Factors Influencing the Lead Corrosivity of Ester Oils during Long-Term Storage

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ESTER-TYPE JET ENGINE OIL of Specification MIL-L-7808 (*14*) is the largest-volume extreme-temperature lubricant and synthetic oil in current use. This and various other ester oils are products resulting largely from the World War II investigations of this laboratory on diester-type lubricants (*3, 4*). Diester oils are excellent lubricants and respond well to additives for improving viscosity-temperature properties, antiwear characteristics, and oxidation resistance. MIL-L-7808 oils permit engine starting at temperatures of − 65° F. and are operable up to 350° F. (*9*). Esters of polyols are promising candidates for operation at temperatures of 400° F. and above (*1*). Both types of esters are apparently satisfactory as regards hydrolytic stability, since they pass the bulk hydrolysis test of Specification MIL-H-8446 (USAF) (*15*). The one serious limitation of Specification MIL-L-7808 oils is that they become corrosive to lead during long-term storage.

Petroleum lubricating oils become corrosive to lead during service, but no difficulty has been reported on their storage instability. As the outstanding structural difference between these oils is the absence of ester groups in petroleum oils, it appeared probable that the reactivity of the ester group was responsible for the increase in corrosivity of MIL-L-7808 oils during storage.

It was reported at service-industry conferences several years ago that the half ester, octyl hydrogen sebacate, OHS (octyl refers to the 2-ethylhexyl radical), was the corrosive constituent in deteriorated oils. It was speculated that OHS production was accelerated by the presence of tritotlyl phosphate (tricresyl phosphate, TCP), and that the catalytic action of TCP was caused by impurities. Some subsequent investigators (*5*) have attributed the deterioration of MIL-L-7808 oils to oxidative attack at ordinary storage temperatures due to the ineffectiveness at such temperatures of the antioxidant, phenothiazine. As these investigators found no correlation between water content and corrosiveness, hydrolysis was dismissed as the mechanism responsible for OHS formation (*5*). Other investigators (*17*) found a correlation between oil acidity and corrosiveness.

The suggestion and tentative conclusion advanced at the service-industry conferences were based on the poststorage properties of commercial oils whose initial properties and compositions were imperfectly known. Hence, the chemical reactions leading to oil corrosivity were not adequately established. Critical examination revealed that the factors suggested to explain oil deterioration could not account for the wide range of storage stabilities exhibited by different lots of oil. Therefore, a more systematic investigation was undertaken of the reactivity of the ester linkage in diester oils and of the development of lead corrosivity both in pure diesters and in MIL-L-7808 formulations. Studies already reported (*11, 13*) dealt with the acidolysis equilibrium between bis(2-ethylhexyl) sebacate and sebacic acid (sometimes included in MIL-L-7808 oils as a lead corrosion inhibitor), with the preparation of pure half ester, 2-ethylhexyl hydrogen sebacate, and with the properties of the lead, sodium, and barium soaps of this half ester. This work confirmed the presence of the half ester in corrosive oils, and showed that in the absence of catalysts the reaction of sebacic acid with bis(2-ethylhexyl) sebacate would be too slow at storage temperatures to account for the amounts of half ester present in highly corrosive oils. It is the purpose to report here the results of a study of the corrosion process, observations on the increase in corrosivity during controlled storage, and the identification of acid-catalyzed hydrolysis as the decisive mechanism for the formation of lead-corrosive oils.

MATERIALS AND EXPERIMENTAL PROCEDURE

Bis(2-ethylhexyl) sebacate (DOS) was the base stock for all of the compositions studied. A highly purified material was obtained by molecular distillation of a commercial lubricant grade of diester, followed by percolation through fuller's earth and alumina to remove remaining polar impurities. The resultant product was a water-white oil with a saponification equivalent 99% of the theoretical, neutralization and peroxide numbers below 0.01, a corrosion number less than 1, and a water content of less than 0.01 weight %. The commercial grade of diester used for parallel studies had a corrosion number of 36, a neutralization number of 0.24, a peroxide number of 1.4, and a water content of 0.08 weight %.

The following chemicals were synthesized or repurified and characterized at this laboratory: 2-ethylhexyl hydrogen sebacate (OHS); methyl hydrogen sebacate; 1,1,7-trihydroperfluoroheptyl hydrogen 3-methylglutarate, and glutaric acid.

The following compounds were commercial products of reagent grade, used as received: phenothiazine (PTZ); sebacic, succinic, malonic, stearic, 2-ethylhexanoic, tricarballylic, and 1,2,4-butane tricarboxylic acids; and 2,6-di-*tert*-butyl-α-dimethylamino-*p*-cresol (2,6-AC). The 2-ethyl-1-hexanol (EHOH), pelargonic acid, and tricresyl phosphate (TCP) used were of technical grade. The latter compound was a mixture of the para and meta isomers, 80 and 20%, respectively. As received, its neutralization number was 0.08 and its chloride concentration was less than 0.1 p.p.m. (*22*). After percolation through columns of activated alumina and Florisil, the neutralization number was reduced to less than 0.01. All concentrations of additives are given in molality or weight per cent.

EXPERIMENTAL

Lead Corrosion Test. This test was used as described in Specification MIL-L-7808; it involves aeration of 500 ml. of oil at 163° C. for one hour in the presence of rotating coupons of lead and copper.

Miniature Lead Corrosion Test. To reduce the volume of oil required, a miniature corrosion test was devised which used the temperature and test duration of the specification, but reduced the sample size from 500 to 40 ml. and the aeration rate to 195 ± 5 ml. per minute, and changed the geometry of the metal coupons as shown in Figure 1. A calibration with oils of known corrosivity established that the corrosion losses in the miniature test, in milligrams of lead dissolved per square inch were very closely one third of those in the specification test. All results from miniature corrosion tests have been translated to specification corrosion numbers by the use of this factor before being reported here.

Water Determination. This procedure was a modification of ASTM Method D 1533-58T (*2*), whereby an excess of Karl Fischer reagent was back-titrated with methanol-water solution to a "dead stop" end point (*26*).

Peroxide Determination. Peroxides were determined in acid medium by the potassium iodide-sodium thiosulfate procedure (*23*). Peroxide numbers were calculated in the following manner: Peroxide No. = (ml. of $Na_2S_2O_3$ for sample − ml. of $Na_2S_2O_3$ for blank) (normality $Na_2S_2O_3$) (1000) ÷ sample weight.

Oxidation Tests. To study the effect of oxidation state on lead corrosivity, oil compositions were oxidized in Erlenmeyer flasks at 280° F. for 40 or 45 hours by rapid aeration with clean dry air. The degree of oxidation was defined by acid and peroxide determinations.

LEAD CORROSION MECHANISM

The corrosion of lead and lead alloys in hydrocarbon solvents has been studied extensively (*8, 10, 18-20, 24, 25*); it is of interest to compare the corrosion effects in the diester oils with those obtained in the more extensively studied systems to ascertain whether the same general mechanism is operative. It is generally agreed that the corrosion of lead in hydrocarbon solvents requires both acidic material and an oxidizing agent. It has been demonstrated (*18, 20*) that the rate of lead corrosion at a high relative concentration of oxidizing agents is proportional to the concentration of carboxylic acid present, and that at a high relative concentration of acid it is proportional to the concentration of oxidizing agent. The corrosion rate is also proportional to the surface of lead available.

For a comparable study of lead corrosion in the diesters, experimental oils were prepared which contained the customary amount of phenothiazine (PTZ) as the antioxidant, and suitably selected concentrations of organic acids whose lead salts were oil-soluble. These acids included 2-ethylhexanoic acid, pelargonic acid, stearic acid, methyl hydrogen sebacate, 2-ethylhexyl hydrogen sebacate, 1,1,7-trihydroperfluoroheptyl hydrogen 3-methyl glutarate, and *p*-cresol. It was found that the corrosion number increased with increasing acid concentration and that the points for the monocarboxylic acids and half esters all fell on a single smooth line which approached linearity at acid concentrations below 1.5 molal (see Figure 2). *p*-Cresol, a compound of lower acidity, was less corrosive than a corresponding concentration of a carboxylic acid. When the concentration of organic acid was held constant and the oxidant concentration reduced by aeration with nitrogen instead of air, the apparent lead corrosion number of the oil dropped from 230 to 1.9. These experiments indicate that the corrosion of lead by carboxylic acids proceeds by the same general mechanism in DOS as in the hydrocarbon solvents.

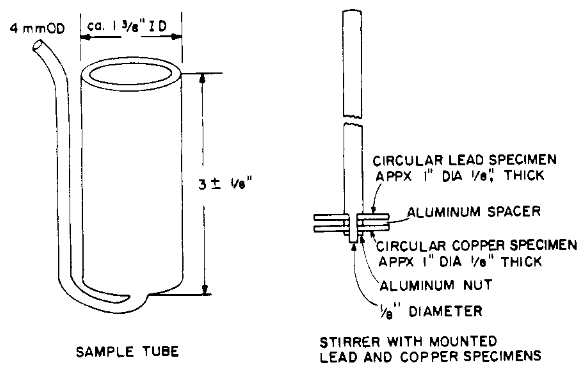

Figure 1. Miniature lead corrosion test apparatus

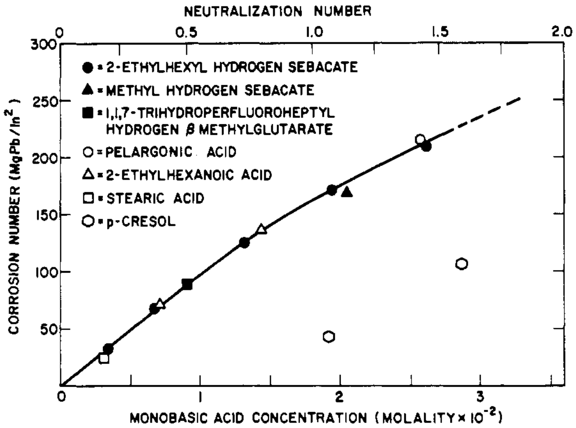

Figure 2. Corrosivity of monocarboxylic acids in bis(2-ethylhexyl) sebacate

When the corrosive acid present in an experimental oil was the half ester, OHS, a precipitate of normal lead sebacate was observed. Analysis of the precipitate gave a lead content of 50.1 ± 0.5% (theory = 50.7%). The identity of the precipitate was further confirmed by the isolation of its acid constituent as free sebacic acid. The production of lead sebacate from the normal salt of the half ester can be formulated either as a simple disproportionation or as a result of further hydrolysis of the half-ester ion. The information available does not permit a decision as to which reaction actually takes place. Similar precipitates of lead sebacate were noted during tests of highly corrosive commercial oils; the analyses indicated lead contents of 44.7 to 50.8%. Sebacic acid was again identified as the acid present.

Lead in the precipitated salt from the experimental oil amounted to about 15% of the lead lost by the test specimen. The remaining 85% of the lead was in solution and could not be precipitated by dilution with common diluents. It was recovered quantitatively as the sulfide. Kaufman (*13*) has reported that the normal lead salt of the half ester, OHS, is extensively soluble in micellar form in a wide variety of organic liquids. No further efforts were made to isolate the soluble lead compound.

INCIDENCE OF CORROSIVITY IN STORED MIL-L-7808 OILS

Field experience showed that it was impossible to predict the stable storage life of MIL-L-7808 oils. In general, oils from a given batch followed the same deterioration pattern, but frequent anomalies were noted. As the composition and initial properties of the commercial oils were imperfectly known, a variety of uncontrolled variables could have influenced their storage characteristics. Therefore, it was considered desirable to study the storage behavior of better characterized compositions under more carefully controlled conditions.

For this purpose two sets of experimental oils were formulated. One set of compositions utilized specially purified DOS as the base fluid; the other, technical DOS with an initial corrosion number of 36 and a neutralization number of 0.24. The results of room temperature storage of these oils are shown in Figure 3. Only the technical DOS samples containing TCP showed large increases in corrosivity; the sample with the "as received" TCP increased in corrosivity at a faster rate than the one with percolated TCP. Neither the technical nor the purified DOS samples without TCP showed appreciable changes in corrosivity. Neutralization numbers obtained before each corrosion number agreed with values predicted from thier corrosion numbers in Figure 2 within approximately 5%.

In order to develop characteristic differences in stability within a practicable storage period, the storage temperature was raised to 125° F. As at room temperature, the samples containing no TCP showed negligible increases in corrosivity, (Figure 4). However, at 125° F., both the purified and technical samples containing TCP increased in corrosivity. The samples with percolated TCP showed an induction period, whereas that with "as received" TCP increased in corrosivity from the initiation of the test. Again the neutralization numbers agreed within about 5% with those predicted from their corrosion numbers.

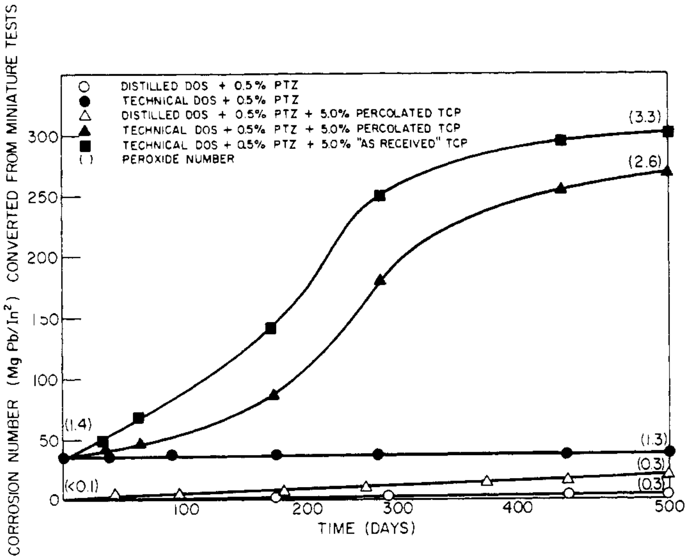

Figure 3. Storage stability of bis(2-ethyhexyl) sebacate compositions (room temperature)

A fortunate circumstance made it possible to supplement the storage tests just described with data on well-characterized diesters which had been stored under laboratory surveillance for as much as 14 years. These were retained samples of diesters procured and tested in connection with the original development of the diester instrument and engine oils (*3*, *4*, *7*). The current properties and corrosivities of these samples are shown in Table I. All of these diesters had corrosion numbers below 50, although their storage lives extended up to 14 years. MIL-L-7808 oils frequently develop corrosion numbers exceeding 200 after 1 to 3 years' storage. A reasonable correlation is again obtained between neutralization and corrosion numbers. These tests show that the corrosive component formed in diesters during storage is acidic, and the shelf life of diesters containing no TCP is sufficiently long to permit stock piling of adequate reserves. However, the data of Figure 3 show that presence of TCP does not invariably result in high lead corrosion after storage. The presence of TCP, then, is a necessary but not a sufficient condition for the development of high corrosivity.

OXIDATION AND CORROSIVITY

The relation of oil oxidation to lead corrosivity was investigated by analysis of the data on peroxide numbers accumulated in the storage test already described, and also by tests of oils oxidized at moderate temperatures. It is generally agreed that oils are oxidized through a hydroperoxide mechanism and that acids are one of the peroxide decomposition products. Furthermore, the oxidation rate of uninhibited diesters is a function of the peroxide concentration (*16*).

Reference to the peroxide numbers developed in the storage samples of Figures 3 and 4 shows no correlation between peroxide numbers and corrosivity in the storage tests either at room temperature or at 125° F. The peroxide numbers gave no indication of extensive oxidation during storage. If low-temperature oxidation were the mechanism responsible for increasing corrosivity, the retained ester samples of Table I should have become highly corrosive. Their current corrosion numbers, however, were 46 or below.

Examining the corrosivity of several experimental oils after they had been subjected to oxidation at 280° F. gave added information on the relation of oxidation to corrosion (Table II). The sample containing PTZ showed only slight changes in peroxide and neutralization numbers and negligible corrosivity. The uninhibited samples showed substantial increases in neutralization and peroxide num-

Table I. Lead Corrosivities of Some Commercial Diesters Without Additives

Identification	Storage, Years	Storage Conditions[a]	Corrosion Number	Neutralization Number	Peroxide Number	Water Content, Wt. %
Bis(2-ethylhexyl) sebacate	14	a-u	36	0.24	1.4	0.08
Bis(2-ethylhexyl) sebacate	5	b-u	23	0.17	2.0	0.03
Bis(2-ethylhexyl) sebacate	¼	c-h	1	0.01	<0.1	0.02
Dicapryl sebacate	11	a-u	46	0.46	<0.1	0.06
Bis(iso-octyl) sebacate[b]	8	a-u	43	0.44	<0.1	0.12
Bis(tetradecyl) sebacate[c]	12	a-u	20	0.23	<0.1	...
Bis(2-ethylhexyl) azelate	10	d-h	45	0.33	...	0.05
Dihexyl azelate	10	a-u	42	0.38	2.3	0.11
Bis(isoamyl) adipate	7	a-u	17	0.08	1.2	0.12

[a] a. Screw-top tin-plated can, partially filled.
b. Screw-top tin-plated can, full but no seal.
c. Screw-top tin-plated can, full, metal seal.
d. Screw-top bottle, partially filled.
u. Stored in unheated building.
h. Stored in heated building

[b] Iso-octyl - oxo alcohol.

[c] Tetradecyl or [1-(2-methylpropyl)-4-ethyloctyl].

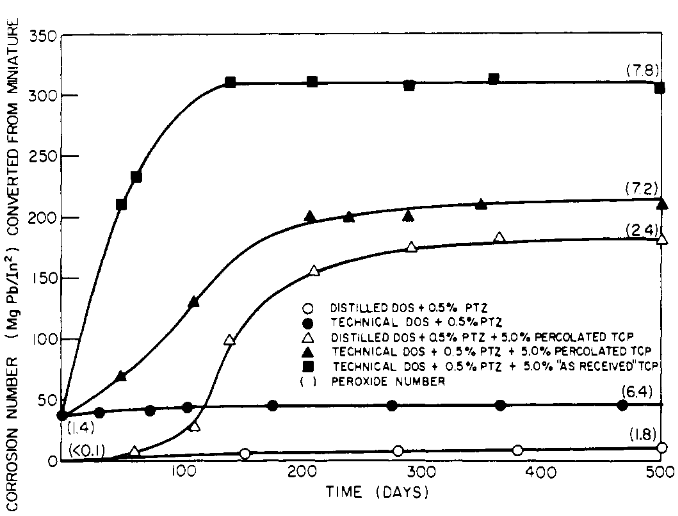

Figure 4. Storage stability of bis(2-ethylhexyl) sebacate compositions (125° F.)

bers, but developed corrosivities which were only moderate when compared with storage samples of equal acidity. This indicates that the acidic products formed by oxidation at 280° F. differ markedly from those produced during storage at ambient temperature. No evidence was obtained that TCP accelerated the formation of corrosive products in these oxidation experiments. Available data do not support the suggestion that low-temperature oxidation of the oil is a major contributor to corrosivity, or that oils inhibited with PTZ require a supplementary oxidation inhibitor to protect the oil at storage temperatures.

WATER CONTENT AND CORROSIVITY

The most consistent relationship discernible in the data thus far presented is that between the corrosivity and acidity of stored oils. Since storage-temperature oxidation appears to provide negligible amounts of corrosive acids, hydrolysis of the diester is the most probable source of such acids. Additional evidence for the hydrolysis mechanism is that OHS, a probable hydrolysis product, is the major acid component in deteriorated MIL-L-7808 oils. The evidence strongly suggests that the initial water content of the oils has been the uncontrolled variable in storage deterioration. Unfortunately, no precise data are available on this property of field-stored MIL-L-7808 oils.

As a first step in investigating the relation of water to corrosivity, the solubility of water was measured in bis(2-ethylhexyl) sebacate and in compositions containing this ester, PTZ, and either EHOH, or TCP, or both. The results in Table III show that the additives in the concentrations used increase the solubility of water in the compositions by a few tenths of 1% at 125° F., but have hardly detectable effects at 68° F. An oil half saturated at 68° F. contains water sufficient for the partial hydrolysis of enough diester to account for a lead corrosion number of 235.

Table II. Changes in Corrosivity of Bis(2-ethylhexyl) Sebacate Compositions with Oxidation at 280° F.

	Oxidation Time, Hr.	Corrosion Number	Neutralization Number	Peroxide Number
DOS, bis(2-ethylhexyl)	0	<1	0.02	<0.1
sebacate	18	61	1.26	46
	40	85	6.88	65
DOS + 5.0% TCP, tricresyl	0	<1	0.03	<0.1
phosphate, "as received"	16	20	0.52	43
	45	37	17.2	32
DOS + 5.0% TCP	0	<1	0.03	<0.1
+ 0.5% PTZ, phenothiazine	16	2	0.08	2
	45	1	0.26	4

Further experiments showed that atmospheric moisture rapidly dissolved in DOS. Two 200-ml. samples of the dry diester (water content less than 0.01%) were exposed to the atmosphere in 400-ml. beakers. One was stirred slowly in a constant temperature room maintained at 68°F. and 50% relative humidity. In 3 ½ hours the water content increased to 0.08%, or three-fourths saturated. The other sample was not stirred, but was exposed where the temperature varied from 78° to 86° F. and the relative humidity from 75 to 92%. The water content of this unstirred sample rose to 0.03% in 6 hours and to 0.08% in 24 hours. It is evident that enough water would be picked up during moderate exposures to humid atmospheres to produce an oil which could develop strong corrosivity during prolonged storage.

Calculations were made of the amount of water per annum that would enter a half-filled gallon can in tropical storage if the can were closed against convection but not sealed against breathing caused by changes in temperature and pressure. The temperature cycle was taken as 70° F. to 115° F. daily, barometric effects were neglected and the water content of the air was assumed equivalent to 80% relative humidity at 100° F. The computation indicated that 1.97 grams of water would enter the can in one year; this amount is sufficient to saturate the dry oil at 70°F. Given an active hydrolysis catalyst, such storage conditions could produce an extremely corrosive oil.

Table III. Solubility of Water in DOS and DOS Compositions

Identification	Solibility of Water, Wt. % 68° F.	 125° F.
DOS, pure bis(2-ethylhexyl) sebacate	0.11	0.15
DOS + ¼% EHOH, 2-ethyl-1-hexanol	0.12	0.17
DOS + ½% EHOH	0.12	0.19
DOS + PTZ (0.5% phenothiazine) + TCP (5.0% tricresyl phosphate)	0.12	0.17
DOS + PTZ + TCP + ¼% EHOH	0.13	0.18
DOS + PTZ + TCP + ½% EHOH	0.13	0.20

Confirmation of the ready solubility of available water vapor is found in the data given in the last column of Table I on the present water content of retained samples of commercial oils which had been stored for various intervals. The water content of diesters from partially filled containers was greater than that from filled containers, but all unsealed samples contained substantial amounts of water. Table I also shows that the other esters listed are as susceptible as the sebacate to atmospheric moisture. The relatively low corrosion and neutralization numbers noted after these long storage periods may be attributed to the absence of TCP additive, some component of which catalyzes hydrolysis.

Determinations of the water content of the diesters from which the experimental oils of Figures 2 and 3 were formulated provided a key to explain the wide range of corrosivities developed during the storage study. The distilled DOS contained less than 0.01% water; the technical DOS contained 0.08%. Only samples containing both TCP and appreciable water developed corrosivity at room temperature. The same general pattern prevailed at

125° F., except that the "dry" sample containing TCP, after an initial period of low corrosivity, became progressively more corrosive as the test schedule was continued. This may have resulted from water absorption when the container was opened to remove samples for test, or an imperfect seal, but no data were taken that would be decisive.

EXPERIMENTS WITH CONTROLLED WATER CONTENTS

The cooperative roles of dissolved water and TCP in producing corrosive oils were established beyond question by the storage behavior of two sets of experimental oils. Each set was prepared from carefully dried and distilled DOS with and without water and with and without the addition of TCP (both "as received" and after percolation). The compositions are given in Figures 5 and 6. The corrosivities and the residual water contents of one set were followed by periodic sampling during storage at 125° F. Figure 5 shows that the dry oils did not become corrosive, even in the presence of TCP. Whereas the wet sample containing no TCP developed only a slight corrosivity and showed no decrease in water content, the wet samples containing TCP became strongly corrosive and the water content dropped to 0.01 or 0.02%.

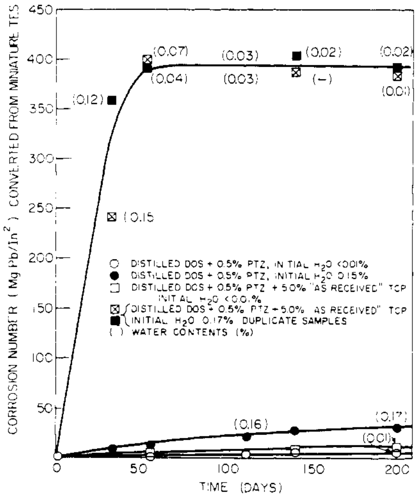

Figure 5. Effect of water content on corrosivity of bis(2-ethylhexyl) sebacate composition (125° F.)

The second set of samples was stored at 185° F. in accordance with a recent Air Force requirement for MIL-L-7808 oils. (The requirement permits corrosion numbers of 20 and 150 after 14 and 45 days, respectively.) The dry oils with and with out TCP and the wet oil without TCP all developed much less than the maximum corrosivity allowed for acceptable oils. The wet oils containing TCP again became strongly corrosive, and the water content fell to less than 0.01%. The "as received" TCP produced more rapid deterioration than the percolated sample, which exhibited an initial period of lower activity, but later became almost as active as the unpurified compound. Assuming that all of the water consumed had hydrolyzed DOS to the half ester, the corrosion number of the resulting oil would be predicted from Figure 2 to be approximately 200. This is in reasonable agreement with the experimental value of 185.

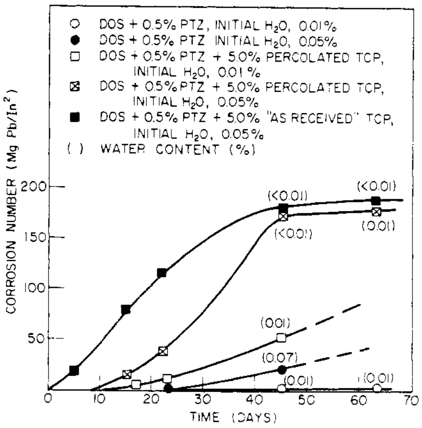

Figure 6. Effect of water content on corrosivity of bis(2-ethylhexyl) sebacate compositions (185° F.)

In the absence of moisture during storage, the DOS compositions investigated show only small increases in corrosiveness. In the presence of water during storage, DOS compositions containing TCP deteriorate rapidly; the corrosiveness is a function of the amount of water consumed by hydrolysis. Two and a half years of storage experience at this laboratory with MIL-L-7808 oils in sealed aluminum cans furnish collateral evidence about the effect of water. Examination of quart samples at 2-month intervals revealed that the water content remained below 0.01% and corrosion numbers did not exceed 1.0.

INHIBITORS OF LEAD CORROSION

Polybasic Acids. Since some suppliers of MIL-L-7808 oils were reported to be adding free sebacic acid as a corrosion inhibitor, the effect of polybasic acids on lead corrosion was studied. A synthetic corrosive oil comprising distilled DOS plus sufficient OHS (2.8×10^{-2} molal) to raise the corrosion number to 220 was used as the reference oil. The effects of increasing concentrations of malonic, glutaric, sebacic, and tricarballylic acids on the corrosiveness of the reference oil are shown in Figure 7. When the concentration of any of these acids exceeded a certain limiting value, the corrosiveness of the half ester was almost nil. Isolated points on the graph indicate that succinic and butane-1,2,4-tricarboxylic acid can also act as effective lead-corrosion inhibitors. The limiting effective concentration of the various polycarboxylic acids is in the same order as their solubilities in DOS. The inhibiting action of these polybasic acids is attributed to the formation of a film of insoluble lead salts on the lead specimen.

It would appear, therefore, that a sufficient concentration of any of these polycarboxylic acids in an otherwise corrosive oil would prevent serious attack (Figure 7).

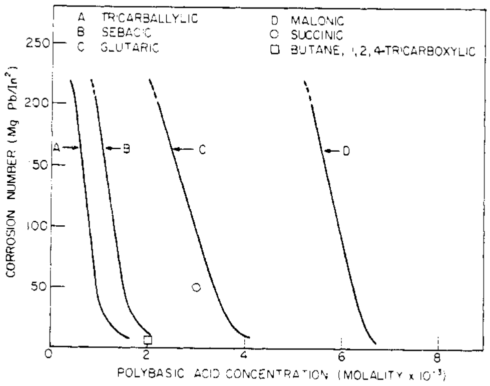

Figure 7. Corrosion inhibition with polybasic acids

However, experiments with polycarboxylic acids in commercial oils that had become corrosive during storage gave very erratic results. It was noticed that the oils least responsive to the inhibiting action of polybasic acids contained appreciable quantities of EHOH. Experiments showed that EHOH was not itself corrosive to lead when present at concentrations found in commercial oils (0.5% or less). When EHOH (8×10^{-3} molal) was added to the reference inhibited oil (DOS + OHS, 2.8×10^{-2} molal + sebacic acid, 4×10^{-4} molal), lead-corrosion losses were of the same magnitude as in the absence of sebacic acid, although the results were less reproducible. Shortening the preheating period before starting the corrosion test improved the inhibition by sebacic acid in the presence of 2-ethyl-1-hexanol. The free sebacic acid must have been removed during the preheating period, probably by esterification.

Storage test results at 185° F. on compsitions with and without 0.1% sebacic acid are compared in Figure 8. The detrimental effect of water on the compositions containing sebacic acid is also shown. The dry sample containing sebacic acid rose to a maximum corrosion number on about the 25th day of storage and then decreased. This phenomenon has been observed with commercial MIL-L-7808 oils during storage. The wet sample containing sebacic acid increased in corrosivity at a faster rate than did the wet sample containing no sebacic acid, but after 45 days both attained the same corrosivity, corresponding to a consumption of 0.045% water.

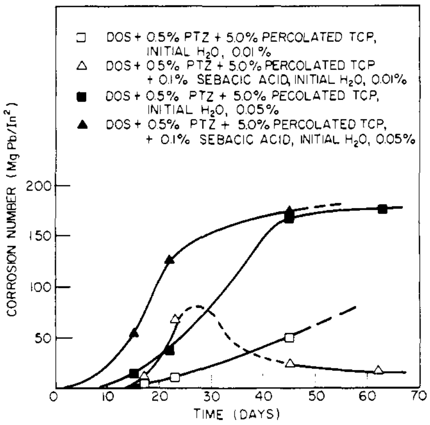

Figure 8. Effect of sebacic acid on corrosivity of bis(2-ethylhexyl) sebacate compositions (185° F.)

Polybasic acids do not appear to be promising lead-corrosion inhibitors for MIL-L-7808 oils because of their limited oil solubility, their erratic behavior in the presence of 2-ethyl-1-hexanol, and their ineffectiveness in the presence of water. The rapid acidolysis reaction between polybasic acids and diesters to from the corrosive half ester (*11*) at temperatures of 200° C. is another serious limitation.

Amine Inhibitors. Other investigators (*5*, *6*) have speculated that a supplementary antioxidant was required to stabilize MIL-L-7808 oils against oxidative attack during storage, with consequent formation of corrosive products. The auxiliary compounds recommended, 2,6-di-*tert*-butyl-α-dimethylamino-*p*-cresol (2,6-AC), was shown to improve the storage life of diester base oils (*5*, *6*). As the work reported here has shown that hydrolysis, rather than oxidation, is the mechanism primarily responsible for the formation of the corrosive component, information is needed about the mode of action of this inhibitor.

It might be thought that the inhibitor operates by neutralizing the corrosive half ester formed in the oil. Aliphatic tertiary amines react with monocarboxylic acids in benzene to form amine complexes containing 2 and 4 acid molecules (*12*). These amine complexes are appreciably dissociated in benzene solution to give free acid and amine. The same amines react with stronger acids in a 1 to 1 ratio to form more stable salts. To determine the effect of the tertiary amine 2,6-AC in reducing corrosivity due to the half ester, experimental oils were prepared containing various ratios of the half ester (OHS) and the amine. The formulation comprising DOS + 0.5% PTZ + 5,0% "as received" TCP was used as a standard fluid, and various concentrations of other compounds were added (Table IV).

Table IV. Lead Corrosion in Presence of Half Ester (OHS)[a] and 2,6-AC[b]

Additive Concn., Molal × 10^{-2}		Corrosion Number	
OHS	2,6-AC	Exptl.	Estd. from Figure 2
1.04	...	97	100
1.04	0.38	73	67
2.20	...	193	189
2.20	0.38	164	163
2.20	2.20	130	0

[a] OHS, 2-ethylhexyl hydrogen sebacate.
[b] 2,6-AC, 2,6-di-*tert*-butyl-α-dimethylamino-*p*-cresol.

Measured corrosion numbers for the samples containing 2,6-AC are given in the third column. The fourth column gives the corrosion number estimated (by the use of Figure 2) on the assumption that the effective acidity was reduced by 1 to 1 reaction with 2,6-AC. The amine deactivated its full equivalent of acid only when the concentration of acid was much greater than that of the amine. When the concentration of amine was comparable with that of the acid, the amine was less than stochiometrically effective. This was to be expected, because only a large excess of acid could prevent appreciable dissociation of the amine-acid complex. Thus, the neutralization of the corrosive half ester cannot be the mechanism by which 2,6-AC maintains the corrosivity of MIL-L-7808 oils at low levels. Furthermore, the concentration of amine recommended, 0.1% or 0.38×10^{-2} molal, is sufficient to neutralize as much acid as is present in a highly corrosive oil.

Results of accelerated storage tests on MIL-L-7808-type oils with and without 2,6-AC and with and without water are shown in Figure 9. These experiments show that in the presence of the amine no water is consumed and corrosivity is maintained at low levels. Similar results were obtained at 125° F. Here a wet sample based on technical DOS, 0.21% water, 0.5% PTZ, 5.0% "as recived" TCP, and 0.1% of 2,6-AC, increased in corrosivity from an initial value of 36 to only 73 after 140 days of storage. Its water content was unchanged during this period. A comparable sample without the amine inhibitor reached a corrosion value of almost 400 and its water content dropped rapidly to about 0.02%.

The hydrolysis of DOS is slow in the absence of TCP. In the presence of "as received" TCP (neutralization number 0.08) corrosion numbers rise rapidly from the initiation of the test, whereas in the presence of percolated TCP (neutralization number less than 0.01) there is an induction period. This indicates that the hydrolysis of DOS is catalyzed by acidic materials present in the "as received" TCP and that catalytic acids are produced form percolated TCP in the presence of water. The most probable products are acid phosphates. The amine 2,6-AC retards hydrolysis by reacting preferentially (*21*) with the strong acid phosphates to form stable neutral salts, thus effectively removing the catalysts. Further confirmation of this mechanism may be deduced from data given in Cart's recent investigation on storage stabilizers for MIL-L-7808 oils (*6*). A variety of compounds having antioxidant activity were studied, including mercaptobenzothiazoles, metal dithiocarbonates, phenols, and aromatic and aliphatic amines. Without exception, the aliphatic amines were found to be effective lead-corrosion inhibitors, whereas the other compounds were ineffective. Aromatic amines, because of thier lower basicity, do not effectively neutralize the acid phosphates which catalyze hydrolysis. The aliphatic amine, 2,6-AC, as well as other aliphatic amines compatible with MIL-L-7808 formulations, should effectively stabilize wet diester oils against rapid deterioration during storage.

RECLAIMING AND DRYING DIESTER-BASE OILS

Attention was also given to the reclaiming of storage-deteriorated MIL-L-7808 oil through the removal of the corrosive component by adsorbents having a selective action toward organic acids. Of the variety of adsorbents investigated (fuller's earth, Florisil, and different grades of alumina), a chromatographic grade of alumina was found to be most efficient. The quantity of alumina required to reduce the corrosion value to specification requirements (*14*) varied approximately directly with the corrosivity of the oil. An oil having a corrosion number of 230 required up to 30 weight % of alumina to reduce the corrosion number to below 1. The treated oil readily passed the corrosion-oxidation and foaming tests (*14*), indicating that there remained sufficient concentrations of the inhibitors to stabilize the oil to the test environments. Quantitative data are not available on the concentration of inhibitors remaining. Percolation through 30 weight % of freshly activated alumina reduced the water content from an initial value of 0.05% to less than 0.01%. Contact or percolation methods appeared to be equally effective in removing the corrosive constituent.

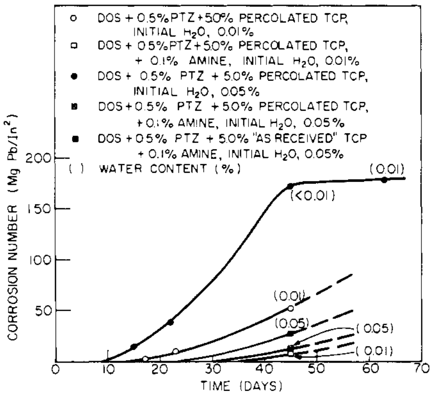

Figure 9. Effect of an aliphatic amine on corrosivity of bis(2-ethylhexyl) sebacate compositions

CONCLUSIONS

The corrosion of lead in diester oil solutions proceeds by the same mechanism as in hydrocarbon solutions–i.e., the reaction of carboxylic acids with the lead oxide surface to form soluble lead salts. The corrosive acid developed during storage of MIL-L-7808 oils based on bis(2-ethylhexyl) sebacate is 2-ethylhexyl hydrogen sebacate. This acid (or half ester) is formed primarily by the hydrolysis of the parent diester, not by oxidation. There is no evidence that phenothiazine is an ineffective antioxidant at storage temperatures. Acidic material present in, or formed from, tritolyl phosphate in the presence of water (acid phosphates) catalyzes the hydrolysis of bis(2-ethylhexyl) sebacate. Aliphatic amines prevent the rapid shelf deterioration of MIL-L-7808 oils because they form stable, noncatalytic, neutral salts with these strong acids. Polybasic carboxylic acids, although effective lead corrosion inhibitors, lose their effectiveness in the presence of free alcohols and moisture. The most positive and generally applicable method for assuring long storage life is to package dry MIL-L-7808 oils in dry sealed cans. This precaution applies with equal force to the packaging of oils formulated from other esters, particularly if components such as acid phosphite antiwear agents or potential sources of strong acid such as TCP are included in the formulation. As an added precaution against the deterioration of oil in defectively sealed containers, the use of a suitable inhibitor containing aliphatic amine groups is recommended.

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