

Effect of Organic Peroxides on the Corrosiveness of Aviation Fuels and Pure Hydrocarbons

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Various amounts of *tert*-butyl hydroperoxide, 0.5 to 2.5 meq. O₂ per liter, were added to aviation gasoline, jet fuel and pure hydrocarbons which had been contaminated with elemental and mercaptan sulfur, 15 mg. per liter each. ASTM copper strip tests at 100° C. were carried out by the standard procedure and in an inert-gas atmosphere. After the copper strip test, the fuel was analyzed for changes in sulfur and peroxide content. An HCl test was devised for a more exact estimation of the corrosion test. The copper strip after the corrosion test was placed in a nitrogen atmosphere in a specially designed apparatus. 1:1 HCl was added, and the evolved H₂S was absorbed in a Cd(OH)₂ suspension and determined from the methylene-blue reaction in a Beckman spectrophotometer at 670 mμ. The results show that an inert atmosphere favors higher results in the copper strip test, and that organic peroxides added to a corrosive fuel reduce corrosiveness. The effect of peroxides in reducing corrosiveness is more pronounced in air and their stability higher than in an inert atmosphere. The proposed HCl test permits linear estimation of the degree of corrosiveness.

HAVING PREVIOUSLY established that a suitable concentration of peroxides formed through ultraviolet irradiation inhibits the corrosive effect of sulfur compounds (3), the authors investigated the effect of organic peroxides on corrosiveness, changes in sulfur compounds and peroxide content after the corrosion test, the use of air *vs.* an inert atmosphere in the standard corrosion test bomb, and improvement of the corrosion-strip evaluation to replace the ordinary visual method.

In the ASTM Copper Strip Corrosion Standard test (1), based on the Indiana scale, a series of copper strips shows a progressive change in discoloration with the degree of corrosiveness established by comparing the tested strips with reference standards. According to Bolt (4), discoloration results from light interference on a thin copper sulfide film. He also believes a reasonably linear relationship exists between the color and the corrosive sulfur content.

Kashima and Nose (9), on the basis of electron diffraction measurements and examination of strip surfaces, found cuprous oxide in the 1a-3a region of the scale and beta-cuprous and cupric sulfide in the higher region, 3b to 4c. They attributed the color change to the oxide film; and were unable to find a linear relationship between color changes and film thickness. Concerning corrosion by elemental sulfur, they believed that the oxide film was overlaid with cuprous sulfide even in the lower region of the scale, and that the presence of peroxides accelerates copper strip corrosiveness.

The present work agrees with Kashima and Nose in that sulfide film was observed even at the lowest level of corrosiveness. However, the authors were able to establish on the basis of ASTM criterion that oxygen and peroxides reduce corrosiveness and that corrosiveness is more severe and peroxide decomposition more pronounced when nitrogen and helium replace air in the corrosion test.

The findings of Claxton and French (5) regarding strip passivation could not be confirmed. It was assumed that the inhibitory effect of peroxides is based on interference with the sulfur-copper reaction and not on any surface phenomenon since no passivation effect was observed at 100° C. Irradiation-formed peroxides, because they may induce free radical reactions and sulfur polymerization, are more active than the added peroxides. This was also mentioned by Pryor (10).

EXPERIMENTAL

Aviation gasoline grade 100/130 (Spec. MIL-G-5572C) and aviation turbine kerosine (JP-1) were artificially contaminated with 0.002% (15 mg. per liter) elemental sulfur and the same amount of *n*-butyl mercaptan. These compositions and concentrations had previously given pronounced corrosiveness and easily evaluable results (3, 7). Organic peroxides were added to these corrosive fuels which were examined under different conditions for corrosiveness. The amounts of sulfur, mercaptans, and peroxides in the contaminated fuels were determined before and after the corrosion test to give an indication of the reaction's mechanism. The deposited sulfide on the copper strip was also determined.

Sample Preparation. The samples were prepared from analytical grade elemental sulfur (recrystallized from benzene) and analytical grade *n*-butyl mercaptan, and dissolved in the fuel or hydrocarbon. *tert*-Butyl hydroperoxide was added to the contaminated fuels. A stock benzene solution (0.5 gram per 100 ml.) was prepared and stored at 0° C. to ensure stability. The pure hydrocarbons and other reagents were of Analar grade. The nitrogen, 99.9% pure, was washed in basic cadmium solution. The helium was of highest purity.

Test Procedure:

Corrosiveness—by ASTM D130 at 100° C. for two hours, rated on the ASTM scale.

Elemental sulfur—by the quantitative benzoin method developed by the authors (11), and by the colorimetric method proposed by Bartlett and Skoog (2).

Mercaptan sulfur—by silver nitrate and potentiometric titration (8).

Peroxides—by iodometric titration, I.P. 88(6). Peroxide number is defined as meq. O₂ per liter.

In addition to these methods, some modifications and new equipment were introduced. The standard ASTM corrosion bomb was modified to permit replacement of the air with an inert gas, Figure 1. The stainless steel closure of the bomb was punched through and equipped with two stainless steel tubes of 8-mm. diameter with a needle valve attached to each end. In addition, a simple glass apparatus was used in the HCl test for determining the deposited sulfur as sulfide on the copper strip [a modification of the Claxton and French procedure (5)], Figure 2. Having been tested

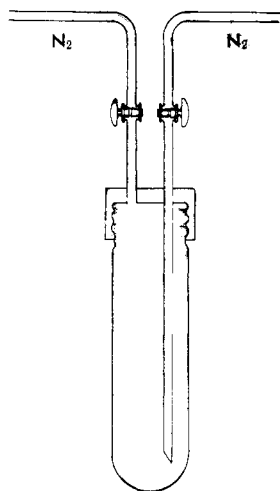


Figure 1. Modified ASTM corrosion bomb

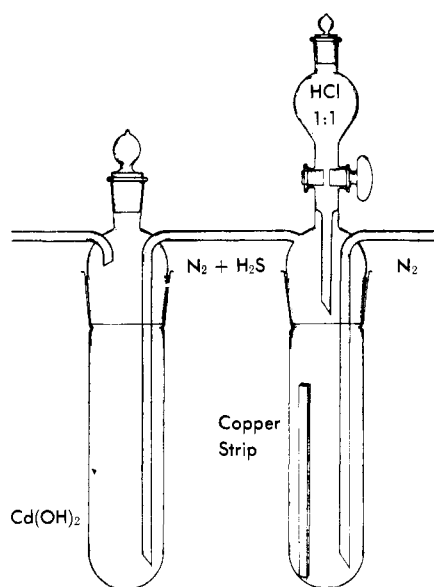


Figure 2. Apparatus for HCl test

and evaluated, the strip was placed in the reaction vessel and the inert gas supply turned on. Through the separating funnel, 15 ml. of 1:1 HCl were added, and the evolved H_2S was absorbed in cadmium hydroxide solution. The flow of inert gas was maintained for 15 to 30 minutes to ensure complete decomposition of the sulfides. The amount of H_2S was determined from the methylene blue reaction in a Beckman spectrophotometer at $670 m\mu$ (11).

PRELIMINARY EXPERIMENTS

A preliminary series was undertaken to select the most effective organic peroxide for reducing the corrosiveness of contaminated fuel, to determine the selected peroxide's thermal stability under the conditions of the standard corrosion test, and to study the mutual effect of strip and peroxides.

The compounds tested were methyl-ethyl ketone peroxide, *tert*-butyl hydroperoxide, the peroxides obtained from ultraviolet irradiation of aviation gasoline (3), and aged cyclohexene (peroxide number 120). All of these were added to sulfur-contaminated aviation gasoline; results of the standard corrosion test are given in Table I. With the exception of the ultraviolet-formed peroxides, TBHP is the

most effective compound, and it was used throughout the experiments. The peroxide number level required for complete elimination of corrosiveness was 2.5.

The thermal stability of TBHP was tested in aviation gasoline at peroxide number 2.8, under conditions of the corrosion test (standard and inert atmosphere), with and without a copper strip. Peroxides were more stable without the strip and were less stable in nitrogen than air. Absence of strip discoloration showed that it is unaffected by peroxides at this concentration, as well as under test conditions.

The stability of the added sulfur and mercaptans was similarly studied, with and without peroxides. In nitrogen, without peroxides, the mercaptan concentration remains unchanged while that of sulfur undergoes little change. In contrast, the highest mercaptan sweetening (15.0 to 2.5 mg. per liter) was observed in air in the presence of peroxides as compared to 15.0 to 6.0 mg. per liter in nitrogen at the same peroxide number.

The preliminary series also included an attempt to verify the finding of strip passivation claimed by Claxton and French.

Polished strips were immersed for two hours in a 0.5% (w./v.) benzene solution of TBHP and in a more dilute solution of peroxide number 2.5, at room temperature and at $100^\circ C$. in a closed corrosion bomb. These strips were used in the standard corrosion test of the contaminated aviation gasoline. After the tests, the strips appeared corroded and no sign of passivation could be observed. Establishing the degree of corrosiveness was difficult because the strips were greyish. The deposit on the strips was easily removable and left a discolored reddish surface. A separate experiment showed that the strips from the $100^\circ C$. experiments could not always be fitted into the Standard ASTM color table. When the same experiment was repeated with iso-octane instead of benzene, the degree of corrosiveness was easier to establish (3b—the same degree as under normal test conditions).

Series 1. The effect of peroxides was further studied in a comprehensive experimental series. Varied peroxide concentration and corrosiveness were determined by the standard corrosion test and by the nitrogen corrosion test. Results are summarized in Tables II, III, and IV, and Figure 3, respectively. The composite diagram clearly indicates the difference between the two corrosion tests—the nitrogen atmosphere is the more aggressive. Smooth curves were obtained for sulfide deposition and residual sulfur after the corrosion test. All results correlated with increasing peroxide number and decreasing corrosiveness. (As no H_2S evolution was observed during the test, the sulfur compounds must have been retained in the fuel or deposited.)

A naturally contaminated aviation gasoline, which had become corrosive during storage, was H_2S and peroxide-free, while containing 5 mg. per liter of elemental sulfur. This gasoline showed 2a-2b corrosiveness on the standard corrosion test scale as compared with 2b-2c in the nitrogen test. The HCl test yielded 14% of sulfur in air and 40% in

Table I. Effect of Organic Peroxides and Concentrations on Corrosive Aviation Gasoline 100/130 Contaminated with Sulfur + *n*-C₁₅H₃₂ (15 Mg. per Liter Each)

Type of Peroxides	Peroxide Number	Corrosiveness, 2 Hr. at $100^\circ C$.
Peroxide-free gasoline	0	3b
Methyl ethyl ketone peroxide	1.1	2c
UV irradiated aviation gasoline 180 sec.	1.1	0
Cyclohexene	1.1	2a
<i>tert</i> -Butyl hydroperoxide	0.44	2c
	0.9	1b+
	1.1	1b
	1.5	1b-
	2.5	0

Table II. Corrosiveness of Aviation Gasoline Contaminated with Sulfur and $n\text{-C}_4\text{SH}$ (15 Mg./Liter Each) in Air and Nitrogen, vs. TBHP Concentration

0		0.5		1.0		1.5		2.5		3.5	
Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
(Peroxide Number)											
Corrosion 2 hrs. at 100° C.											
3b	3b-4a	2a ⁻	3a	1b	2e	1a ⁻	2d	0	1b	0	1a ⁻
Sulfide Deposition, HCl Test, γS											
170	266	30	110	6	60	2	40	0	6	0	2
Residual ^a Peroxide Number											
...	...	0.25	0	0.9	0.5	1.1	0.5	2.1	2.0	3.3	2.3
Residual ^a Sulfur, Mg./Liter											
3.5	2.5	9.5	3.5	10	6	13	9	15	13	15	13
Residual Sulfur, % ^b											
25	16.5	50	25	66	40	87	60	100	87	100	87
Residual ^a $n\text{-C}_4\text{-SH}$, Mg./Liter											
0-1.5	9	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5	0-1.5

^aConcentration of corresponding compound in contaminated fuel after corrosion test. ^bPercentage of added sulfur.

Table III. Corrosiveness of Aviation Gasoline (after Removal of TEL, Antioxidant and Dye) Contaminated with Sulfur and $n\text{-C}_4\text{SH}$ (15 Mg. per Liter Each) in Air and N₂ vs. TBHP Concentration

0		0.5		1.5		2.5	
Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
Corrosion 2 hr. at 100° C.							
3b	4a	2c	4a	1a	1b ⁻	0	0
Sulfide Deposition, HCl Test, γS							
162	220	70	122	4	13	0	0
Residual peroxide number							
0	0	0.2	0.1	0.6	0.3	2.5	2.45

Table IV. Corrosiveness of JP-1 Contaminated with Sulfur and $n\text{-C}_4\text{SH}$ (15 Mg. per Liter Each) in Air and N₂ vs. TBHP Concentration

0		0.5		1.5		2.5	
Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
Corrosion 2 hrs. at 100° C.							
3a ⁻	3a	3a	3a	1b	1b ⁻	1a ⁻	1a ⁻
Sulfide deposition, HCl test, γS							
71	112	100	109	9	13	0	0
Residual peroxide number							
...	...	0.35	0.25	1.45	1.35	2.35	2.30

nitrogen. Again, a higher degree of corrosiveness was found in the nitrogen test which was confirmed by higher sulfide.

Series 2. A parallel series was carried out on various hydrocarbon constituents of gasoline and included paraffins, cycloparaffins, and aromatics. Admixtures included, in addition to TBHP, TEL (aviation mix), and an antioxidant (n,N -di-*sec*-butyl-*p*-phenylene diamine). In addition to the air and nitrogen tests, some of the typical experiments were repeated in helium. Results are summarized in Tables V and VI.

The conclusion drawn from this series is basically the same as from Series 1. Allowing for experimental error, cyclohexane (peroxide number 0.5) is the one exception. The nitrogen test is again more severe than its standard

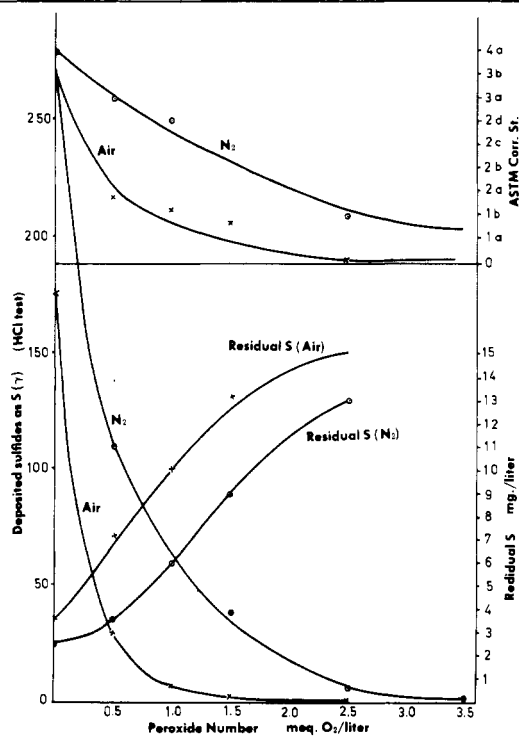


Figure 3. Corrosiveness of contaminated aviation gasoline 100/130 with sulfur and n -butyl mercaptan (15 mg. per liter each), vs. peroxides, residual sulfur, and deposited sulfide on copper strip

counterpart, and is in turn slightly exceeded by helium. Only in iso-octane did TEL and the antioxidant contribute to reduction in corrosiveness. The effect of TBHP on hydrocarbons is more pronounced than in aviation fuels.

DISCUSSION AND CONCLUSIONS

The HCl test was developed and is recommended as a quantitative method for corrosiveness evaluation. A fuel showing above 15γ of deposited sulfur is regarded as corrosive. Addition of organic peroxides resulted in progressive reduction of corrosiveness. Replacement of air by a nitrogen atmosphere leads to higher corrosiveness and should be considered where metal parts are in contact with corrosive fuels in an air-free atmosphere. They may be

Table V. Corrosiveness of Hydrocarbons Contaminated with Sulfur and $n\text{-C}_4\text{SH}$ (15 Mg./Liter Each), in Air and Inert Atmosphere vs. Peroxide Concentration

	(Peroxide Number)										
	0			9.5			1.5			2.5	
	Air	N ₂	He	Air	N ₂	He	Air	N ₂	He	Air	N ₂
Iso-octane											
Corrosion 2 hr. 100° C.	3b	3b	4a	2e ⁻	4a-	1a	1b+	1b+	0	0	
Residual peroxide number	0	0	0	0.25	0.1	0.1	1.45	1.0	0.2	2.35	1.0
Sulfide deposition HCl test, γS	146	145	187	79	84	170	2	2	16	0	0
Cyclohexane											
Corrosion 2 hr. 100° C.	3b+	4a-	4a-	4a	4a	4a	1a+	1b+	...	0	1a
Residual peroxide number	0	0	0	0.2	0.1	0.1	1.2	0.35	...	2.85	1.05
Sulfide deposition HCl test, γS	159	197	181	229	220	230	6	19	...	0	3
Benzene											
Corrosion 2 hr. 100° C.	3a+	3a+	...	1a	1b+	...	1a	1a+	...	1a-	1a-
Residual peroxide number	0	0	...	0.5	0.3	...	1.45	0.7	...	2.2	1.0
Sulfide deposition HCl test, γS	142	162	...	2	18	...	1	3	...	0	0

Table VI. Corrosiveness of Hydrocarbons Contaminated with Sulfur and $n\text{-C}_4\text{SH}$ (15 Mg. per Liter Each) with 3.6 ml./l.G. TEL and 50 P.P.M. Antioxidant in Air and N₂

Iso-octane Peroxide No. 0.5		Cyclohexane Peroxide No. 1.5		Benzene Peroxide No. 0.5	
Air	N ₂	Air	N ₂	Air	N ₂
Corrosion 2 hr. at 100° C.					
1b+	1b+	1a	1b+	1a	1b
Residual peroxide number					
1b+	1b+	1a	1b+	1a	1b
Residual peroxide number					
0.5	0.5	1.4	0.9	0.2	0
Sulfide deposition HCl, test γS					
13	13	2	17	2	7

attacked much more severely than predicted by the standard corrosion test. Contrary to claimed findings, no copper strip passivation under the action of peroxides was observed either in aviation fuels or in pure hydrocarbons. The effect of peroxides in a corrosive fuel is inhibitory and reduces the activity of the corrosion-inducing sulfur compounds.

The effect of added peroxides on corrosive fuels is less in the air-free test than in the standard ASTM corrosion test. In these circumstances, the residual sulfur compounds were higher in the standard test and sulfide deposition and corresponding corrosiveness were higher in the air-free test. Residual peroxides were higher in the standard test because of the stabilizing effect of atmospheric oxygen.

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