

## DISCUSSION

### F. B. Peterson<sup>4</sup>

The authors have performed an interesting piece of work. However, there are several aspects that possibly should be considered in greater detail. In Fig. 12, an experimental current density is compared with that predicted from the theory developed in the text. This theory was based on a perfectly smooth wall assumption and on a knowledge of the velocity distribution near the wall. The experimental values were determined by considering the amount of material removed by corrosion in a 28 1/2 hour period. Since the authors showed that the boundary layer thickness was as little as 1/6 of the corrosion pit depth, the assumption of a smooth wall does not seem valid. If the comparison is to be made, the boundary layer thickness should be substantially greater than the corrosion pit depth. It was stated that the actual current measured with the ring disk electrode system was 5 microamperes. In view of the above comments, it would appear that this measured current should vary with time.

If in fact the experiment was time-dependent, a knowledge of the variation in fluid electrical conductivity and dielectric constant would be useful. To what extent did these properties change as corrosion progressed?

### M. S. Plesset<sup>5</sup>

The authors have proposed the possibility that significant wear can be produced by the current generated by the liquid flow. It is, of course, known that such currents are produced under suitable conditions, and the authors have apparently made observations of it with a particular liquid—Skydrol. Questions remain regarding the validity of their suggestion regarding wear production by such currents.

The  $\zeta$ -potential and the currents measured in this report seem rather high and naturally suggest that inadequate precautions were taken to eliminate corrosive contaminants. Also, it is most regrettable that similar observations have not been made by the authors with other liquids including those with values of dielectric constant,  $\epsilon$ , as high as the value quoted for Skydrol, as well as for values of  $\epsilon$  in the lower range characteristic of petroleum-based liquids.

In view of the limited nature of the study reported, it would appear reasonable to adopt a reserved attitude toward the authors conclusion that the electrokinetic current is the source of the observed wear. This conclusion does not appear to be established.

### Authors' Closure

Subsequent to submission of the manuscript it was realized that the Klinkenberg apparatus did not give an accurate value for the  $\zeta$  potential for moderate conductivity fluids such as phosphate esters (see footnote 3). The charges carried with the flowing stream out of the exit nozzle are in part conducted back to the nozzle. A new streaming current measuring device illustrated in Fig. 14 was therefore designed to obtain a more accurate value of the  $\zeta$  potential [8]. In essence a high velocity stream of fluid flows past a narrow insulating gap and the current carried across the gap is measured. Even with this device, there is some back conduction across the gap and experiments were

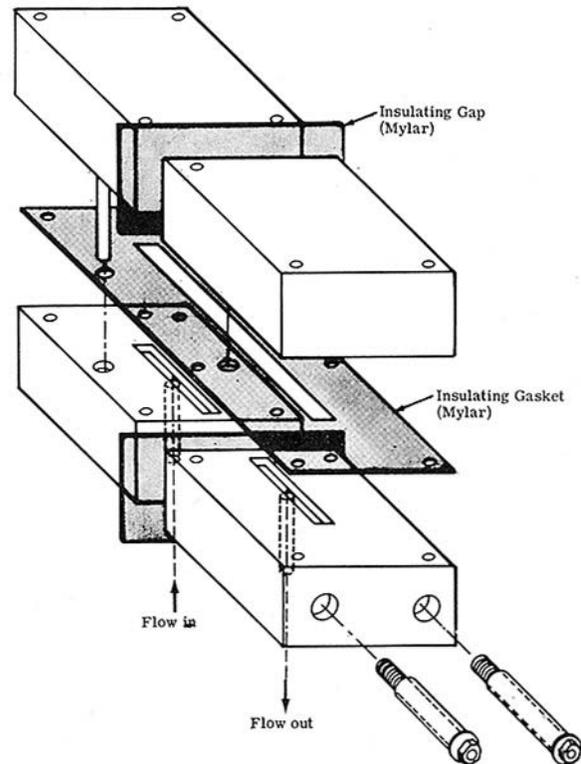


Fig. 14 Apparatus to measure streaming current for moderate conductivity fluids

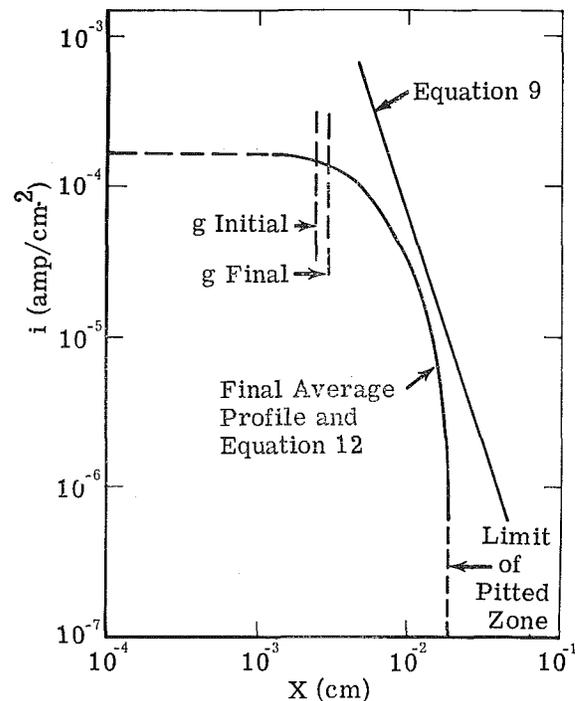


Fig. 15 Comparison of measured corrosion current density and equation (9) for  $\zeta = 0.2$  volts

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**Table 4 Comparison of three fluids**

Type of fluid	Electrical conductivity	Dielectric constant	$\zeta$	$I_w$ at 2000 psi
Phosphate Ester	$10^{-7}$ mho/cm	8	200 mV	$1.0\mu A$
Humble WSX-7597	$10^{-11}$ mho/cm	2.4	< 8 mV	$0.002\mu A$
MIL-H-5606	$<10^{-13}$ mho/cm	2	33 mV	$<0.001\mu A$

done at several gap widths and the results extrapolated back to zero gap width. This instrument gave a new value of 0.2 volts for the  $\zeta$  potential for phosphate ester against steel. Inserting this new value of  $\zeta$  potential in equation (9) increases the predicted current density at all positions  $x$  above the current density based on the wear profile as shown in Fig. 15. The deviations of the measured profile below theory can be qualitatively accounted for by conduction from the fluid and by other electrochemical reactions, such as those causing the polymer films.

The question of F. B. Peterson on geometry changes due to wear and their effect on the current distribution has not been fully examined. The theory as it stands predicts only the initial current distribution from a smooth surface. Yet, it is probably a good approximation for the worn state. A distinction must be made between wear depth as given in Table 2 and pit size as seen in Fig. 13(b). The total wear, i.e., sum of all pits, produces a gradual undulation of the surface seen in Fig. 11 and has only a small effect on the hydrodynamics. The pit depth is about 0.2 micron, a small depth compared to the boundary layer thickness.

Variations with time as the wear progresses are observed. During the 28½-hour run the flow rate increased by 85 percent. However, the fluid properties do not change significantly with time. During 476 hours of use in an airplane, the dielectric constant remained constant and the fluid conductivity increased by 53 percent. Thus the geometry changes from the wear are by far the most important changes leading to time dependence.

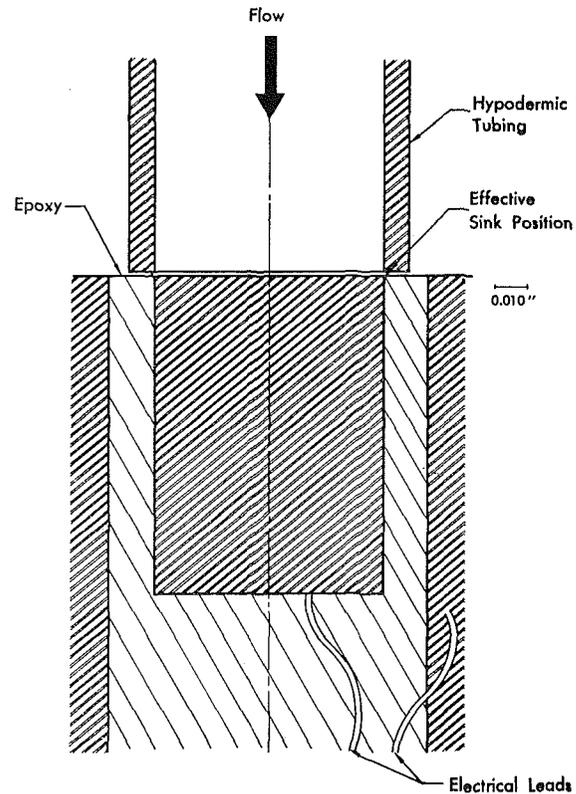
Dr. Plesset is, of course, correct that streaming currents are well known. Electrokinetic streaming currents in low conductivity hydrocarbon systems result in buildup of high voltage and sparks that have resulted in explosions [1]. The magnitude of streaming currents flowing parallel to a surface have been satisfactorily accounted for by electrokinetic theory. It is the wall current that is of concern in the present paper and this occurs normal to the wall in the zone where the streaming current is generated. Previously wall currents have apparently not had any technological importance and have not been studied. It is the wall currents, not streaming currents, that cause the formation of deposits and corrosion.

The value given for the  $\zeta$  potential is not unusually high as values up to 0.2 volts are common for organic liquids against glass.<sup>6</sup> There is no prior standard by which the magnitude of wall current densities may be judged, but the values observed were consistent with the prediction of equation (10). Moreover, the wall current varied with flow rate in the device illustrated in Fig. 16 in a manner that was consistent with equation (10). Fig. 17 shows the relationship between the experimentally measured current and pressure drop across the orifice. The wall current should vary as the ¾ power of the pressure drop because  $Q$  in equation (10) varies as the square root of the pressure drop.

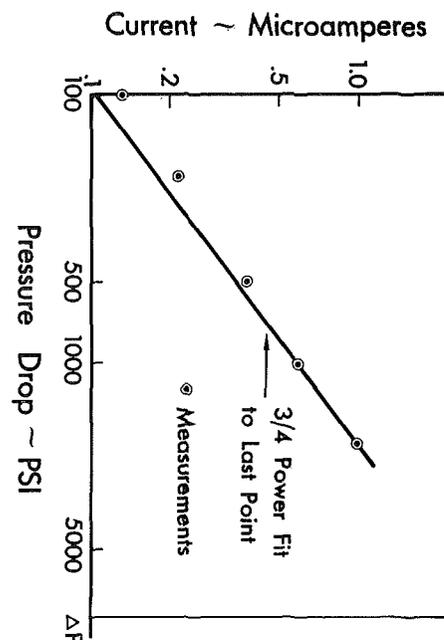
Corrosive contaminants cannot be invoked as causes for the observed currents and wear. The strong variation of current with flow as predicted and observed in Fig. 17 shows that the wall current is not due to corrosion by a contaminant.

Measurements were made for other fluids as indicated in Table 4. The wall currents were measured with the device of Fig. 16 and are consistent with values of electrical conductivity,  $\epsilon$  and  $\zeta$ . No wear was observed in 2½-hour tests with either

<sup>6</sup> Kruyt, H. R., *Colloid Science*, Vol. I, p. 230, Elsevier, New York, 1952.



**Fig. 16 Wall current measurement apparatus**



**Fig. 17 Relation between current and pressure drop in wall current measurement apparatus**

Humble WSX-7597 or the hydrocarbon oil, MIL-H-5606, in the wear test apparatus of Fig. 8.

On the strength of all of the direct and supporting evidence the authors consider that the relationship between the observed wear of steel in contact with high velocity phosphate ester fluids is established. The direct and supporting evidence is reiterated here.

1 Elimination of cavitation by increasing the back pressure had no effect on the wear.

2 Installation of a 1-micron filter did not decrease the wear, thus eliminating erosion as a mechanism.

3 An electrical wall current, larger than required to account for all of the wear by corrosion was measured with a ring disk electrode system.

4 The magnitude of this current was consistent with the theory developed.

5 Pitting corrosion was obtained under anodic conditions in phosphate ester fluids without flow. Corrosion was observed only in the presence of electrical currents either imposed by an external source or generated by flow of the fluid.

6 The sign of the wall current was consistent with the location of the wear.

7 The wear could be eliminated on one part of the orifice by an externally applied electric field of appropriate sign.

8 No wear was observed on an insulating aluminum oxide insert.

9 Good agreement was observed between the theory and the experimental profile of wear and the deviations were accountable.

10 Film deposits were observed in the flow experiment similar to those found in the electrochemical experiment without flow.

11 No measurable wall current or wear was observed with Humble oil or hydrocarbon oil in the wear apparatus.