Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Effect of Ultraviolet Irradiation on the Corrosiveness of Aviation Gasoline

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CORROSIVENESS of petroleum products, or, more precisely, copper strip corrosion, is tested by the well-established copper strip method at fixed temperatures, described both in ASTM standards (*1*) and in the Institute of Petroleum standard (7, I.P. 154/59).

Primarily, the degree of corrosiveness depends on the amount of corrosive substances dissolved or suspended in the product. This refers to hydrogen sulfide, organic polysulfides, elemental sulfur, and tertiary mercaptans (thiols), other organic sulfur compounds being only very slightly or not at all active with regard to copper (*8*, *10*).

Happel and Cauley (*6*) recognized that not only is the corrosiveness of petroleum products dependent on the concentration of the various corrosive substances, but a certain interaction of the inactive compounds is also a factor in inducing it.

The authors have observed several cases of aviation gasoline becoming corrosive on prolonged storage, the cause being elemental sulfur (*3*), but contrary to other reports they were unable to detect hydrogen sulfide formed by bacterial action. Furthermore, this corrosiveness disappeared completely in the samples in question on exposure to sunlight.

In the light of these observations, a more detailed study of this phenomenon was justified, to an extent which, to the authors' knowledge, had not hitherto been undertaken.

EXPERIMENTAL

Preliminary experiments showed that 0.002% (15 mg. per liter) of elemental sulfur and 0.002% of *n*-butyl mercaptan caused pronounced corrosiveness in commercial corrosiveness-free aviation gasoline grade 100/130 (specification Mil-G-5572 C). These rather high concentrations were used to facilitate the study under the various conditions.

This artificially contaminated gasoline, on exposure to sunlight in a transparent glass bottle, gradually lost its corrosiveness and a whitish precipitate was formed. It was also realized, at an early stage, that the presence of air in contact with the gasoline surface is a highly important factor in the irradiation experiments.

A Mineral Light lamp Type R-51 (Ultraviolet Products) with peak intensity at 2500 to 2600 A. was found most suitable for irradiating the aviation gasoline, which had shown a characteristic high absorbance at 2620 A.

Procedure. The samples (prepared from analytical grade elemental sulfur recrystallized from benzene and analytical grade *n*-butyl mercaptan and dissolved in gasoline or hydrocarbons) were placed in a Petri dish and subjected to direct irradiation at varying distances either in contact with air (filled to a depth of 12 mm. and left uncovered) or air-sealed (completely filled and covered with a thin quartz plate), with time of irradiation and sulfur (elemental and mercaptan) contents as additional variables. In a special test the air-exposed samples were subjected to magnetic agitation.

The samples were tested before and after irradiation, for:

Corrosiveness (*1*) at 50° C. for 3 hours and at 100° C. for 2 hours, with results given by the ASTM scale.

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

Mercaptan sulfur, by the $AgNO_3$ potentiometric titration method (*9*).

Peroxides, by iodometric titration (7, I.P. 88).

Existent gums, by the air jet glass dish method (7, I.P. 38).

Octane number, by the knock rating method (7, I.P. 42).

SERIES 1. The sample, containing 15 mg. of elemental sulfur per liter and an equivalent amount of *n*-butyl mercaptan (having a corrosiveness of 3b at 100° C.) was irradiated for 150 seconds. Under air-sealed conditions corrosiveness remained unaffected and no peroxides were formed, whereas the sulfur content remained 15 mg. per liter and the mercaptan sulfur was reduced to 13 mg. per liter. On the other hand, on air exposure corrosiveness completely disappeared and the elemental sulfur was reduced to 13 mg. per liter and the mercaptan sulfur to 12 mg. per liter, whereas the peroxides increased to 0.7 meq. of O_2 per liter. The series showed that reduction of corrosiveness is closely related to peroxide formation, which is in turn dependent on contact with air.

SERIES 2. This series dealt with the effect of sulfur contents on corrosiveness, peroxides, existent gums, and octane number in air-exposed samples. Results are summarized in Table I and Figure 1.

The conclusions are:

Corrosiveness is dependent on sulfur content.

Peroxide formation and reduction in corrosiveness are dependent on irradiation time.

Decrease of mercaptan sulfur is higher than that of elemental sulfur for the same irradiation time; the higher the initial mercaptan content the higher the relative decrease. Stirring intensifies the reduction in mercaptan sulfur, with other data almost unchanged.

The higher the two sulfur contents, the higher the amount of peroxides required for reducing corrosiveness.

The 100° C. corrosiveness test shows higher reduction in corrosiveness compared with the 50° C. test.

Existing gums remain below the prohibitive level for short irradiation times.

The octane number is unaffected.

Precipitation is negligible for short irradiation times.

These results again demonstrate that corrosiveness is primarily dependent on the amount of peroxides formed on irradiation, and the relatively small decreases in sulfur content appear to be of secondary importance under the conditions of the tests.

SERIES 3. This dealt with the response to irradiation of various hydrocarbon constituents of gasoline, including the combined effects of the commonly used TEL (tetraethyllead) octane number improver and antioxidant inhibitor. The types tested comprised an unsaturated paraffin, a cycloparaffin, a cyclo-olefin, and an aromatic hydrocarbon in the gasoline distillation range, with aviation gasoline 100/130, which had been previously examined, included for comparison. Results are summarized in Tables II and III.

Here again, the presence of peroxides appears to be the decisive factor in reducing corrosiveness. The most outstanding case is that of cyclohexene, where even the unirradiated hydrocarbon, with a high peroxide content, failed to show any effect on the copper strip, and irradiation resulted in an appreciable decrease in both sulfur contents.

In saturated hydrocarbons the presence of TEL [known as an oxidation accelerator (*4*)] had a marked effect on peroxide formation, resulting in a decrease in both sulfur contents and corrosiveness. Aromatics, on the other hand, behaved differently and appeared to be unaffected by irradiation even in the presence of TEL. In the case of contaminated benzene, different discoloration of the copper strip was observed, for which no satisfactory explanation has been found.

Peroxide formation was reduced in the presence of an active antioxidant (such as *N,N'-sec*-butyl-*p*-phenylenediamine) which binds the available oxygen, thus protecting the hydrocarbons against oxidation.

SERIES 4. The irradiation test was carried out on a sample of naturally contaminated aviation gasoline, which had become corrosive on storage (Table IV). A very short irradiation time rendered the gasoline noncorrosive.

The possibility of utilizing this technique for large-scale treatment of corrosive gasolines requires further study.

As a further proof of the role played by peroxides in counteracting corrosiveness, the effect of their removal was studied in a special experiment. For this purpose, the gasoline samples were shaken with a saturated aqueous solution of ferrous sulfate, washed, and filtered (*12*). In the case of artificially contaminated gasoline, corrosiveness reappeared (2d at 50°, 3b at 100° C.). Furthermore, addition of oxidized or peroxidized gasoline to contaminated gasoline resulted in disappearance of the copper strip discoloration.

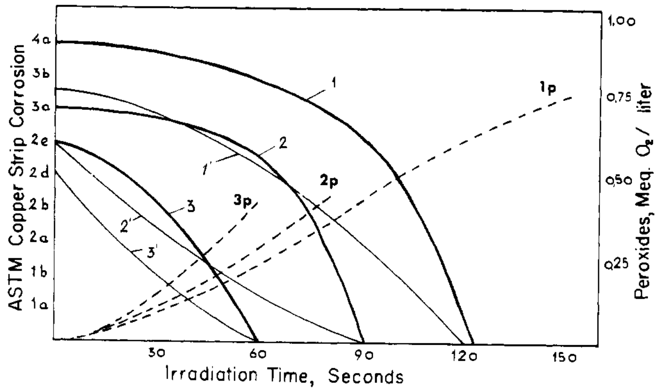

Figure 1. Decrease of corrosiveness of contaminated aviation gasoline as a function of irradiation time and peroxide content

▬ Corrosion at 100° C.

— Corrosion at 50° C.

– – – Peroxides

1,1', 1p. 15 mg./liter S°, R-SH each
2,2', 2p. 10 mg./liter S°, R-SH each
3,3', 3p. 5 mg. liter S°, R-SH eoch

Table I. Effect of Sulfur Content of Air-Exposed Aviation Gasoline

(Irradiation at 5 cm., 2000- to 3000-A. wave length)

	S° and R-SH, Mg./Liter Each									
	5			10			15			
	Irradiation Time, Seconds									
Corrosiveness	0	30	60	0	60	90	0	90	120	150
At 50° C., 3 hours	2d	1b	0	2e	1b	0	3a	2a	0	0
At 100° C., 2 hours	2e	2b	0	3a	2b	0	4a	3a	1a	0
Elemental sulfur, mg./l.	...	...	4	...	...	9	...	...	...	12.0
Mercaptan sulfur, mg./l.	...	...	2.9	...	...	5.1	...	...	...	5.1
Peroxides, meq. O_2/l.	0	0.14	0.42	0	0.3	0.52	0	...	0.61	0.74
Existent gums, mg. ml.	1.5	2.0	2.3	1.5	2.0	2.0	1.5	...	3.0	5.0
Octane No. F-3							100		100	

Table II. Effect of Elemental and *n*-Butyl Mercaptan Sulfur on Pure Hydrocarbons

(15 mg./l. each, irradiation time 150 seconds at 5 cm., 2000- to 3000-A. wave length, air-exposed, and air-sealed conditions.)

		Before Irradiation			After Irradiation									
					Air-Exposed					Air-Sealed				
		Corrosiveness			Corrosiveness					Corrosiveness				
Hydrocarbon	TEL, Ml./IG	50° C.	100° C.	Per-oxides, meq. O_2/l.	50° C.	100° C.	Per-oxides, meq. O_2/l.	S°, mg./l.	R-SH, mg./l.	50° C.	100° C.	Per-oxides, meq. O_2/l.	S°, mg./l.	R-SH, mg./l.
Iso-octane	3.6	2e	3b	0	0	0	0.8	12.5	11.5	2c	3b	0.1	13.0	12.0
Benzene	3.6	2d	4a	0	3a	4a	0.08	14.0	14.0	2d	4a	0	14.0	14.0
Aviation gasoline	3.6	2e	3b	0	0	0	0.7	13.0	12.0	2d	3b	0	13.0	13.0

IG = Imperial Gallon.

Table III. Effect of Elemental and *n*-Butyl Mercaptan Sulfur on Hydrocarbons

(15 mg./l. each, irradiation time 150 seconds at 5 cm., 2000- to 3000-A. wave length, air-exposed.)

	Before Irradiation					After Irradiation				
				Corrosiveness					Corrosiveness	
Hydrocarbon	TEL, ml./IG	Inhibitor, p.p.m.	Peroxides, meq. O_2/l.	50° C.	100° C.	S°, mg./l.	R-SH, mg./l.	Peroxides, meq. O_2/l.	50° C.	100° C.
Iso-octane	0	0	0	2e	3b	14.5	13.0	0	2c	3b
	3.6	0	0	2e	3b	12.5	11.5	0.8	0	0
	3.6	50	0	2e	3b	...	...	0.24	0	1b
Cyclohexane	0	0	0	2c	4a	15.0	14.0	0.04	2c	3b
	3.6	0	0	2c	4a	12.0	5.0	1.8	0	0
Benzene	0	0	0	2d	4a	14.5	14.0	0	2a	3a
	3.6	0	0	2d	4a	14.0	14.0	0.08	3a	4a
Cyclohexene	0	0	50	0	0	12.0	12.0	120.0	0	0
	3.6	0	50	0	0	9.0	1.0	170.0	0	0
Aviation gasoline	3.6	20	0	2e	3b	13.0	12.0	0.7	0	0

IG = Imperial Gallon.

Table IV. Effect of Irradiation Time on Naturally Contaminated Aviation Gasoline

Irradiation time, sec.	0	30	60
Corrosiveness at 50° C., 3 hours	2b	0	0
Corrosiveness at 100° C., 2 hours	2d	0	0
Elementary sulfur, mg./l.	4	...	0.42
Mercaptan sulfur, mg./l.	9	...	...
Peroxides, meq. O_2/l.	0.08	0.32	0.42
Existent gums, mg./100 ml.	5.6	...	6.0

Another aspect studied was retention of noncorrosiveness by the irradiated samples on prolonged storage. Samples were stored in dark glass bottles at room temperature and their corrosiveness and peroxide contents were measured at various time intervals. The test showed gradual reduction in peroxide content, combined with an increase in corrosiveness; the irradiated aviation gasoline sample of Series 4 still remained noncorrosive after 60 days of storage. The reappearance of corrosiveness probably depends on the type of peroxides formed and their stability (5).

CONCLUSIONS

Peroxide formation is the first reaction on ultraviolet irradiation. At suitable concentration, these peroxides inhibit the action of the corrosiveness-inducing sulfur compounds. The decrease in mercaptans was greater than the equivalent amount of elemental sulfur. All these reactions ensue in a comparatively short time at suitable ultraviolet wave length and under air- exposed conditions, and are accelerated in the presence of TEL. Different degrees of corrosiveness were found in irradiated gasoline and pure hydrocarbons, in spite of the identical amount of sulfur contamination.

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RECEIVED for review March 2, 1961. Accepted June 9, 1961.