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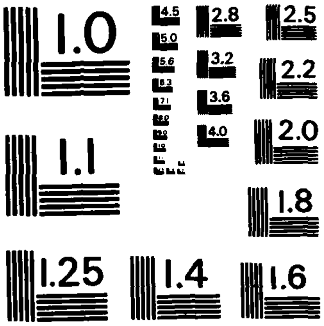

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The kinetics of lubricant antioxidant depletion in an aircraft gas turbine engine were treated as those of a stirred flow reactor. Depletion rates of p,p′-dioctyl diphenylamine and phenyl-alpha-naphthylamine, based on zero and first order reaction models, were calculated. First order reaction rates most closely fit the engine test data.

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A KINETIC STUDY OF LUBRICANT ANTIOXIDANT DEPLETION IN AIRCRAFT GAS TURBINE ENGINES

INTRODUCTION

Improved antioxidant technology is, to a large extent, responsible for the development of current high-temperature lubricants. Navy jet engine lubricants, based on neopentylpolyol esters, frequently contain secondary amine antioxidants such as p,p' - dioctyl diphenylamine (DODPA) and N-phenyl-alpha-naphthylamine (PAN).

The operational characteristics of such additives are obviously of significance both to their efficacy and the successful performance of the engine/lubricant system. Antioxidant reaction kinetics can be adequately explained by free radical theory (1,2). For engineering evaluations of the relative merits of lubricant/additive systems, various laboratory tests have been devised. One widely used method is to pass air through the hot thermostated oil in contact with various metals. The oil is then examined for acid and viscosity increases, the metal specimens for corrosion and deposits etc. If the results of these and other laboratory and engineering evaluations are satisfactory, the final requirement to qualify the oil for use is an engine test. For final Navy qualification of jet engine lubricants, a T-63 turboshaft engine containing the candidate lubricant is run and monitored under carefully specified conditions (3). After completion of the test, the oil and engine components are examined critically, and a determination is then made as to whether the oil has fully qualified for Navy use.

Antioxidant depletion studies have been carried out on steam turbine (4,5) and diesel engine (6) lubricants. Little comparable information is available, however, for aircraft jet engines. In the present investigation, a cooperative effort between the Naval Air Propulsion Center, Tren-

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ton, N.J. and this Laboratory, periodic oil samples obtained during several engine tests were analyzed for their antioxidant contents. The data were fitted into model engine schemes, providing significant information on antioxidant degradation modes under actual service conditions.

EXPERIMENTAL

The T-63 test engine employed in this study was a helicopter turboshaft type. Its oil capacity is 6600 ml (7 qts.); total oil flow is 10.67 kg (23.52 lbs)/min and flow through the turbine hot section is 1.59 kg (3.5 lbs)/min.

Four engine tests, identified as Runs 1,2,3 and 4 were performed, employing four different neopentylpolyol ester based formulations; two were qualified under Military Specification MIL-L-23699; the third a candidate oil; and the fourth a modified MIL-L-23699 type. The oils in Runs 1,2, and 3 contained both PAN and DODPA; that in Run 4 contained an unidentified antioxidant mixture. The data plotted in Figures (1-4) correspond to these runs. Analyses of PAN and DODPA were carried out by liquid-liquid chromatography with a stainless-steel column 4.6 mm I D and 250 mm long. The packing was a standard commercial polar phase bonded to silica particles 10 micrometers in diameter. The carrier solvent was heptane pumped through the column at 3 mi/min. A 0.01-ml sample of the oil was diluted with 1 ml of heptane, and 0.01 ml of this solution injected into the chromatograph. The antioxidants were analyzed with a UV detector monitoring at 254 nm; quantitative results were obtained by a linear comparison of peak heights. Figure 5 shows, as an example, the antioxidant peak heights for oil samples from Engine Run No. 1. The analysis of the unknown antioxidant mixture (Run No. 4) was carried out by thin-layer chromatography. The oil samples were diluted 3:1 with heptane; one-microliter aliquots were spotted on precoated silica gel glass plates which were then developed in toluene. All

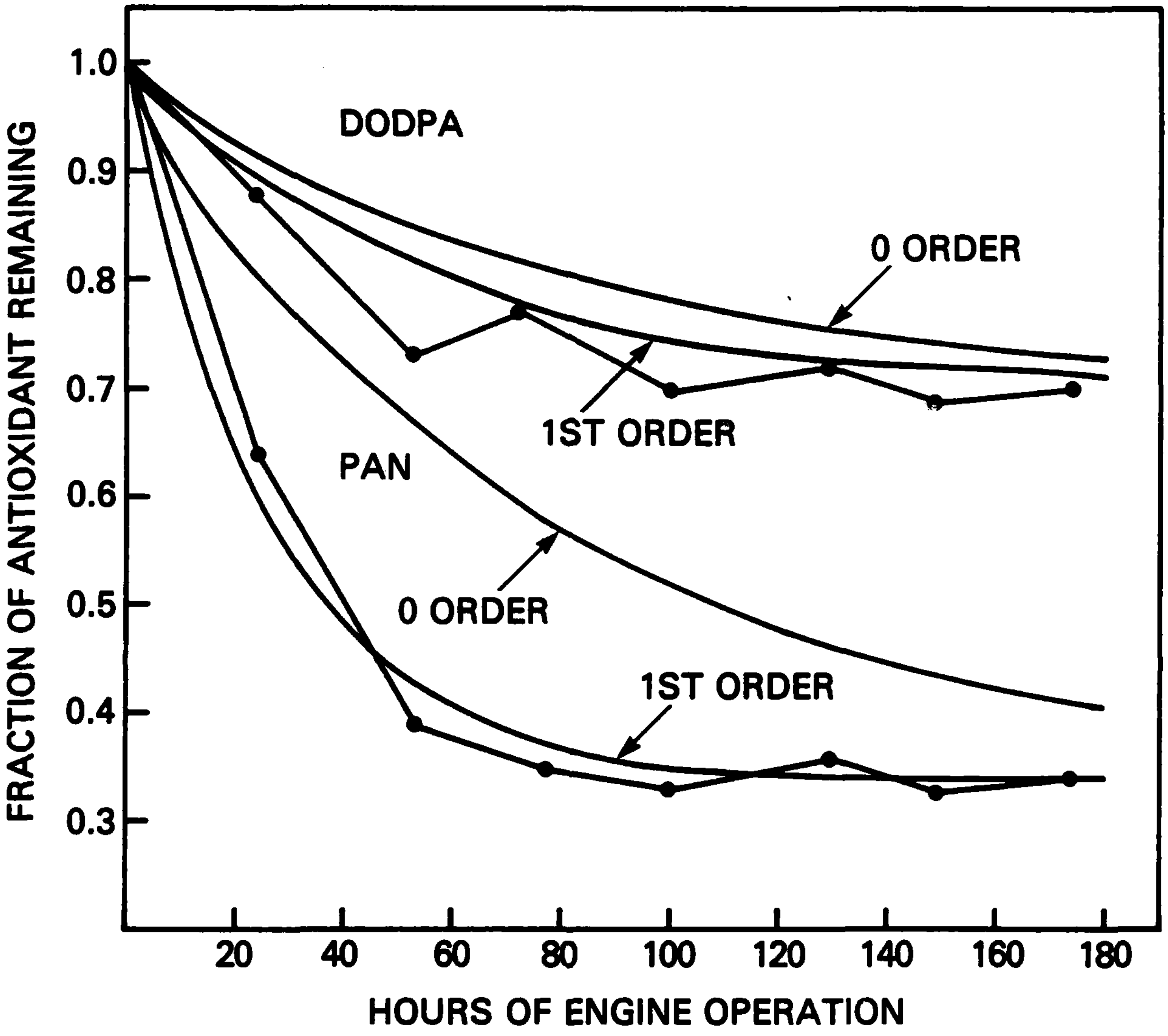

Fig. 1 — Calculated and experimental antioxidant levels during T-63 engine test Run 1

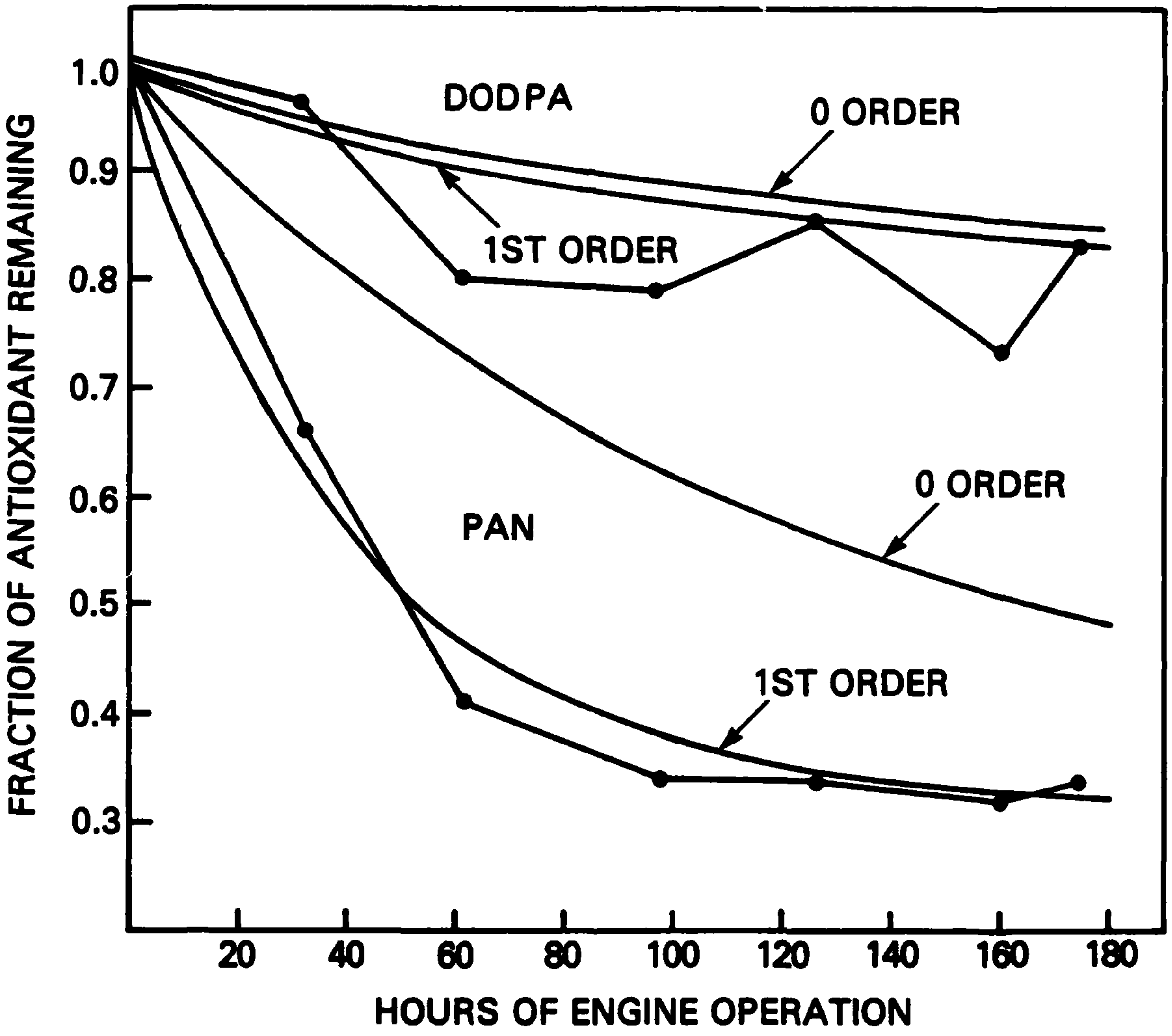

Fig. 2 — Calculated and experimental antioxidant levels during T-63 engine test Run 2

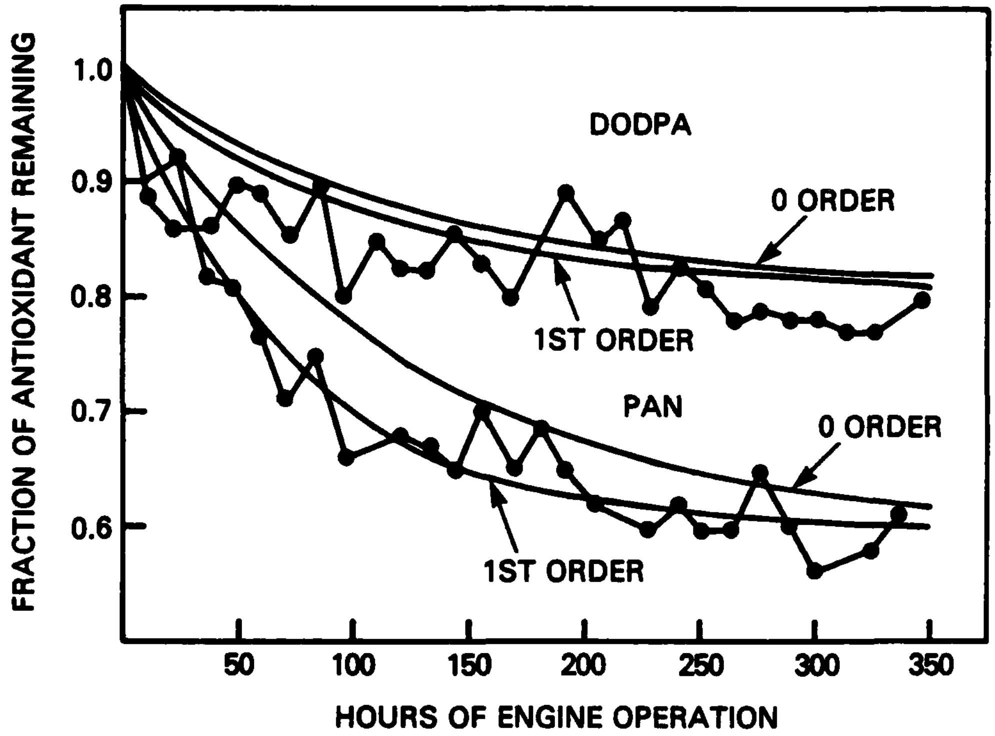

Fig. 3 — Calculated and experimental antioxidant levels during T-63 engine test Run 3

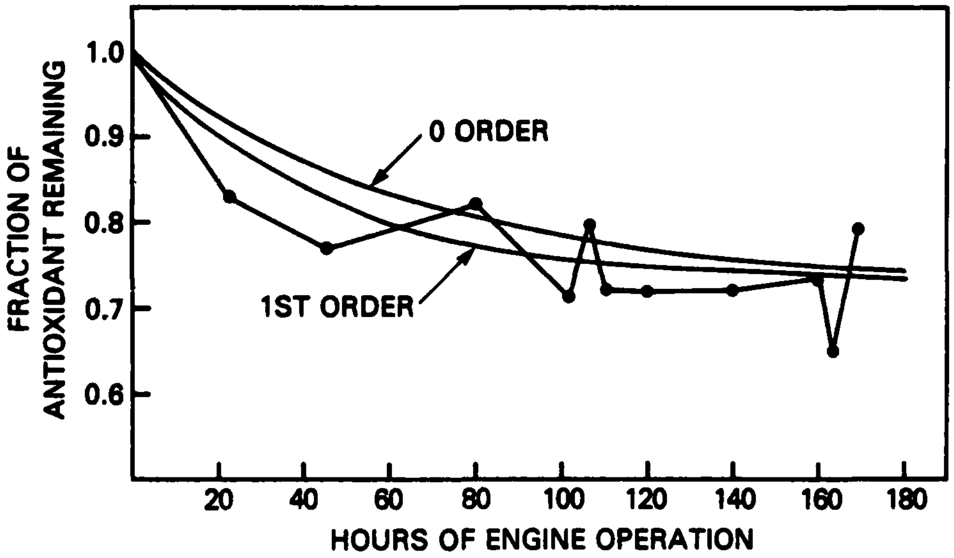

Fig. 4 — Calculated and experimental antioxidant levels during T-63 engine test Run 4

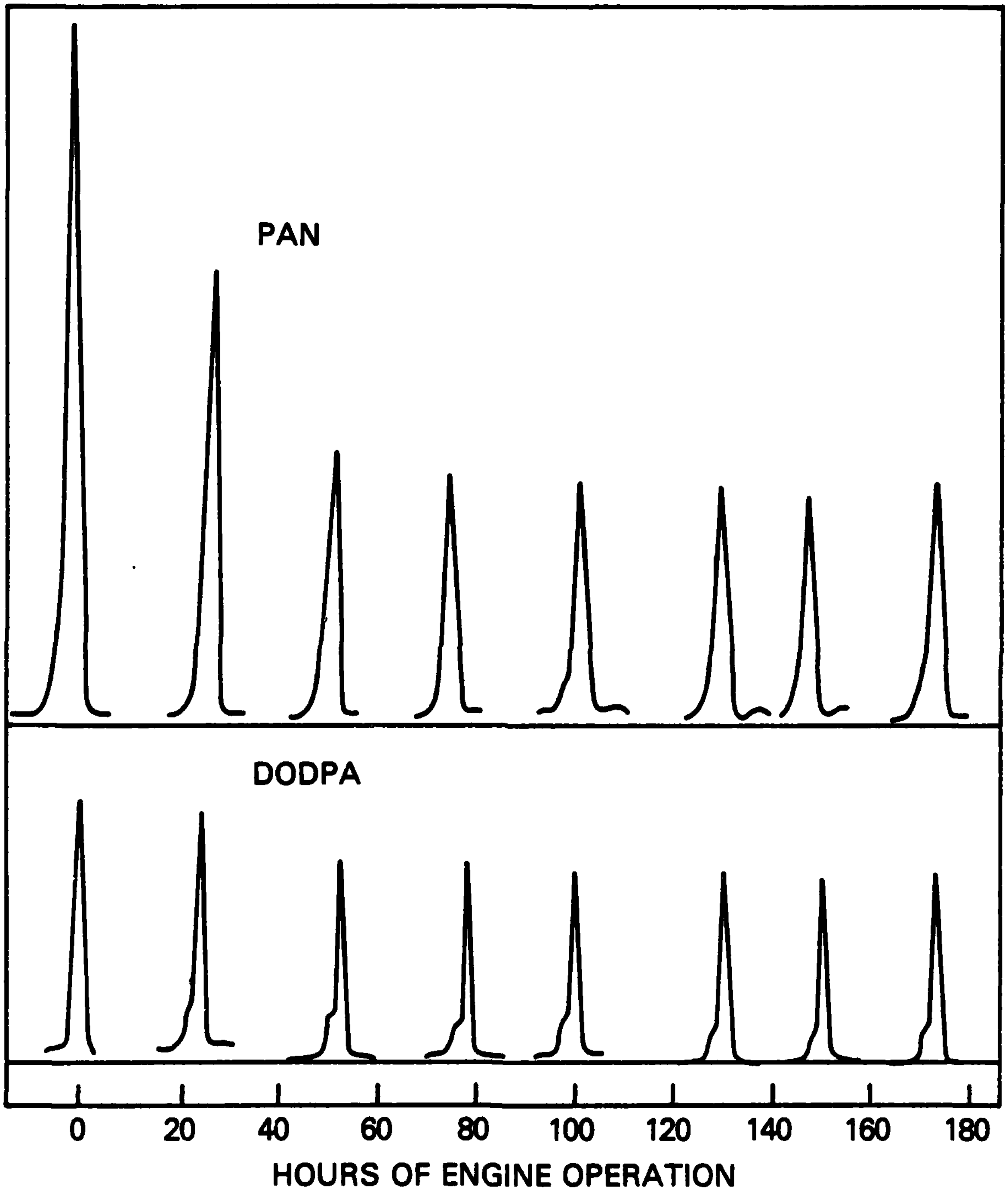

Fig. 5 — Liquid chromatograph peaks for antioxidants in lubricant samples from T-63 engine test Run 1

antioxidant components appeared as one composite spot on the plate. The samples were immediately analyzed with a densitometer operating in the long wave UV fluorescence mode. The analyses were quantified by employing the original oils as references. Acid number and viscosity data for the lubricant in Run (2) are given in Figure (6). These are typical of results with the other lubricants.

RESULTS AND DISCUSSION

Based on results with steam turbine (4,5) and diesel (6) engines, antioxidant degradation in a jet engine may be described approximately by the kinetics of a stirred flow reactor; i.e. antioxidant in the engine is consumed, oil is lost by various routes, and new make-up oil is added. For stirred flow reactor kinetics to be strictly applicable in such a system, it is necessary that oil and antioxidant be depleted at the same rate, oil be continuously added at a constant rate, and temperature and other factors that affect the degradation rate remain constant. Although these requirements are not fully met in the T-63 engine test, over a sufficiently long test period they should average out to provide valid data. Table 1 shows equations derived for the antioxidant state in a stirred flow reactor, for both zero and first order kinetics. These equations are employed to treat the engine test data.

One of the advantages of the stirred flow reactor method for determining the kinetics of a reaction is that it is mathematically less intricate than more conventional methods. This simplicity results from the determination of the steady state of the system in which reactant loss is balanced by its addition. It has been calculated that seven reactor volumes must pass through the system before the concentrations of the reactants are less than 0.1% from their steady state(7). A lesser number of volumes, however,

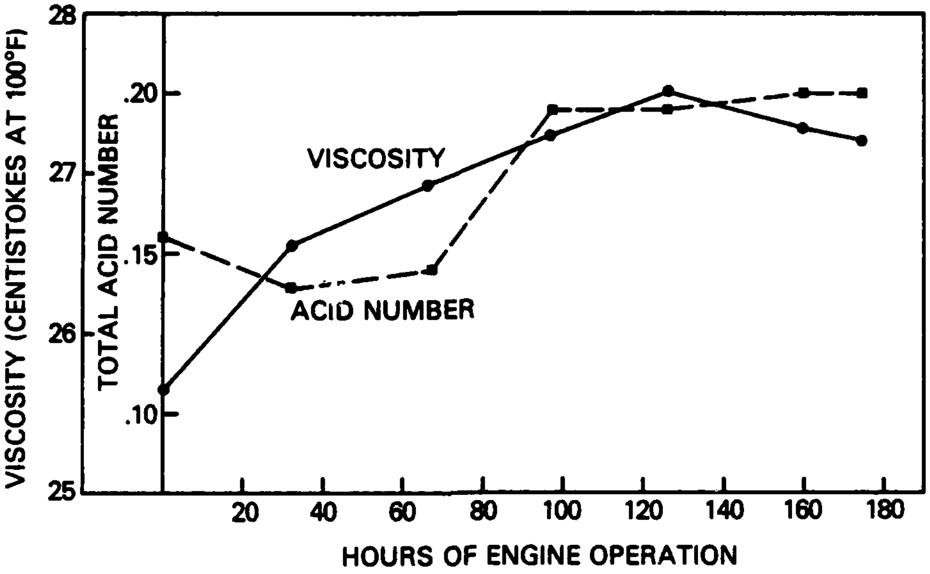

Fig. 6 — Viscosities and total acid numbers of lubricant samples from T-63 engine test Run 2

Table 1 — Zero and First Order Dynamics for Antioxidant Depletion with Continuous Make-up Oil Addition

t = measured period of engine operation, hours
C_i = concentration of antioxidant in the make-up oil, g antioxidant per g of oil
C = concentration of antioxidant in the engine oil
C_s = concentration of the antioxidant at the steady state
W = lubricant capacity of the engine, g
m = rate of make-up oil addition, g per hour
k_0 and k_1 = zero and first order rate constants for total antioxidant depletion in the engine system

Description of Equation	Zero Order	First Order
Differential expressing change of antioxidant concentration in the engine	(1) $\frac{dC}{dt} = \frac{mC_i - mC - k_0}{W}$	(2) $\frac{dC}{dt} = \frac{mC_i - mC - Ck_1}{W}$
Antioxidant concentration after t, starting with engine filled with make-up oil	(3) $C = C_i - \frac{k_0(1 - e^{\frac{-mt}{W}})}{m}$	(4) $C = \frac{mC_i + k_1 C_i e^{\frac{-(m+k_1)t}{W}}}{m + k_1}$
Steady State Concentration	(5) $C_s = C_i - k_0/_m$	(6) $C_s = \frac{mC_i}{m + k_1}$
Concentration of antioxidant in the engine when C_s is known	(7) $C = C_s + (C_i - C_s)e^{\frac{-mt}{W}}$	(8) $C = C_s + (C_i - C_s)e^{\frac{-mtC_i}{WC}}$
Total rate of antioxidant degradation in the engine at the steady state	(9) $k_0 = m(C_i - C_s)$	(10) $k_1 C_s = m(C_i - C_s)$

is in many cases adequate to approximate the steady state. Table 2, constructed from equations (7) and (8) in Table 1, shows the number of reactor refills required to be less than 5% from the steady state concentration for given fractions of antioxidant remaining at the steady state. As reactor conditions become more severe, i.e., higher temperatures, the steady state concentrations decrease. Under typical conditions less than 4 refills are required to approach steady state. It is also seen that a given steady state is more rapidly approached (fewer reactor volumes) by first order than by zero order kinetics.

Table 3 summarizes relevant engine oil consumption and additive data from the four T-63 engine tests. As shown in Figures (1-4), the engines were run for a sufficient length of time and the make-up rate was high enough that all fractions of additive remaining reached an essentially steady state. The saw tooth appearance of the graphs of the experimental data is primarily a result of the incremental addition of make-up oil, but temperature changes and engineering adjustments may also have contributed to the effect.

Considering the experimental data for the engine tests as for a stirred flow reactor, zero and first order antioxidant depletion curves were calculated for each test, Figures (1-4) based on equations (7) and (8) of Table 1 and the appropriate values for W, m, C_s, and C_i. Several results of interest can be noted:

1. The first order curves lie below those for zero order, having steeper initial declines. The lower the steady-state antioxidant concentration, the greater the difference between the curves. Thus, where both PAN and DODPA were present in the oil, the DODPA calculated and experimental curves are closer together because of its higher steady-state concentration.

Table 2 — Reactor Volumes Necessary to be Within 0.95 of the Steady State

Fraction of Antioxidant Remaining at the Steady State ($C_i = 0.01$)	Zero Order Volumes	First Order Volumes
0.9	0.8	0.7
0.8	1.6	1.3
0.7	2.2	1.5
0.6	2.6	1.6
0.5	3.0	1.5
0.4	3.4	1.4
0.3	3.8	1.2
0.2	4.4	0.9
0.1	5.2	0.5

Table 3 — Data and Results from the Engine Tests

Run Number	1	2	3	4
Oil capacity of engine (g)	6600	6600	6600	6600
Rate of oil addition (g/h)	85	53	54	105
No. of refills	2.2	1.4	2.7	2.8
Duration of test (h)	174	174	336	174
% DODPA in the make-up oil	0.96	1.28	0.97	2.0*
% PAN in the make-up oil	0.94	0.98	0.92	
Fract. of DODPA remaining at steady state	0.70	0.80	0.81	0.73*
Fract. of PAN remaining at steady state	0.34	0.32	0.60	
Steady state consumption of DODPA (g/h)	0.24	0.14	0.10	0.57*
Steady state consumption of PAN (g/h)	0.53	0.35	0.20	
Steady state consumption of antioxidant (g/h)	0.77	0.49	0.30	0.57

*Antioxidant of unknown components

2. The data for the loss of PAN during engine operation are consistent with first order kinetics. Those for DODPA also appear to follow first order kinetics, but because of the near congruency of the zero and first order rate curves, the assignment is not definitive.

3. In Run 4, Figure (4), in which the antioxidant mixture was analyzed as a single entity, no clear assignment as to the reaction order can be made.

The more rapid loss of PAN as compared with DODPA may reflect its greater volatility, reactivity, or both. Its behavior, however, is consistent with other data which suggest that antioxidant degradation from a hot steel surface, as in an engine, in the presence of air proceeds by first order kinetics (8). The steady state rates of antioxidant degradation in the engine can be calculated from equation (10), Table 1. In the engine runs reported here, these rates are comparatively small, approximately one-half gram/hour, (Table 3). The major portion of this loss likely occurs in the turbine hot section. Only 15 percent of the total lubricant flow through the engine, containing approximately 2 kg of antioxidant per hour, experiences this extreme environment, and that for only a very short time period. Under these operational conditions, only a minor proportion of the original antioxidant is lost under steady state conditions. As might be intuitively deduced, viscosity and acidity of the lubricant increase somewhat during engine operation, but level off to an approximate steady state at about the same time as do the antioxidant levels.

Equation (6), Table 1, shows the dependency of the steady state concentration on the rate of make-up oil, i.e., the more rapid the rate of oil addition, the larger the steady state concentration of antioxidant. This leads to the somewhat surprising conclusion that the ''tighter'' the engine and consequent reduced rate of make-up oil, the lower the steady state antioxidant concentration and the shorter the useful life of the lubricant. Denherber and Vienna (4) give an illustration of how overhaul of an engine to reduce oil loss could lead to the pronounced reduction of antioxidant protection.

CONCLUSIONS

The concept of a stirred flow reactor as a model system for rationalizing the kinetics of lubricant/antioxidant depletion in aircraft gas turbine engines has been shown to be valid. The data provide a basis for estimating the useful life of lubricants based both on engine operational characteristics, i.e., lubricant loss rate and frequency of refills, and the efficacy of the antioxidants.

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