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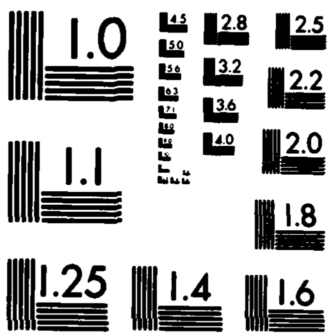

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Chapter 6 in the Russian book by E. T. Denisov and G. I. Kovalev, "Oxidation and Stabilization of Jet Fuels", is reviewed. It deals with the effects of many metal and alloy surfaces on gum and deposit formation from a stable jet fuel (T-6) produced by "hydrodearomatization". The metals affect oxidations mostly by assisting or retarding the initiation of a subsequent homogeneous oxidation. The effects of the metals and the differences among them are small to moderate. Originator furnished keywords include

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OXIDATION AND GUM FORMATION IN JET FUELS

Interim Technical Report No. 1

By

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U. S. ARMY RESEARCH OFFICE
Contract No. DAAG 29-84-K-0161

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OBJECTIVE

One of the objectives of my present contract with the ARO is to determine the effect of metal surfaces on fuel stability. However, a book has recently appeared that treats this subject competently, "The Oxidation and Stabilization of Jet Fuels" by E. T. Denisov and G. I. Kovalev[1]. The book has been translated but not published by NASA;[2] both versions have a very limited availability in the U. S. Chapter 6 in the book deals with relative rates of oxidation and gum formation in the presence of many metal and alloy surfaces. The object of this Interim Technical Report is to review this chapter, draw some conclusions, and consider whether and how the direction of my contract research should be altered.

BACKGROUND

The first five chapters of the book consider in great detail the kinetics and mechanism of oxidation of hydrocarbons and some jet fuels. They make available in one place the extensive and detailed Russian work in this field but I found little that is new in principle. However, I am not aware of much other work on the effects of metal surfaces.

Denisov's experiments used 0.5 g of metal powder in 50 g of T-6 jet fuel. This fuel was produced by hydrodearomatization. It contains no significant quantities of O, N, and S has a low tendency toward deposit formation in fuel systems. Some properties are: <10% boiling below 220°C, >98% below 315°C; density at 20°C, 840 g/L; <22% aromatic hydrocarbons, <1.5% bicyclic aromatic hydrocarbons. Oxygen absorption was measured over an unstated period at 150°C and presented as the quotients of the rates of oxygen absorptions with and without metal. At the ends of the experiments, solid products and soluble gum were determined. These are presented as milligrams of material/100 g fuel

[1] Khimiya Press, Moscow, 1983.
[2] NASA Technical Memorandum 77490, 1984.

and also as the quotients of these weights in the presence and absence of metal surfaces. Denisov treats these gum data as if they were rates over the same periods as the corresponding oxygen absorptions and I shall treat them the same way.

RESULTS

Table 1 summarizes the results in Denisov's Table 6.3 on pages 208-209 of his book. I have added code letters and arranged the relative rates of oxidation in order of decreasing rates. These relative rates range from 8 times to one-seventh the rate in the absence of metal (q). The second column of figures gives the relative rates of gum formation in order of decreasing rates; the code letters are repeated because the orders in the two columns, though similar, are not identical. The spread in rates of gum formation is small, from one-half to twice the rate in the absence of metal. The third column of figures shows the quotients of the same code numbers in the first two columns, arranged in order of decreasing magnitude. The larger numbers at the top of this column show that more oxygen is required to produce a milligram of gum with these metals; the small numbers at the bottom show that these metals give the most gum for the oxygen absorbed.

Denisov and Kovalev conclude that the principal effect of the metal surfaces is to affect the rate of homogeneous oxidation by decomposing hydroperoxides on the metal surface. If this decomposition produces free radicals, the oxidation is accelerated; if it does not, the oxidation is retarded because the hydroperoxide is wasted.

CONCLUSIONS

My Figure 1 is a revision of Denisov's Figure 6.2 on page 210. The straight line corresponds to his correlation of the data. His line has the advantage that it comes close to the blank with no metal (q), but the disadvantage that it predicts considerable gum formation without any oxidation. My curve put a different emphasis on the data. It says that for many metals, s to h, there is a close proportionality between rates

Table 1

Oxygen Absorption and Gum Formation by T-6 Jet Fuel

Code Letter	Metal Surface[a]	Relative R_o [b]		Relative R_g [c]		Relative R_o/R_g
a	100 Cr	8.12	a	no datum	a	no datum
b	Cu +20 Pb[e]	5.16	d	2.16[d]	c	2.54
c	Cu +11 Pb +10 Sn	5.16	b	2.04[d]	b	2.53
d	100 Pb	5.08	c	2.03	d	2.35
e	Cu +11 Al[f]	3.12	f	1.76	e	1.91
f	65 Cu +33 Zn + 2 Pb	3.10	e	1.63	g	1.90
g	Cu +10 Al[g]	3.02	g	1.59	p	1.84
h	Cu + 6.2 Sb	2.57	h	1.51[d]	o	1.77
i	100 Cu	2.51	i	1.49	f	1.76
j	Stainless Steel	1.96	w	1.44	m	1.75
k	60 Cu + 40 Zn	1.86	j	1.31	h	1.70
l	Fe + 12 Cr	1.86	k	1.18	i	1.68
m	100 Fe	1.56	l	1.13	l	1.65
n	100 Al	1.55	q	1.000	k	1.58
o	100 Sn	1.47	n	0.99	n	1.57
p	Low-Ni stainless	1.42	m	0.89[d]	s	1.56
q	no metal	1.000	x	0.88[d]	j	1.50
r	100 Zn	0.88	u	0.86	r	1.09
s	100 Mo	0.78	o	0.83	q	1.000
t	100 Nb	0.78	v	0.81	t	0.99
u	100 Mg	0.70	t	0.79	w	0.81
v	100 Ni	0.24	p	0.77	v	0.39
w	100 V	0.14	v	0.62	x	0.16
x	100 W	0.14	s	0.50[d]	w	0.097

[a] Metal powder, composition in weight %, with a surface area of about 300 cm^2/L. However, a, m, n, r, t, and v apparently have surface areas up to 19000 cm^2/L.

[b] (Rate of oxygen absorption with metal)/(Rate of oxygen absorption without metal). Latter rate was 1.97×10^{-5} $M^{1/2}/sec$.

[c] (Gum + deposit with metal)/(gum + deposit without metal). Latter number is 57.0 mg /100g fuel.

[d] Deposit noted. [e] +3 each Zn, Sb. [f] +5.5 each Fe, Ni. [g] +3 Fe + 1.5Mn.

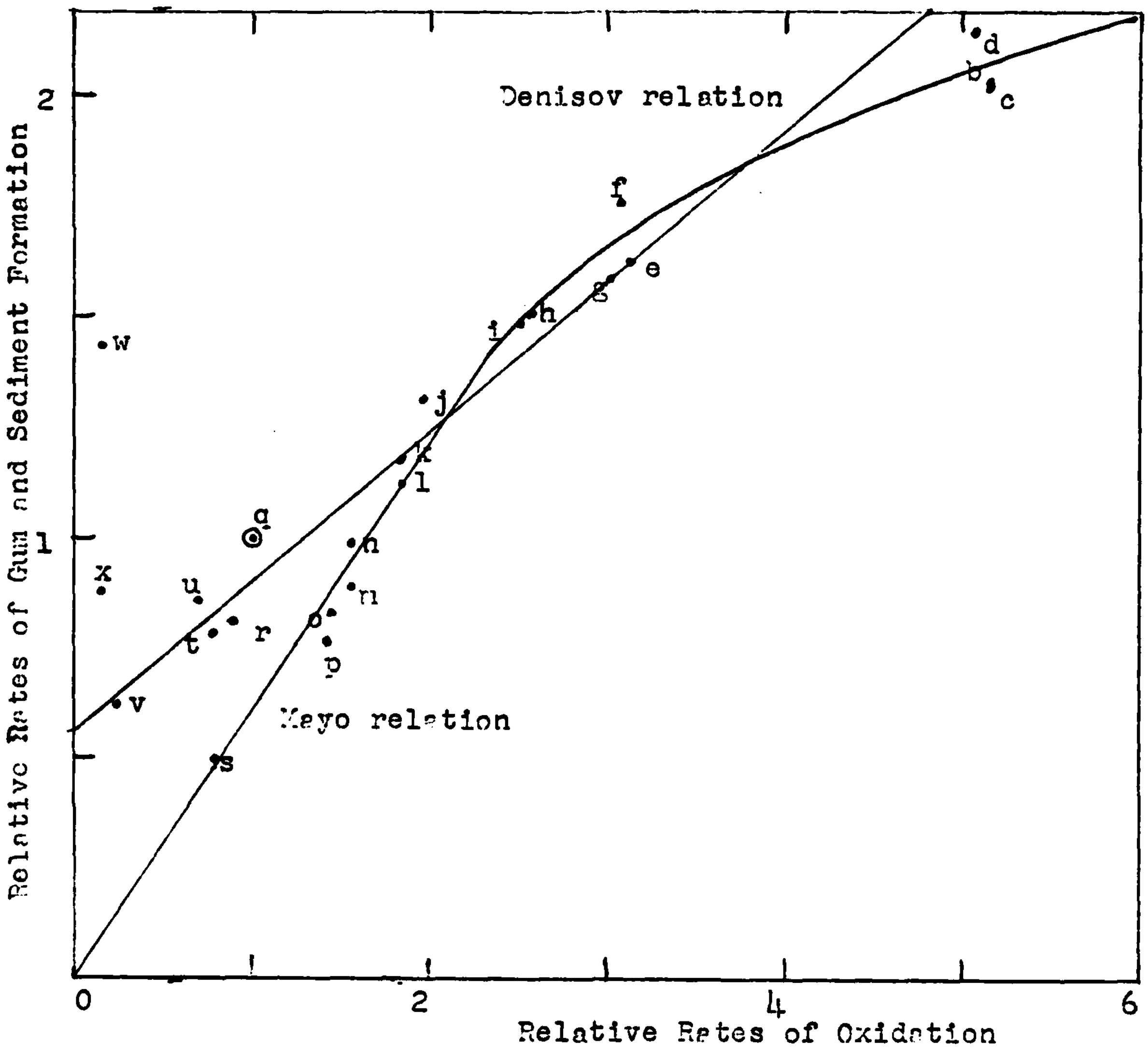

Figure 1, Comparison of Relative Rates of Oxidation and Gum Formation

of oxidation and gum formation and that when there is no oxidation, there is no gum formation. The place of sample q, without any metal, then suggests that the metals on or near the line have accelerated oxygen absorption more than gum formation. Points that lie above my line, especially w (V) and x (W), then accelerate gum formation more than oxygen absorption. The metals that cause the fastest oxidations (b, c, d) give relatively less gum formation than the metals that fit the straight part of the line. Chromium (a), which causes the fastest oxidation, does not appear in Figure 1 because no gum data are available.

I conclude that the effects of metal surfaces on rates of oxygen absorption and gum formation are not now a promising field for investigation. Even with 300 cm^2 of surface per L of fuel, the effects of the metals and alloys tested are small to moderate and the effects in larger containers would be less. My own data suggest that differences among fuels are greater than the differences among effects of metals. Although W and V are outstanding gum formers in Figure 1, gum is formed no faster than on several other metals, but the rate of oxygen absorption is so small. Further, they are unlikely to appear in fuel systems. Use of the proper stabilizers (e.g., BHT, Ionol) will probably essentially eleiminate the effects of metals on the homogeneous reactions.

IMPLICATIONS FOR FURTHER WORK

The missing effect of a chromium surface on gum formation should be checked to see if it is interesting.

The results cited here were obtained with a stable jet fuel. A few results might be checked with a stable U. S. fuel (diesel and/or jet) to see if results are analogous, and then a few experiments might also be done with an unstable fuel. A few oxidation and gum experiments might be done with dissolved metals. The effects of the soluble metals might be larger but the pattern should be the same, assuming that both dissolved metals and surfaces mostly affect peroxide decomposition and free radical production.

Metals seem to be necessary to convert soluble gums to hard deposits. The effects of dissolved metals and surfaces on this reaction should be checked. This field could be the most important remaining problem in fuel stability.

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