DISCUSSION

D. Godfrey[1]

The authors have found that mineral oil forms an Fe_3O_4 film on steel and the surfaces becomes smoother during run-in. Their work supports earlier research and emphasizes the role of oxygen in boundary lubrication. I will comment on some of their techniques, point out some old papers that came to the same conclusion and discuss the important role of dissolved oxygen.

Techniques

Describing a mineral oil by viscosity only is inadequate characterization in boundary lubrication studies. The paraffinic, naphthenic, sulfur, oxygen and nitrogen content would be helpful. It was a mistake to compare a mineral oil and a synthetic engine oil probably containing zinc dialkyldithiophosphate. Anti-wear compounds should have been added to the mineral oil, or a mineral oil based engine oil used for a better comparison. The identification of Fe_3O_4 described reference [10] was, in my opinion, weak. The use of X-ray or electron diffraction would have been positive.

The cycling of the friction traces is probably an apparatus problem. At one time the Chevron Research Company pin-on-disk tribometer developed similar friction cycling. We found that a journal bearing was rubbing the disk support shaft on one side due to misalignment and vibrating the disk once per revolution [16]. Vibration would also increase contact resistance by momentary separation of surfaces.

The reduction of contact resistance with continued sliding shown in Fig. 3 was surprising. One would expect a run-in surface to induce thicker elasto hydrodynamic lubrication films and thus increase contact resistance.

Profiles

The microscopic conformity of the roughness of sliding surfaces, shown in Fig. 6 has been observed on cam and cam followers in automotive engines.

Older Literature

Many tribologists in the 1940's reported on the importance of oxygen and Fe_3O_4 on lubrication. Most pertinent were Teeter [17], Simard, Russell and Nelson [18], Webb [19], Finch [20], Powell [21], Larsen and Perry and Davis [23] who, for example, wrote that wear rate was reduced by the accumulation of finely divided iron oxide particles on rubbing steel surfaces.

My first recognition of Fe_3O_4 on worn, unfailed, lubricated surfaces was in 1948 at NACA [24] where the dark film on steel was found to consist of a mixture of Fe_3O_4, α iron and iron carbide, identified by X-ray diffraction. The Fe_3O_4 was shown to facilitate break-in. About the same time we at NACA found a preformed Fe_3O_4 film to be better than a preformed αFe_2O_3 film [25]. In 1962 I reported on finding Fe_3O_4 by electron diffraction in the film on most unfailed lubricated specimens and discussed its importance [26]. Also, in a tribometer the dark debris in the oil around the rider nose was identified as Fe_3O_4 approximately 100A in size.

Importance of Dissolved Oxygen

The role of oxygen in boundary lubrication has been of primary interest in my career. It has not been studied enough in oil lubricated systems, possibly because it is ubiquitous. Dissolved oxygen in the oil is the anti-wear agent. Ordinary mineral oil contains a surprisingly large amount of dissolved air, about 10 percent by volume, and water, sufficient to maintain the protective oxide film. In 1963 I used deaerated medicinal white oil to lubricate a pin-on-disk apparatus under nitrogen. Scuffing occurred instantly at low loads. When air was admitted to the bell jar covering the apparatus, mild wear occurred. Oil deaeration (in a rotary evaporator) is a very powerful technique to reveal the role of oxygen and oxides in lubrication. Also, the small amount (averaging 0.5 percent by wt.) of sulfur in mineral oil is surprisingly active and forms mixed oxide-sulfide films which are better than either alone [26].

The authors comments on these points would be appreciated.

Additional References

16 Godfrey, Douglas, "Vibration Reduces Metal to Metal Contact and Causes an Apparent Reduction in Friction," *ASLE Trans.*, Vol. 10, 1967, pp. 183–192.

17 Teeter, M. O., "Load Carrying Capacity Phenomena of Bearing Surfaces," *SAE J.*, Vol. 47, 1940, pp. 497–502.

18 Simard, G. L., Russell, H. W., and Nelson, H. R., "Extreme Pressure Lubricants – Film Forming Action of Lead Naphenate and Free Sulfur," *Ind. Eng. Chem.*, Vol. 33, 1941, pp. 1352–1359.

19 Webb, W. A., "The Influence of Iron Oxide on Wear of Rubbing Surfaces," *Science*, Vol. 99, 2575, 1944, pp. 369–371.

20 Finch, G. I., "The Structure of Sliding Surfaces," *Engr.*, Vol. 159, No. 4, 1945, p. 131.

21 Powell, A. S., "Reactions with Steel of Compounds Containing Chemical Groups Used in Lubricant Additives," NACA TN 1207, 1947.

22 Larsen, R. C., and Perry, G. L., "Chemical Aspects of Wear and Friction," *Mechanical Wear*, ASM, 1950.

23 Davis, C. B., "Influence of Roughness and Oxidation on Wear of Lubricated Sliding Metal Surfaces," *Ann. N. Y. Acad. Sci.*, Vol. 53, No. 4, 1951, p. 919.

24 Good, J. N., and Godfrey, D., "Changes Found on Reciprocated Steel, Chromium Plate, And Cast Iron Surfaces," *ASTM Proceedings*, Vol. 48, 1948, pp. 841–853, or NACA TN 1432.

25 Johnson, R. L., Godfrey, D., and Bisson, E. E., "Friction of Solid Films on Steel At High Sliding Velocities," NACA TN 1578, 1948.

26 Godfrey, Douglas, "Chemical Changes on Steel Surfaces During Extreme Pressure Lubrication," *ASLE Trans.*, Vol. 5, 1962, pp. 57–66.

[1] Wear Analysis, San Rafael, Calif.

Authors' Closure

We are not able to answer all of the questions raised by the esteemed discusser, probably because we have a very different approach to tribology problems than he does. He quotes work in which the major thrust was to make a phenomological connection between the presence of selected elements and compounds in liquid carriers and the function of that liquid in some mechanical apparatus. He and his contemporaries have made many advances in tribology in this manner, and they did some fine detective work on the way.

However, they "left a few stones unturned." For example, whereas preformed Fe_3O_4 is less offensive than is Fe_2O_3 on a lubricated surface, the Fe_3O_4 formed by sliding in "mineral oil" exhibits a lower coefficient of friction *when dry* ($\mu \approx 0.12$) than do otherwise preformed Fe_3O_4 ($\mu \approx 0.25$) and Fe_2O_3 ($\mu \approx 0.6$). This difference was asserted to be very influential in the prevention of scuffing.

In defense of the identification of Fe_3O_4 films in earlier work (10), it was found that the film was too absorbing to obtain results from either Raman or infra-red spectroscopy, and too thin to give satisfactory results by x-ray diffraction. Dr. S.

K. Rhee of Allied-Signal and Dr. W. France of General Motors independently provided the identity of films of Fe_3O_4 and Fe_2O_3, by Auger spectroscopy using spectroscopic pure oxide for comparison. X-ray diffraction of debris showed no metal and no other crystalline material than Fe_3O_4.

Further, it has often been mentioned that rubbing pairs such as cams and non-rotating followers wear conforming grooves into each other. We found no definitive statement in the technical literature on the mechanism by which this occurs. It is usually difficult to prove that the system is free of abrasive species which will scratch grooves in the sliding surfaces. The coincident presence of Fe_3O_4 had been noted in some papers but its exclusive role in *developing* the conformity has, to our knowledge, not been reported previously.

The discusser should note that the reduction in contact resistance in Fig. 6 is due to the step loading sequence. Finally, we regret having to deny our discusser the delight of attributing the "anomolous" results in Fig. 9 to something as simple as a defect in the test machine!