

## REACTIONS INVOLVING HYDROPEROXIDE FORMATION IN JET FUELS

By

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### INTRODUCTION

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Problems have been associated with Jet A, JP-4, and JP-5 jet fuels. The first reported incidents occurred with Jet A in Japan in 1962 when fuel hoses of neoprene or nitrile rubber cracked and leaked (1). In 1976 the U.S. Navy experienced attack on neoprene fuel pump diaphragms on jets operating in the Philippines (2). More recent problems have been encountered in Thailand with JP-4 when Buna-N O-rings cracked and leaks from fuel pumps occurred. All incidents involved fuels which had been hydrotreated and had peroxide levels from 1 to 8 milliequivalents of active oxygen per kilogram of fuel (peroxide number, P.N.).

Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated. The U.S. Navy has continuing concerns with this topic due to increasing hydrogenation for jet fuel processing. In addition, shale-derived fuel production will involve more extensive and higher pressure hydrotreatment. It has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (3). It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation.

Hydroperoxide concentration has been found to be a factor in fuel instability. Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term high-temperature stress (thermal oxidative stability) (4-7). The latter situation is found during flight conditions, where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is found to occur in nonoxidizing atmospheres, the presence of oxygen or active species such as hydroperoxides will greatly accelerate oxidative degradation

as well as significantly lower the temperature at which undesirable changes in fuel take place. The rates of reactions in autoxidation schemes are dependant on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature (8-10). If sufficient oxygen is present, the hydroperoxides will reach a high level. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated with both hydroperoxide formation and decomposition.

Several solutions to the problem of fuel peroxidation have been suggested. Antioxidants have been mandated by some authorities, particularly for hydrotreated fuels. Viton elastomers and other materials have been proposed as replacement materials but their low temperature properties make them marginal for aircraft use. Clay filtration has been suggested as a means for field removal of hydroperoxides but this treatment has been found to be too expensive (2). Although hindered phenols have given satisfactory peroxide control, those phenols which are permitted in the jet fuel specifications were developed for gum control in gasoline. Their effectiveness for peroxide control was found to be marginal, depending on structure (11). It is necessary to investigate the relationship of temperature on peroxide concentration in fuel as it relates to peroxide formation as well as fuel stability.

Sulfur is the most abundant heteroatom present in jet fuels (up to 0.4% allowed by specifications). Deposits formed in jet fuel in the presence of oxygen contain a higher percentage of sulfur than that present in the fuel itself (12). The formation of these deposits has been attributed to the participation of sulfides, disulfides, and thiols (mercaptans) (13). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (14). Examination of the reactions between both alkyl and aromatic thiols with tert-butylperoxide have indicated that aromatic thiols are more reactive than other classes of sulfur compounds with hydroperoxides. The reaction of thiophenol with tBHP was found to produce trace amounts of sulfonic acid while depleting the amount of both reactants in solution (15). It is desirable to test the relationship between sulfur compound reactivity and peroxide formation using an aryl thiol as a model dopant under accelerated storage conditions.

This paper reports on the hydroperoxide formation in hydrotreated JP-5 jet fuels at various temperatures, in both the presence and absence of antioxidants. The results of using thiophenol as a model dopant for four stable, hydrotreated jet fuels under 65C accelerated storage conditions and the effect on peroxide formation versus added sulfur concentration are also reported.

## EXPERIMENTAL

Fuels and Reagents. The fuels examined for the temperature effects study included a shale JP-5 with antioxidant, a hydrotreated petroleum JP-5 with and without antioxidant, and a petroleum JP-4 without antioxidant. The four fuels investigated for the sulfur versus peroxide concentration study were the same Shale-II JP-5 used in the temperature study (J-22), a Jet-A, a Hydrocracked JP-5 and a Hydrofined JP-5 from Esso Petroleum Corporation, Ontario, Canada. Thiophenol was obtained from Aldrich Chemical Co. and was

distilled in vacuo to 99.9% purity.

Method. Tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Test for temperature effects on peroxidation were carried out at 43, 65, 80 and 100C. To test the relationship of added sulfur to peroxide concentration, duplicate samples of the four other fuels were prepared, with 0.10 and 0.05% sulfur in the form of thiophenol weighed into one sample of each fuel. Stress tests were conducted at 65C for five weeks. Samples were analyzed weekly for peroxide concentration by ASTM method D3703-85. Sulfur concentration was monitored weekly with a Tracor 565 gas chromatograph equipped with a sulfur specific 700A Hall electrolytic conductivity detector.

#### RESULTS AND DISCUSSION

Rolls-Royce defined the peroxidation potential of a fuel with an accelerated 100C test for 24 hours (1). The relevance of this test to ambient storage conditions was of interest, so stress tests were conducted at 43, 65, 80 and 100C.

The peroxide numbers for the different temperatures are listed in Table I. The stress times were selected according to the Arrhenius relation, namely doubling (or halving) of reaction rate for every 10°C change in temperature, and then modified based on previous results from our laboratory. Thus time factors of 30:1 and 10:1 were used for 43C and 65C test instead of the calculated values of 52:1 and 11.3:1. Columns in the Table are labeled "equivalent hours at 100C." The actual storage times at the several temperatures are shown at the end of the data table.

Data for the two JP-5 samples, with and without oxidant are plotted in Figures 1 and 2. Time factors for multiplying the abscissa are listed on the graphs for the various temperatures.

The data reveal appreciable variation in peroxide number as a function of time, temperature and fuel. Two fuels, petroleum JP-5 and JP-4 both without antioxidant, show fair agreement between the temperatures based on equivalent time periods. In at least two cases (Fuels 3 and 4), peroxide levels at all times were lower at the lower temperatures. With the two fuels containing antioxidants (Fuels 1 and 3), results at the lower temperatures were quite different from results at the higher temperatures, and therefore not predictable from the higher temperature test.

Important difference in fuel response to temperature is illustrated by comparing Figures 1 and 2. The hydrotreated JP-5 without antioxidant (Fuel 2), Figure 1, produces peroxide at a linear rate with respect to time for the initial portion of the tests. The time factors are also reliable in the 1-3 day equivalent time frame.

Shale-II JP-5 (Fuel 1) containing an antioxidant behaves quite differently. Peroxidation follows an exponential rate. The most probable explanation for this observation is the depletion with time of the antioxidant. The rate of peroxidation was not predictable from the time factors. Specifically, the rate was much faster at 80 and 100C than the low temperature data would indicate.

Based on these observations, the 65C stress test was chosen for the sulfur concentration study. Added sulfur concentrations of 0.10 and 0.05% sulfur (weight/volume) were used. The data for these tests are represented in

Tables II and III respectively.

For both sulfur concentrations, the control samples, fuel only, exhibited similar behavior. Differences in actual peroxide numbers between the two tests could be attributed to thermostatic differences in the ovens that were used. It was interesting that in Jet A peroxide formation occurred in a cyclic pattern. The petroleum derived JP-5 samples formed peroxides at a greater rate than the shale JP-5 or Jet A.

The most important aspect of both sets of data was that the samples doped with sulfur in the form of thiophenol did not undergo peroxidation as rapidly as the fuel by itself. In fact, thiophenol addition eliminated ROOH present in starting samples in most tests, and after the first week in the other tests. In the samples doped with 0.10% sulfur, peroxide formation was not observed until the fourth week of the stress test. When the concentration of added sulfur was reduced (halved) peroxide formation began one week earlier with three of the fuels, indicating a relationship between added sulfur concentration and peroxide formation (or peroxide inhibition). Neither of the doped samples of the hydrocracked JP-5 showed evidence of peroxide formation throughout the duration of the tests.

The sulfur concentration of the samples was found to decrease throughout the tests as measured by the sulfur specific detector on the gas chromatograph. The emergence of new peaks on the chromatogram indicated the formation of new sulfur-containing compounds, however concentrations were too low to permit identification. Since aromatic thiols are quite reactive in the presence of peroxides, the thiophenol most likely undergoes oxidation by the peroxide species. These reactions could be similar to other observed liquid phase oxidation reactions that take place between thiophenol and t-butyl hydroperoxide (15).

#### CONCLUSIONS

The effect of adding sulfur in the form of an aromatic thiol, thiophenol, was significant to peroxide formation. Thiophenol has been found to act as an inhibitor or controller of peroxide formation in Jet A, Shale-II derived JP-5, and petroleum derived JP-5. Hydrotreated jet fuels exhibited higher peroxide formation and concentration than other fuels. Hydrotreatment reduces the sulfur content of the fuel, which removes those naturally occurring sulfur compounds which act as inhibitors to peroxide formation. There appeared to be a "critical concentration" of sulfur at which peroxide formation was inhibited. If this concentration was decreased or consumed, peroxidation took place in an uncontrolled manner.

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TABLE I

## Peroxidation at Various Temperatures

Fuel	Temp. °C	Time Factor	Equivalent Hours at 100°C							
			3	7	24	48	72	96	168	
1. Shale JP-5 w/A.O.	43	30:1	-	-	1.03	1.10	1.38	1.74	2.66	
	65	10:1	-	-	1.45	1.80	2.44	3.90	8.69	
	80	4:1	-	1.10	2.53	7.43	18.4	43.3	1.48	
	100	1:1	.85	1.05	2.66	9.11	23.3	19.3	0.96	
2. Petroleum JP-5	43	30:1	-	-	13.2	41.0	82.5	111	133	
	65	10:1	-	-	13.5	53.3	86.3	121	198	
	80	4:1	-	7.41	34.3	60.7	82.4	95.2	78.9	
	100	1:1	1.61	5.52	24.6	48.0	66.8	72.0	61.5	
3. Petroleum JP-5 w/A.O.	43	30:1	-	-	0	0	0	0	0	
	65	10:1	-	-	0	0	0	0	.12	
	80	4:1	-	0	0	.10	.16	.35	39.7	
	100	1:1	0	0	0	.29	.78	2.31	42.9	
4. Petroleum JP-4 No A.O.	43	30:1	-	-	.07	.03	.12	.14	.19	
	65	10:1	-	-	.10	.16	.12	.16	.14	
	80	4:1	-	0	.24	.25	.25	.20	.30	
	100	1:1	.07	.10	.22	.23	.22	.26	.22	
All Fuels	43	ACTUAL STORAGE TIMES					60d	90d	120d	210d
	65	3.8d	8.8	30d	30d	20d	30d	30d	40d	70d
	80	30h	70h	10d	8d	8d	12d	16d	28d	
		12h	28h	4d	4h	4h	72h	96h	168h	
	100	3h	7h	24h	48h					

TABLE II

Jet Fuel Peroxidation at 65°C with Added Thiophenol  
0.10% Sulfur Dopant

Week	<u>Shale-II JP-5</u>		<u>Jet A</u>		<u>Hydrocracked JP-5</u>		<u>Hydrofined JP-5</u>	
	Control	Doped	Control	Doped	Control	Doped	Control	Doped
0	0.25	0.25	0.00	0.00	0.00	0.00	0.16	0.16
1	0.24	0.00	0.19	0.00	0.18	0.00	0.57	0.00
2	0.31	0.00	0.44	0.00	0.49	0.00	1.16	0.00
3	0.37	0.00	0.19	0.00	1.10	0.00	1.73	0.00
4	0.51	1.29	0.40	0.51	4.08	0.00	5.38	0.26
5	0.48	0.97	0.26	0.40	10.82	0.00	8.47	0.25

TABLE III

Jet Fuel Peroxidation at 65°C with Added Thiophenol  
0.05% Sulfur Dopant

Week	<u>Shale-II JP-5</u>		<u>Jet A</u>		<u>Hydrocracked JP-5</u>		<u>Hydrofined JP-5</u>	
	Control	Doped	Control	Doped	Control	Doped	Control	Doped
0	0.69	0.00	0.12	0.00	0.10	0.00	0.24	0.00
1	0.70	0.00	0.18	0.00	0.60	0.00	1.58	0.00
2	0.73	0.00	0.16	0.00	2.09	0.00	6.01	0.00
3	0.94	0.45	0.28	0.54	12.41	0.00	37.66	0.61
4	1.11	0.68	0.26	0.22	25.27	0.00	62.05	0.51
5	1.56	0.88	0.29	0.81	56.67	0.00	59.92	0.25

FIGURE 1

HYDROPEROXIDE FORMATION  
AT VARIOUS TEMPERATURES  
--HYDROTREATED JP-5--NO A.O.

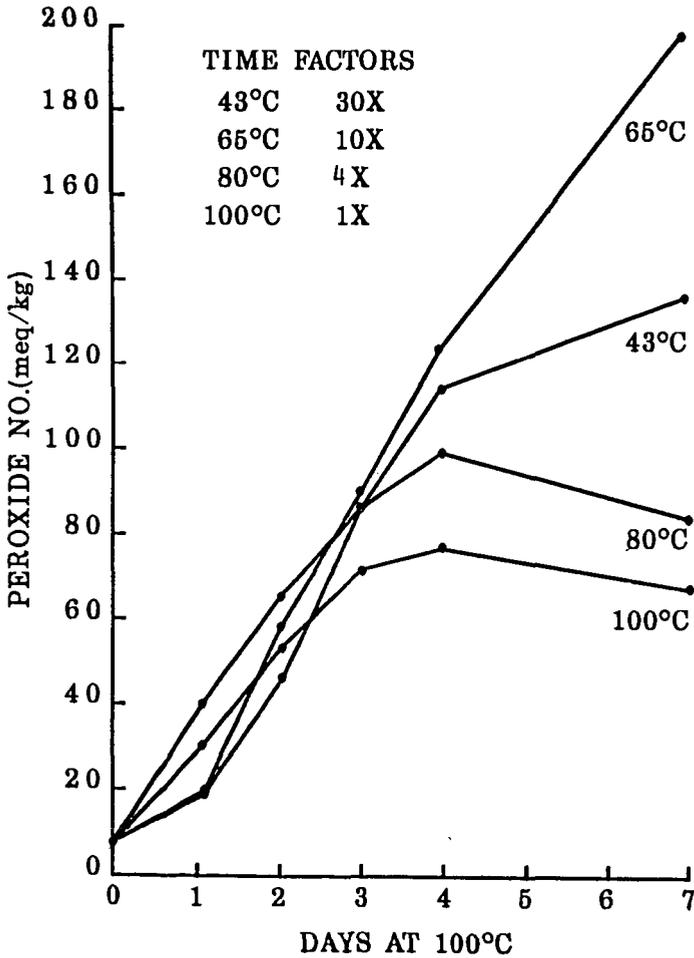


FIGURE 2

HYDROPEROXIDE FORMATION  
AT VARIOUS TEMPERATURES  
--SHALE-II JP-5--WITH A.O.

