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Letter

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Sir:

In Volume 1, January 1969, of *The Journal of Adhesion*, I noticed in the discussion on Page 47 (H. Schonhorn and F. W. Ryan: "Adhesion of Polytetrafluoroethylene") the following speculation:

"This change in wettability is thought to arise from an increase in the surface density of the PTFE."

Yet, a few lines earlier, (Page 46), the authors state:

"The critical surface tension of wetting is about 40 dynes/cm for the treated surface, more than twice the value of the untreated polymer."

This last observation is mechanically incompatible with the first statement. Any densification is caused by compressive stress, and such compressive stress is opposed to any pre-existing tensile stress like surface tension. In this situation, Newton's third law applies, and if we find increased tensile stress in the surface (the observation), we cannot explain this by an assumption based on a compression in the same plane.

A forthright explanation of the observed facts follows from Langmuir's theory of molecular orientation in the surface of a homogeneous liquid [1].

A classical demonstration of this theory is a thick layer of molten stearic acid being solidified on a water-wet surface. The free surface of the now solidified stearic acid is formed of the lowest energy groups in the molecule, the methyl end-groups, facing the low energy gas phase. This surface shows high contact angles with non-solvent liquids having surface tensions larger than about 25 dynes/cm.

The surface of the stearic acid which was formed in contact with high energy water contains the high energy carboxyl-groups, and will show low or zero contact angles with the same liquids which showed high contact angles on the upper surface.

In the case of molten PTFE, the trifluoromethylene end-groups will cause the low critical surface tension, whereas higher energy difluoromethylene chain groups (and maybe polar impurities) will diffuse in the molten state toward the high energy gold surface; after the gold is dissolved, a relatively high energy surface is left as shown in the experiments in the paper under discussion.

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[1] Irving Langmuir: "The Constitution of Liquids with Especial Reference to Surface Tension Phenomena." *Metallurg. and Chem. Engng.*, Vol. 15 (1916), pp. 468-470.