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Lead Corrosion and Oil Oxidation

THE reaction between metallic lead and hydrocarbon peroxides has been extensively studied[1-5] but always from the standpoint of what happens to the lead. Little attention has been given to the way this reaction can alter the subsequent oxidation reactions of the hydrocarbons. We show that when lead is corroded by the oxidizing hydrocarbon, the oxidation chain reaction is stopped as effectively as if a classical oxidation inhibitor was present. In this respect, lead seems to be unique among metals. Other metals such as copper, iron or aluminium tend to catalyse the oxidation reaction; lead inhibits it.

This reaction is not interesting only because of its unique character chemically, but also because it has a very practical application in the behaviour of motor oils. Copper–lead bearings are used in many engines, and their corrosion can be a limiting factor if the motor oil is not properly inhibited. Several engine test procedures have been set up to measure this property (for example, CRC L-4 and L-38, Petter W-1). Again, there has been little interest in what happens to the oil in these tests, but only in what happens to the lead.

The reaction is complicated by the fact that lead surfaces tend to be rapidly passivated. Static oxidation tests using strips of lead or pieces of copper–lead bearings do not reproduce the rubbing conditions of the engine. As a result none of these tests has gained any wide acceptance as a screening test for the engine.

Wilson[5] partially solved this problem by brushing the lead strips at intervals of 15 min in order to remove the passivated layer. We now report a further improvement, which consists of running the test under conditions of cavitation erosion. This erosion action provides a metal surface that is continuously clean.

Table 1 Oxidation Results in Cavitation Conditions (Iron Tips)

Ball	Oxidized products, %	Acids, %	Colour
Fe	3.2	0.47	Dark brown
Al	2.7	0.34	Brown
Cu	2.4	0.34	Brown
Pb	2.2	0.20	Yellow
Fe*	1.5*	0.30*	Dark brown*

* No cavitation.

The apparatus is the same as that used by Tao[6] to study cavitation in liquids. A 20 kHz ultrasonic horn is vibrated close to a metal ball immersed in an oil. In our tests the horn was AISI 304, the balls were variously high purity Al, Cu, SAE 52100 steel, and Pb. The oil was a refined paraffinic mineral oil into which air was bubbled at a rate of 2.7 l./h; the temperature was 140° C. After 7 h of reaction the oil was analysed for total oxidized products using a Florisil column, and for organic acids using an ion-exchange resin. In the presence of lead, oil degradation is much less than for the other metals (Table 1). This is especially obvious in the visual appearance, lead giving a transparent yellow oil, whereas with the other metals (or even in the absence of metals) the oil is an opaque brown. Similar results were obtained when the horn was made from other metals, for example, aluminium.

In a parallel set of experiments, the oil was analysed for peroxide content and soluble metals. As expected, the oil oxidized over lead showed only half the peroxide content and contained appreciable amounts of soluble lead in the form of basic lead soaps.

These results are exactly matched by actual engine runs, using the old CRC L-4 procedure which requires inspection of the engine for sludge and carbon deposits and inspection of the oil for oil-insoluble matter (Table 2). Two separate tests were run on each oil, first with the standard Cu–Pb bearings and then with non-corroding Babbitt bearings. With Cu–Pb bearings, the weight loss due to corrosion was often very high, but the engine was relatively clean and the oil was not seriously degraded. With Babbitt bearings there was no corrosion of bearing metal, but engine deposits were heavy and the oil had a large amount of oxidized products.

Table 2 CRC L-4 Engine Test Data

Oil	Bearing metal	Engine sludge demerit*	Used oil acidity mg KOH/g	Bearing weight loss, g
SAE 10	Cu–Pb	0.1	8.5	8.91
SAE 10	Babbitt	3.3	15.2	0.0
SAE 20	Cu–Pb	0.4	3.6	3.10
SAE 20	Babbitt	4.3	7.4	0.0

* 0=clean; 10=maximum deposits.

Other deposits in the engine, such as ring-zone carbon and piston-skirt lacquer, paralleled the sludge deposits: other used-oil properties, such as viscosity increase and insoluble matter, paralleled the acidity.

It is obvious that the lead, in being corroded, has altered the course of the oxidation reactions. Probably the peroxides, which are the chain carriers of reaction, have reacted with the lead and have thus destroyed themselves. The lead has thus acted as an oxidation inhibitor in the classical sense.

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Stability of Swivel Wing Supersonic Aircraft

THE model[1,2] presented by R. T. Jones for a swivel wing supersonic transport does not reveal the inherent stability of trim when the wing is rotated. This stability may very simply be demonstrated by a paper model (Fig. 1). A straight strip of paper is taken and trim tabs are cut as shown. For the subsonic flight condition, wing tip fins are bent up at right angles to the span and the nose weight, a wooden match split halfway along its length, is set parallel to the fins. To convert to the supersonic swivel winged condition, new fins are bent at 45° to the span and the match is moved to a new position parallel