

**ACCELERATED PEROXIDE FORMATION IN JET FUEL USING  
CONVENTIONAL AND OXYGEN OVERPRESSURE METHODS**

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**INTRODUCTION**

In recent years the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of more severe refinery processes in order to produce jet fuels of higher thermal stability and cleanliness. Unfortunately, these processes remove species that inhibit the formation of hydroperoxides during storage. As a result the storage stability of some jet fuel products, as measured by hydroperoxide formation, has decreased.

Hydroperoxides in jet fuel have a deleterious effect on elastomers in aircraft fuel systems. (1-3) This problem was first recognized in the early 1960s when an unusually large number of flexible fuel manifold hose failures occurred in aircraft operating in the Far East. (4) To investigate the cause for these failures, a rubber immersion test was developed to distinguish between good and bad fuels. Rubber samples were immersed in jet fuel at 100±1°C and their rate of deterioration, from visual inspection, was recorded. Peroxides, which were known to cause rapid deterioration of elastomers, were monitored during the immersion test. The peroxides in a fuel as received were designated existent peroxides. The peroxides that formed after the fuel was heated to 100°C for 100 hours were designated potential peroxides. In general, as the concentration of potential peroxides in a fuel increased, the failure time for a rubber sample decreased. (4)

During the 1970s and 1980s, additional hydroperoxide induced elastomer failures in aircraft fuel systems occurred. In one instance the failure resulted in the loss of an aircraft. As a result of these failures, a cooperative program was initiated to develop a method to predict a jet fuel's tendency to form hydroperoxides during storage. Six laboratories participated and seven fuels, some of which contained a phenolic antioxidant, were included in the first Coordinating Research Council, Inc., (CRC) cooperative interlaboratory testing (round robin).

A procedure similar to the rubber immersion test was used. Fuel samples were stressed in capped brown borosilicate glass bottles at 100°C for up to 168 hours. The fuel samples were periodically analyzed for hydroperoxide concentration at intermediate intervals by ASTM D3703-78. (5) The results indicated that this procedure had fair repeatability and poor reproducibility. The participants concluded that additional work was needed to achieve better values.

Prior to further developmental work, it was suggested that testing at 100°C may not be indicative of peroxidation at ambient conditions. To verify this possibility, an experiment was performed in which four

fuels from the first round robin were stressed at 43°C, 65°C, and 80°C. Aliquots of the fuels were periodically removed for peroxide analysis. Peroxidation rates at these temperatures were compared to the rates obtained at 100°C in the first interlaboratory round robin.

The fuel samples were, unfortunately, stressed in capped bottles. This limited the amount of oxygen available to the samples. At higher temperatures, 80°C and 100°C for instance, the frequency at which aliquots were removed allowed for more frequent replenishment of atmospheric oxygen. At the lower temperatures where aliquot removal was less frequent, oxygen starvation led to a decrease in the peroxidation rate. This suppression of peroxidation rate in turn led to the erroneous conclusion that peroxidation occurs by a different mechanism at elevated temperatures. In further studies, therefore, the temperature at which fuels were stressed was limited to 65°C.

Two additional interlaboratory round robins were performed. This work culminated in a set of standard test conditions that are useful in research studies. (6) These conditions, however, have serious limitations for fuel quality use. These include the duration, 4 weeks, and the limitation as a Go/No Go (pass/fail) test. The use of a pass/fail criterion does not allow fuels to be ranked relative to each other. Furthermore, under these conditions antioxidant additives cannot be easily or quickly tested for their relative effectiveness. Clearly a more rapid and meaningful test must be developed.

This paper describes experiments that compare fuels stressed at 65°C in capped and vented bottles. Also described is a method for distinguishing between various antioxidant additives using a serial dilution technique.

#### EXPERIMENTAL

Five fuels were used in this study and included: Three JP-5 blending stocks; coded Fuel #1, #2, and #3; Shale II, a finished JP-5 jet fuel; and n-dodecane. The n-dodecane was treated with silica gel to remove polar species that may have influenced peroxidation rate. This was done by adding 250g of 100-200 mesh activated silica gel to two liters of n-dodecane. The mixture was magnetically stirred for six hours. Two liters of each sample were prefiltered through a pair Gelman type A/E glass fiber filters prior to accelerated aging.

Two sets of each sample were prepared. The first set remained exposed to atmospheric oxygen, and the second set remained tightly capped for the duration of the test. For each anticipated hydroperoxide analysis period, two 125mL brown borosilicate glass bottles each containing a 100mL sample were prepared. The duplicate samples were initially to be analyzed for hydroperoxide concentration in duplicate every two weeks for eight weeks. This was later modified and single samples were analyzed in duplicate for up to twelve weeks. The samples were stressed in an oven at 65°C for the duration of the test.

Phenolic antioxidant experiments were performed using a serial dilution technique. Two pure compounds, 2,6-di-t-butyl-4-methyl phenol (26dtb4mp) and 2,4-di-t-butyl phenol (24dtbp), were used in this study.

Stock solutions were prepared by dissolving 24mg of an additive in 1.0L Fuel #1. This is the maximum concentration allowed in JP-5 jet fuel by MIL-T-5624N. (7) Aliquots of the stock solution were diluted to 100mL, with an appropriate volume of neat Fuel #1, in 125mL brown borosilicate glass bottles. A series of samples for each additive were produced with concentrations between 24.0mg/L and 0.3mg/L.

An entire sample set of either additive, including a 100mL additive-free Fuel #1 aliquot, was simultaneously stressed in a low pressure reactor (LPR) at 100°C and an oxygen overpressure of 793kPa. (8) After 24 hours under these conditions, the samples were removed and analyzed for peroxide concentration.

A Mettler DL20 automatic titrator was used for peroxide determinations. Analyses were performed according to ASTM D3703-85: the Standard Test Method for Peroxide Number of Aviation Turbine Fuels. (5)

## RESULTS

The results of accelerated aging at 65°C in capped bottles are shown in Figure 1a. It can be seen that four of the samples approached hydroperoxide concentrations of approximately 90ppm. The fifth sample, Shale II JP-5, continued slow peroxidation for the duration of the test. The results of accelerated aging at 65°C in vented bottles is shown in Figure 1b. It can be seen that three samples, Fuels #1, #2, and #3, produced extremely high concentrations of hydroperoxides under these conditions. In Figure 1c the peroxidation of n-dodecane and Shale II JP-5 in vented bottles is shown with an expanded ordinate.

Comparison of Figures 1a and 1b shows that peroxidation rate in the capped bottles is significantly reduced. This is a result of the limitation of atmospheric oxygen. Although not apparent from these figures, the hydroperoxide concentration in the two sets of fuels significantly differed at two weeks. At four weeks Fuel #3 had the highest hydroperoxide concentration in both sets of fuels. It can be seen, however, that the concentration in the vented sample was nearly eight times that of the capped sample. After four weeks, the hydroperoxide concentration in Fuel #3 continued to increase in the vented bottle. In the capped bottle, however, the concentration of hydroperoxides remained relatively constant. This indicates that oxygen starvation has occurred.

In Figure 1b it can be seen that Fuels #1 and #2 also exhibited a tendency to form high concentrations of hydroperoxides. Both of these fuels undergo a relatively slow rate of peroxidation for six weeks. After six weeks, both fuels rapidly form hydroperoxides. In the vented bottle, Fuel #1 undergoes peroxidation at a linear rate until ten weeks. In the capped bottle, however, Fuel #1 peroxidizes at much slower rate. Unlike Fuel #3, Fuel #1 slowly approaches what appears to be a limit of approximately 100ppm.

Similar characteristics are exhibited by Fuel #2. In the vented bottle this fuel undergoes a rapid rate of peroxidation after six weeks. The peroxide concentration continues to increase for the duration of the test. In the capped bottle, however, Fuel #2

peroxidizes at a much slower rate finally reaching a concentration limit similar to that of Fuels #1 and #3. These results indicate that accelerated aging in capped bottles not only limits the amount of hydroperoxides formed, but reduces the rate at which peroxidation occurs.

Figure 1c shows the rate of peroxidation for n-dodecane and Shale II JP-5 in vented bottles. Both fuels exhibited a relatively slow and linear peroxidation rate. When compared to Figure 1a, it can be seen that Shale II exhibited similar characteristics in capped bottles. The Shale II sample reached a maximum hydroperoxide concentration of 28ppm in the vented bottle. In the capped bottle the maximum concentration formed is approximately 18ppm. In general, the rate of hydroperoxide formation in the capped bottles was approximately  $68.6 \pm 7.8\%$  of the rate in vented bottles for the Shale fuel. This again shows that accelerated aging in capped bottles reduces peroxidation rate.

The rate of hydroperoxide formation in n-dodecane in capped bottles seemed to exhibit a periodicity. This was much less apparent in the vented samples. The maximum concentration of hydroperoxides formed was similar in both sets of samples. It is expected that after twelve weeks the hydroperoxide concentration in the capped n-dodecane sample would remain constant.

A cursory examination of phenolic antioxidant effects at 100°C and 793kPa oxygen for 24 hours was also performed. It is well known that hindered phenols significantly reduce liquid phase free-radical autoxidation of hydrocarbon fluids. (9-11) The relative effectiveness of these compounds has been shown to be structure dependent. (9) In general, the presence of a t-butyl group in the 2-position or both the 2- and 6-position increases its effectiveness as an antioxidant. The presence of an alkyl group in the 4-position also leads to an increase in its antioxidant properties. If the alkyl group in the 4-position possesses  $\alpha$ -branching, such as a t-butyl or an isopropyl group, however, the additive's antioxidant characteristics are diminished. (9)

Figure 2a shows the effect of 26dtb4mp in Fuel #1 using the serial dilution technique. It can be seen that this additive exhibits an antioxidant effect to concentrations as low as 0.3mg/L. Figure 2b shows the effect of 24dtbp in Fuel #1. It can be clearly seen that under these conditions, 24dtbp is a significantly less effective antioxidant than 26dtb4mp as would be expected.

Figure 2c is a side-by-side comparison of the effect of the two additives. This shows that 26dtb4mp is approximately 20 times more effective than 24dtbp at various concentrations, e.g., 0.3mg of 26dtb4mp is as effective as 6.0mg of 24dtbp; 0.6mg of 26dtb4mp is as effective as 12.0mg of 24dtbp, etc. These results show that under these conditions it is possible to evaluate the effect of various antioxidants relative to each other.

#### SUMMARY

In the past additive-free fuels have been ranked relative to each other by the length of their induction period. This period is

characterized by slow peroxidation until a readily discernible change in rate occurs, i.e., the "breakpoint". Antioxidants have also been compared by their ability to increase the induction period in a particular fuel. Unfortunately at higher temperatures the induction period for additive-free fuels is either minimal or non-existent. This renders its measurement quite subjective. Furthermore, the end of the induction period, or breakpoint, often occurs at hydroperoxide concentrations higher than are allowed by MIL-T-5624N. (7) The use of the breakpoint as a criterion for ranking fuels or additives is, therefore, not appropriate.

The rate at which a fuel approaches the military specification peroxide limit, 8ppm, would be more useful. For example, a fuel with a longer induction period than another fuel is not necessarily better. If the first fuel's induction period rate is greater, it will reach the specification limit sooner. Unfortunately, the use of induction period rate also presents problems. At lower temperatures the induction period for additive-free fuels is long enough to objectively measure an induction period rate. At higher temperatures, 100°C and 120°C for instance, the induction period rate measurement, like its length, is too subjective.

If more objective measurements of induction period rates are desired, it is necessary to remove and titrate samples for hydroperoxide concentration at very frequent intervals. At 100°C and 120°C, it may be necessary to analyze fuel samples every 30 minutes, or less. For additive-free fuels, or fuel samples obtained from field activities, these labor intensive induction period rate measurements are necessary.

For antioxidant evaluations, the use of the serial dilution technique has advantages over induction period rate and length measurements. First, it is not a subjective test. All samples of a particular fuel and additive combination are stressed under exactly the same conditions. The technique is not concerned with either the length or rate of the induction period. It simply compares the concentration effect of various antioxidants on peroxidation in a given fuel. Second, the technique is far less labor intensive. These advantages make this technique useful for further antioxidant evaluations.

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**ACCELERATED PEROXIDE FORMATION  
12 Wks @ 65C & Atm. Air (Capped Bottle)**

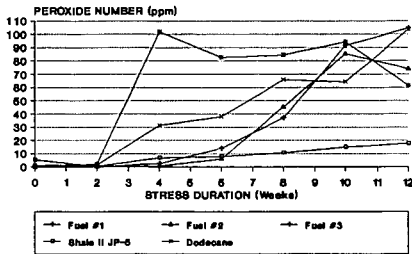


FIGURE 1a

**ACCELERATED PEROXIDE FORMATION  
12 Wks @ 65C & Atm. Air (Vented Bottle)**

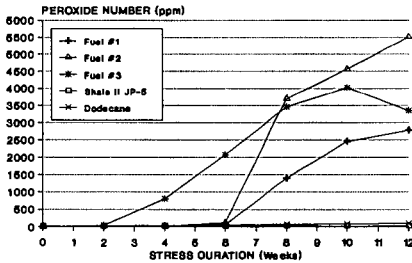


FIGURE 1b

**ACCELERATED PEROXIDE FORMATION  
12 Wks @ 65C & Atm. Air (Vented Bottle)**

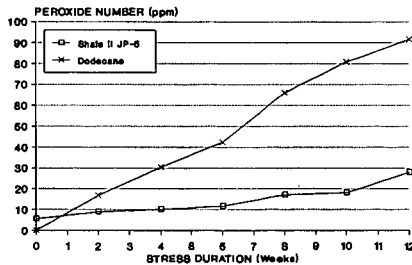


FIGURE 1c

**2,6-di-t-Butyl-4-Methyl Phenol**  
**LPR @ 100C & 793kPa Oxygen**

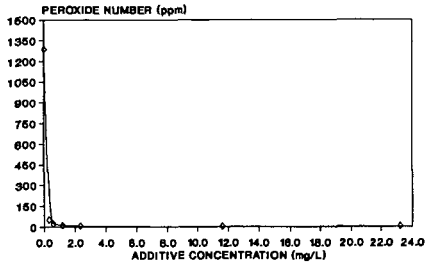


FIGURE 2a

**2,4-di-t-Butyl Phenol**  
**LPR @ 100C & 793kPa Oxygen**

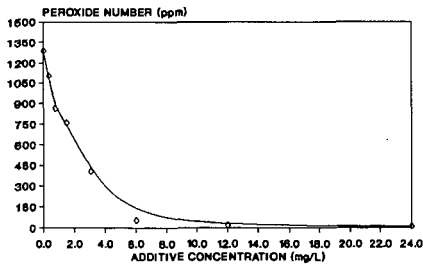


FIGURE 2b

**PHENOLIC ANTIOXIDANT EFFECT**  
**LPR @ 100C & 793kPa Oxygen**

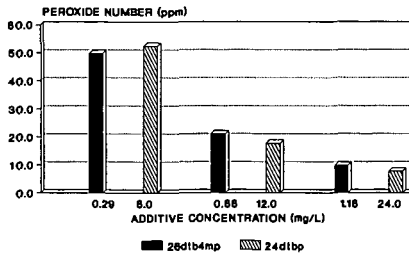


FIGURE 2c