that F-1041 was generally unaffected in storage. The 24-month results on this lubricant were comparable for all storage conditions; however, the overall level of deterioration was somewhat higher than that obtained at 12 months. This effect, though generally consistent for a given sample set, is not conclusive due to the fact that rather poor oxidation-corrosion test repeatability has been demonstrated<sup>(2)</sup> with this lubricant.

Table 9 presents neutralization number data derived from the oxidation-corrosion test series. These results generally confirm observations made concerning lubricant viscosity increase and agree with the individual levels of deterioration shown by viscosity.

Metal specimen corrosion obtained in oxidation-corrosion tests on the storage samples was insignificant. Lubricant O-64-2 gave no evidence of significant attack with any of the metal specimens used. Certain of the other test lubricants have a history of metal corrosion with some metals. However, specimen attack with a particular oil was consistent for all storage samples and thus did not reveal any trends specifically connected with this program.

#### d. Lead Corrosion Test Results

In view of the equivocal oxidation-corrosion test results relating storage stability to test performance, particularly with O-62-25, it was decided to conduct standard lead corrosion tests on the 24-month samples. Lead corrosion data have been the criteria of storage stability for diester lubricant types. Previous lead test data were not available for this group of lubricants; however, since three of these fluids are related to the ester class, it was thought that some indication of storage deterioration might be obtained. A lead corrosion tendency was not expected to exist for O-64-20 or 5P4E polyphenyl ether and, as shown in Table 10, none was obtained. The remaining test lubricants did exhibit a susceptibility to lead corrosion and were significantly affected by the storage atmosphere.

Lead corrosion test data for O-62-25, O-64-2, and ATL-401 demonstrate that the controlling factor in storage deterioration was again not oxygen availability but the presence of moisture. The 50-percent RH samples of O-62-25 gave severe lead weight losses regardless of gas type, whether air or nitrogen. Similarly, lead corrosion was moderate for the dry gas samples and was of the same level with or without oxygen present.

TABLE 9. OXIDATION-CORROSION TEST SUMMARY FOR  
NEUTRALIZATION NUMBER DATA

Sample Condition	Neut. No. , mg KOH/g				
	0 Months	6 Months	12 Months	24 Months	
				Metal	Glass
<u>O-62-25</u>					
A	--	--	0.63	2.49	0.73
B	--	--	1.57	4.38	0.56
C	--	--	0.49	5.78	3.58
D	--	--	0.63	0.66	0.87
E	--	1.15(a)	0.62	1.03	--
<u>O-64-2</u>					
A	--	6.08	7.56	8.47	8.15
B	--	6.94	7.42	8.59	8.65
C	--	6.39	7.71(b)	8.56	8.53
D	--	6.28	6.56(b)	8.21	8.82
E	5.84	4.49	8.22	9.08	--
<u>O-64-20</u>					
A	--	0.04	0.04	0.04	0.05
B	--	0.04	0.04	0.07	0.06
C	--	0.04	0.04	0.06	0.05
D	--	0.04	0.04	0.07	0.04
E	0.03	0.04	0.05	0.04	--
<u>ATL-401</u>					
A	--	1.64	1.73	1.91	1.82
B	--	1.66	1.75	1.68	1.96
C	--	1.64	2.01	1.95	1.95
D	--	1.62	1.73	1.78	1.99
E	1.48	1.54	1.74	1.87	--
<u>F-1041</u>					
A	--	0.03	0.05	0.13	0.10
B	--	0.06	0.05	0.11	0.10
C	--	0.05	0.05	0.14	0.08
D	--	0.07	0.05	0.11	0.10
E	0.10(a)	0.08	0.04	0.11	--

(a) Average results for duplicate determinations.

(b) C and D samples suspected of being reversed for this determination.

TABLE 10. LEAD CORROSION TEST RESULTS ON LUBRICANT STORAGE STABILITY SAMPLES

Sample Code	Storage Atmosphere	Lead Weight Change (a), mg/in. 2			
		O-62-25	O-64-2	O-64-20	ATL-401
A	0% RH, air	- 14	- 9	+5	- 1
B	50% RH, air	-139	-50	+1	-19
C	0% RH, N <sub>2</sub>	- 14	- 8	+5	0
D	50% RH, N <sub>2</sub>	-126	-49	+1	-14
E	Variable RH, air, cold storage	- 16	- 5	+2	0

Metal container samples.

(a) Federal Test Method 5321.

A similar relationship was observed for O-64-2 and ATL-401 although lead corrosion was less severe for these lubricants, particularly the latter.

Thus, storage deterioration, as evidenced by lead corrosion for the three lubricants, is apparently due to hydrolytic instability. The lesser role of oxidation in the degradation process is again demonstrated by the lack of any significant effect when air was excluded (by the use of nitrogen).

## SECTION V

### CONCLUSIONS

It has been demonstrated conclusively that the presence of dissolved moisture is the controlling factor in the deterioration of one typical MIL-L-7808 lubricant, and that the presence or absence of oxygen has essentially no effect. The additive Ethyl 703 stops the development of corrosivity, apparently by an antihydrolytic rather than an antioxidant mechanism, but it causes some additional precipitation of insoluble material from moist samples.

In the storage program with five other type lubricants, several performance criteria were evaluated. Over the 24-month period, only lubricant O-62-25 indicated significant consumption of available moisture. Several instances of increased sample water were noted, primarily in glass containers. The phenomenon is tentatively ascribed to a photochemical reaction. This theory, however, offers no explanation for results on F-1041 or an O-64-2 sample in metal which also gave increased water contents. Viscosity data obtained on the storage samples revealed no permanent change of this property over the 24-month period, although moist-gas samples gave a depressed viscosity apparently due to the presence of dissolved water. With the exception of F-1041, all moist-gas samples also indicated some neutralization number increase in storage. This effect was most pronounced for O-62-25 and O-64-2.

Oxidation-corrosion test results on the five fluids showed essentially no performance change except for lubricants O-62-25 and O-64-2. Sample performance for O-62-25 unexpectedly showed the most severe deterioration for the dry nitrogen atmosphere. All O-64-2 samples indicated slight deterioration with time regardless of the storage atmosphere. A similar performance was shown for both dry-gas samples. The moist-gas samples, also quantitatively similar in performance, showed the greatest degradation. This relationship implies a hydrolytic storage instability rather than oxidative deterioration.

Lead corrosion test results showed the development of significant corrosion products for the 24-month moist-gas samples of O-62-25, O-64-2, and ATL-401. The effect was quantitatively similar for both air and nitrogen atmospheres. Lead corrosion was suppressed for both gas atmospheres by the exclusion of moisture. Thus, as with the earlier study on the MIL-L-7808 lubricant, it is concluded that the presence of moisture, not oxygen, is the controlling factor in the storage deterioration of these ester type fluids.

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13. ABSTRACT Lubricant storage stability data are presented for two separate programs, each of 2 years' duration, using controlled storage conditions. One study dealt solely with the stability characteristics of a MIL-L-7808 lubricant. The second program involved five lubricant types including one MIL-L-9236B lubricant, one MIL-L-23699 type fluid, one MIL-L-27502 fluid, a 5P4E polyphenyl ether, and one experimental lubricant formulation related to polyphenyl ether. On the basis of lead corrosion test results, the presence of dissolved moisture is shown to be the controlling factor in the deterioration of the MIL-L-7808 lubricant, and the presence or absence of oxygen (air) had essentially no effect. Similarly, in the second study, three fluids of the ester class showed degradation, as evidenced by lead corrosion, in the case of the moisture-containing samples. The presence of an oxidative atmosphere had no measurable effect on fluid stability. The polyphenyl ether and the modified polyphenyl ether formulation did not indicate measurable storage deterioration over the 2-year period under any of the storage conditions investigated.			

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