

### Preferential Adsorption of Long-chain Normal Paraffins on MoS<sub>2</sub>, WS<sub>2</sub> and Graphite from *n*-Heptane

I REPORTED recently that cast iron<sup>1</sup> and graphite<sup>2</sup> adsorb preferentially long-chain normal paraffins from hydrocarbon solvents such as *n*-heptane or benzene. It was thought that the adsorption is relevant to effective lubrication of sliding surfaces of cast iron and graphite by mineral oils. Adsorbed films of hydrocarbons are most likely to reduce the extent to which the rubbing surfaces come into contact, under a given pressure, which would result in less transfer of solid material across the interface and, therefore, a reduced rate of wear.

It was reported in the literature that films of MoS<sub>2</sub> and WS<sub>2</sub> deposited on steel surfaces reduce their wear rates when lubricated by mineral oils<sup>3</sup>. These two sulphides were examined, therefore, in the flow micro-calorimeter to discover whether they also have the property of preferentially adsorbing long-chain paraffins from low-boiling solvents. The flow calorimeter used has already been described<sup>2</sup>. The solvent in which the adsorption was examined was *n*-heptane purified by percolation through silica gel and alumina. *n*-Heptane percolated through a bed of MoS<sub>2</sub> or WS<sub>2</sub> in the calorimeter cell and  $\mu$ g quantities of dotriacontane were injected into *n*-heptane. Contact between dotriacontane and graphite was accompanied by a heat effect registered by a potentiometric recorder.

MoS<sub>2</sub> and WS<sub>2</sub> used in the experiments were commercially available materials. Examination by X-ray diffraction showed that these disulphides have a high degree of crystallinity, the diffraction patterns corresponding to those of MoS<sub>2</sub> and WS<sub>2</sub>. Some weak unidentified lines were present in the WS<sub>2</sub> pattern. The Brumauer-Emmett-Teller surface areas of the disulphides were 8.3 and 2.2 m<sup>2</sup>/g respectively. The amount of the disulphides placed in the calorimeter was 0.15 g. Results of the preferential adsorption experiments are illustrated in Figs. 1 and 2.

It can be seen that as the amount of *n*-C<sub>32</sub> that comes into contact with the disulphides increases from 2 to 40  $\mu$ g the heat effects increase. This increase is approximately linear for WS<sub>2</sub>. For MoS<sub>2</sub> the heat effects per unit weight of solute decrease with the amount injected. Thus, although for 2- $\mu$ g quantities of *n*-C<sub>32</sub> the heat effects are very similar for both MoS<sub>2</sub> and WS<sub>2</sub>, the heat effects produced when 40  $\mu$ g of *n*-C<sub>32</sub> come into contact with the disulphides are higher for WS<sub>2</sub> than they are for MoS<sub>2</sub>. These results are obtained in spite of the fact that the surface area of MoS<sub>2</sub> is four times that of WS<sub>2</sub>. Thus in the calorimeter cell the total Brumauer-Emmett-Teller area available for the adsorption of *n*-C<sub>32</sub> is 1.25 m<sup>2</sup> for MoS<sub>2</sub> and 0.32 m<sup>2</sup> for WS<sub>2</sub>. (If all this area was available for adsorption and the adsorbed molecules lay flat on the surface, a monolayer would be formed by 75  $\mu$ g of dotriacontane on WS<sub>2</sub>.)

In separate experiments it was established that up to 40  $\mu$ g of dotriacontane was adsorbed almost completely on 0.15 g of both disulphides when injected into *n*-heptane percolating through the solids. This made it possible to estimate heats of adsorption of dotriacontane on the disulphides from *n*-heptane. The results are given in Table 1. It can be seen that the heats of adsorption on MoS<sub>2</sub> are somewhat lower than those on WS<sub>2</sub>. The difference is, however, small in comparison with that

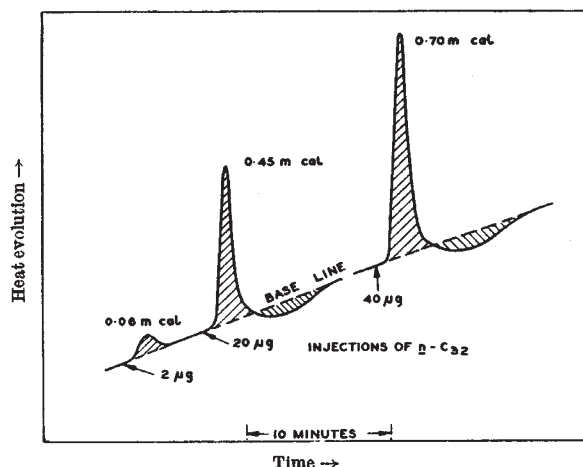


Fig. 1. Adsorption of *n*-C<sub>32</sub> on MoS<sub>2</sub>.

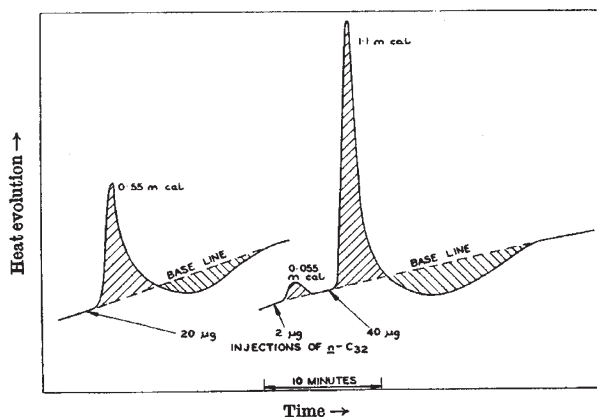


Fig. 2. Adsorption of *n*-C<sub>32</sub> on WS<sub>2</sub>.

between the heat adsorption on graphite and WS<sub>2</sub> or MoS<sub>2</sub>, the latter heats being about one-third of the heat of adsorption on graphite. This indicates that dotriacontane adheres to graphite surfaces more strongly than it does to the surfaces of the disulphides.

In view of the observed specific adsorption properties of graphite, MoS<sub>2</sub> and WS<sub>2</sub> and, also, the fact that these solids are reported to increase the load-carrying capacity of metal surfaces on which they are deposited, it is possible that the relatively strong tendency of long-chain hydrocarbons to adhere to the surfaces of these layered solids is an essential factor in increasing their load-carrying capacity.

It was shown by various investigations<sup>4</sup> that adsorption of long-chain compounds on metal surfaces in sliding contact decreases their wear and friction. This leads me to postulate that the value of graphite, MoS<sub>2</sub> and WS<sub>2</sub> in their performance as solid lubricants depends in part on their property of adsorbing tenaciously compounds with long normal hydrocarbon chains, which are usually present in mineral oils. The adsorbed hydrocarbons may be expected to reduce the frequency of solid-to-solid contact, in much the same way as the adsorption of stearic acid reduces the contacts of steel surfaces on which it is adsorbed.

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Table 1. HEAT OF ADSORPTION OF *N*-DOTRIACONTANE FROM *N*-HEPTANE ON SOME SOLID LUBRICANTS

Solute adsorbed ( $\mu$ g)	Heat of adsorption (kcal/mol)		
	Graphite	MoS <sub>2</sub>	WS <sub>2</sub>
2	50	12.3	12.3
10	36	10.0	12.0
20	34	10.1	12.4
40	—	7.9	12.3

<sup>1</sup> Groszek, A. J., *Nature*, **196**, 531 (1962).

<sup>2</sup> Groszek, A. J., Paper presented at a meeting of the Surface Activity Group, Soc. Chem. Indust. (March 9, 1964).

<sup>3</sup> Middleton, K., Second Lubrication and Wear Convention, Inst. Mech. Eng., Eastbourne (May 28-30, 1964).

<sup>4</sup> Bowden, F. P., and Tabor, D., *The Friction and Lubrication of Solids* (Oxf. Univ. Press, 1950).