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Re-addition of antioxidant to aged MEROX and hydroprocessed jet fuels

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HIGHLIGHTS

- Effect of re-addition of antioxidant to aged and processed fuels.
- Addition of antioxidant to hydroprocessed fuel past mandated time.
- Antioxidant depletion rates for aged fuels.
- Influence of readdition of antioxidant on induction times.

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ABSTRACT

Long term storage of aviation turbine fuels often requires the use of antioxidants with many military fuel specifications mandating its addition for hydroprocessed fuels. This work examines the influence of antioxidants on aged and freshly refined aviation turbine fuels of various types, some containing antioxidant at manufacture and others not. The rate of antioxidant depletion is reported along with the re-stabilised fuel's oxidation induction periods. It was found that some fuel types do not benefit from re-addition of antioxidant and no improvement was observed for inhibition of hydroperoxide formation in aged fuels, however oxidation induction times were improved for re-addition of antioxidant for all fuels examined. A simple method for assessing the degree of hydroprocessing of an unknown fuel was also examined with limited success.

1. Introduction

Storage stability is a significant concern for long term and strategic storage of jet fuels. Storage stability is defined as a fuel's resistance to peroxide and sediment formation. Other measures of stability also exist and include oxygen induction times. Jet fuels are manufactured by various processing methods including straight run, MEROX and hydroprocessing [1]. Different fuel refinery processing methods are known to affect the storage stability of fuels. Some fuels are known to have poor storage stability based on their processing such as hydroprocessed fuels which are generally considered to be fast oxidisers [2,3]. Hydroprocessing will remove naturally occurring antioxidants including oxygen, sulfur and nitrogen heteroatoms [4]. Unstabilised fuels will tend to react with oxygen to form hydroperoxides which will affect aircraft fuel system seals, diaphragms and materials made of neoprene, nitrile rubber and Buna-N [5–9]. Rates of formation and decomposition of peroxides are driven by storage temperatures, duration and the availability of oxygen [10,11]. Peroxides once formed in a fuel, will initiate autoxidation reactions ultimately forming sediments and gums which lead to increased maintenance, poor performance and engine failures [3,12,13].

To ensure satisfactory storage stability and inhibit peroxide formation, some military and civil fuel specifications require the addition of antioxidant to hydroprocessed fuels immediately after processing and before the fuel is exposed to the atmosphere [14,15]. This is done with the purpose of preventing gum formation and peroxidation after manufacture [16]. Previous studies have shown that hydroprocessed fuels will exhibit peroxide formation rates 200 times greater than a non hydrotreated fuel [9]. Once all available antioxidants are depleted the rate of formation is so rapid that for the antioxidant to be effective it should be added at the time of processing.

Synthetic phenolic antioxidants have routinely been used to stabilise fuels by preventing peroxide build up [17–19]. Synthetic phenolics act to disrupt the chain of peroxidation reactions by

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Table 1
Ambient aged fuels peroxide concentrations pre and post addition of antioxidant and measured after 26 weeks aging at 43 °C. *Note* PV = peroxide value.

Sample name	Fuel type	Finishing process	Years in ambient storage	PV initial	PV 26 weeks at 43 °C with 25 ppm antioxidant added (ppm)	Initial antioxidant present (ppm)
Aging 7	F-34	MEROX blend	0.5	0.0	0.0	0.0
Aging 6	F-34	MEROX blend	3	0.0	7.2	0.0
Aging 5	F-34	MEROX Blend	10	0.5	8.5	0.0
Aging 4	F-34	MEROX blend	11	0.0	6.4	0.0
Aging 3	F-34	MEROX blend	12	0.0	7.4	8.1
Aging 2	F-34	MEROX Blend	17	0.0	7.3	9.4
Aging 1	Jet A1	MEROX blend	17	0.0	3.4	0.0

forming a stable radical but are not known to be effective in inhibiting those peroxides already in the fuel [20].

Work by Love et al. [7] on fuel related problems in gas turbine engines summarised the effect of peroxide formation finding the following;

– "Fuels that contained peroxide that attacked rubbers showed little or no improvement following addition of antioxidant, as the useful properties of the additive were quickly absorbed without a reduction in peroxide content.
– Little improvement was achieved when all traces of existing peroxides were removed from the fuel by chemical treatment as they quickly reform.
– Removal of existent peroxides from the fuel, followed by immediate addition of an antioxidant inhibited peroxide reformation.
– Blending of fast oxidising fuels with non-hydroprocessed fuels improved resistance to peroxide formation."

Normally once a jet fuel has been stabilised with antioxidant it has no further requirement for re-addition under normal storage conditions. Fuels in storage have no defined in-service deterioration limits with respect to peroxide formation, but the deterioration may be monitored via other properties such as existent gum formation. Currently for some fuels in long term storage there is no limit placed on life as long as those fuels pass periodic recertification testing.

Fuel samples of uncertain provenance may be mixtures of fuels produced by varied finishing processes. Currently there is no simple method for determining the level of an unknown fuel's hydrotreatment, or the degree of hydroprocessed component of a mixture. A simple method to establish unknown fuels level of hydrotreatment based on the conversion of naphthalene to tetralin and decalin as a guide was examined.

This work explores the potential for re-addition of antioxidant to aged hydroprocessed fuels and to a hydroprocessed fuel that did not have antioxidant added during production. These hydroprocessed fuels are compared with a range of straight run and MEROX fuels of various ages.

2. Experimental

2.1. Samples

Three different fuel types were examined plus a 'model fuel' assessed as a possible reference fuel. Fuel samples used in the experiment were either Jet A-1, F-34 (Jet A-1 plus military additive package) or F-44 (military aviation fuel for use on ships with additive package). The F-34 and F-44 all met the DEF(AUST) 5240D aviation turbine fuel specification [16] and all had the fuel system icing inhibitor (FSII), static dissipater additive and corrosion inhibitor additive package. All samples were taken either directly from the refinery or from air base tankage where the fuel was supplied to the base consistently from a single refinery. All were stored in 1 L amber glass bottles at ambient conditions.

2.1.1. MEROX fuels

Seven ambiently aged fuels were included from a refinery known to use a MEROX finishing process. These fuels have no requirement for antioxidant addition. The Aging 1 and Aging 2 samples were the same fuel with Aging 2 containing the military additive package. It was found that Aging 2 still contained 9.4 ppm of antioxidant even after 17 years in ambient storage, Table 1.

2.1.2. Hydrotreated fuels

A range of ambient aged hydrotreated jet fuels, and a fresh 100% hydrotreated fuel with no antioxidant added was used as a reference standard. The reference hydroprocessed fuel, designated AO-24, was obtained from a local refiner and was 1 day old when received; this sample was subsequently stored at −18 °C. All of the F-44 samples were taken from a single location and known to be 100% hydrotreated, Table 3.

2.1.3. Model fuel

The model fuel composition was chosen to examine storage stability of the alkane and aromatic fractions of fuel and did not contain any diaromatics as added to other model fuels compositions [21]. The model fuel used was as that of Webster et al. [22] and was made up of the following components;

a. 50 mL methyl cyclohexane.
b. 50 mL 2,2,4-trimethylpentane.
c. 100 mL toluene.
d. 100 mL *o*-xylene.
e. 100 mL nonane.
f. 50 mL decane.
g. 100 mL undecane.
h. 250 mL dodecane.
i. 200 mL tetradecane.

Table 2
MEROX and model fuel PetroOxy results.

Sample	Years in ambient storage	PetroOxy time, min
Model fuel	0	297
Model fuel + 24 ppm AO	0	1356
Aging 6 – MEROX	3	1715
Jet A1 69% MEROX	6	923
Aging 5 – MEROX	10	1760
Aging 4 – MEROX	11	1790
Aging 3 – MEROX	12	1417
Aging 1 – MEROX	17	974
Aging 2 – MEROX	17	1734

Note Aging 2 sample is Aging 1 that had the military additive packed added when produced.