

much larger than the area obtained at the maximum adsorption on silica. This appears to indicate that linoleic acid monolayers are neither a closely packed array of fatty acid molecules, as in the case of the air-water interface, nor lying flat on the silica surface (2).

It should be pointed out, however, that for most adsorbents the values obtained for surface area are dependent on the cross-sectional area of the molecules used for monolayer coverage. This is due to the fact that small yardsticks, e.g. nitrogen, can follow many more of the fine details of an irregular surface than larger molecules, e.g. stearic acid, and consequently give relatively large surface area values (12, 13). Avnir and Pfeifer (14) reported a fractal dimension of 2.94 for silicic acid, reflecting the labyrinthine nature of this adsorbent, and concluded that molecules adsorbed on silicic acid may thus experience a nearest-neighbor geometry that resembles that of a three dimensional, rather than a planar array of the adsorbate. It can be seen that the surface available for monolayer binding of stearic or linoleic acid molecules on silica may be far less than indicated from measurements made with nitrogen as a probe molecule (BET).

The reflection points observed in the Scatchard plots of some substrates suggest that two different binding constants may be involved for one substrate. From IR studies, it has been shown that, at low surface coverage, adsorption of acid monomer onto pairs of adjacent silanol groups occurs. As the concentration of acid in solution increases, adsorption of monomer onto isolated surface silanol groups becomes predominant. Therefore, it is possible that there are two different forms of binding between substrate and silica. Either the same substrate binds at different sites, e.g. paired silanol groups and isolated silanol groups, or different forms of substrate bind to the same site with different

binding strengths, e.g. monomer at low concentration and dimer at high concentration as described previously for alcohol.

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☼ Sunflower Oil Diesel Fuel: Engine Wear Implications

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ABSTRACT

Diesel lubricating oil contaminated with sunflower oil fuel was degraded under conditions simulating an engine crankcase environment for metal wear testing. Wear analyses were performed using a four-ball apparatus according to ASTM D 4172. Lubricity of oils was characterized by ball scar dimensions. Contaminated lubricating oils exhibited lower metal wear indexes than pure lube oil control samples, even when the former were severely degraded as measured by thickening and loss of alkaline reserve.

INTRODUCTION

Seed oils such as sunflower ultimately may prove acceptable as substitute diesel fuels in emergency situations. However, a variety of problems including unburned fuel contamination of engine lubricating oil must be solved first. Unsaturated seed oils undergo addition polymerization and acid-forming oxidation reactions at conditions present in a diesel crankcase environment (1), leading to thickening and a loss of alkaline reserve in lubrication oil.

In an earlier paper (2), we reported the polymerization thickening and loss of alkalinity of SAE 30 diesel lubricating oil contaminated with 5.0% sunflower oil when the mixture was exposed to simulated engine conditions; cf. (2) for a

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complete description of experimental apparatus and procedures. Sample mixtures were treated for up to 70 hr at 150 C in an immersion bath heater. Oxygen was percolated vigorously through test cells of contaminated oil in the presence of metallic copper catalyst. Viscosity rise and alkalinity loss responses are shown in Figure 1. Viscosities given were determined at 40 C; alkalinity as expressed is a total base number (TBN) according to ASTM D 2896 (3).

The thickening and alkalinity losses shown in Figure 1 pose definite lubricant distribution and possible corrosion problems for a diesel engine in extended operation on sunflower oil fuel. After only 30 hr exposure to a simulated crankcase environment, viscosity is increasing sharply and alkaline reserve is largely exhausted. An additional problem of progressive decline in lubricity for degraded oil mixtures has also been widely speculated, but reliable in-engine testing of the wear preventive characteristics of contaminated lubrication oil is costly and difficult (4).

RESULTS AND DISCUSSION

Oil mixtures degraded as shown in Figure 1 were tested for lubricity according to ASTM D 4172, "Wear Preventative Characteristics of Lubricating Fluid (Four-Ball Method)."

SUNFLOWER OIL DIESEL FUEL

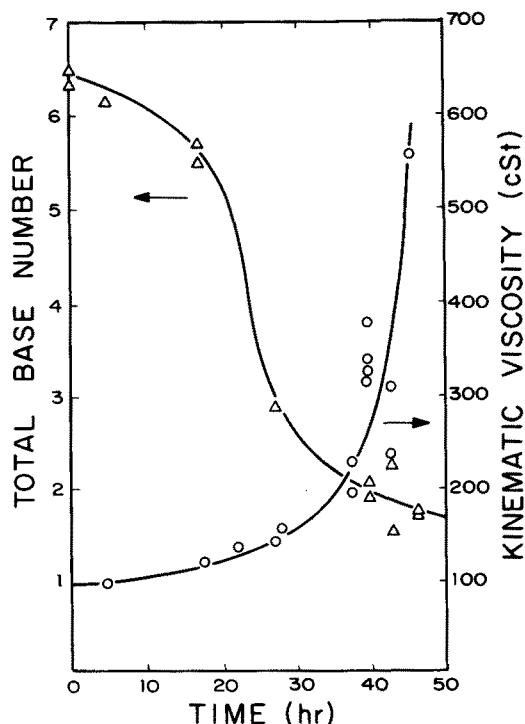


FIG. 1. Oil mixture viscosity and alkalinity vs. time of exposure to simulated engine conditions.

Mixtures were 5.0% refined sunflower oil (Agricom) having an IV of 138 in API CD SAE 30 (Amoco MIL-L-2104C) diesel lube oil. In the four-ball method, three 12.7 mm stainless steel balls are clamped together and immersed in the oil sample at 70 C. A fourth ball having the same diameter is rotated at 1200 rpm against the stationary balls (3-point contact) for one hr under a load of 392 N. At the conclusion of the test, scars on the stationary balls are measured both across and in parallel with the wear striations and then averaged to yield the test result in millimeters.

Lubricity value vs. exposure to simulated engine conditions is presented in Figure 2. The lower curve represents the 5.0% sunflower-lube oil mixture while the upper curve is a pure lube oil control exposed to identical conditions. Spot testing on the control sample showed that viscosity rise and TBN loss were each less than 20% at 50 hr exposure.

Results given in Figure 2 indicate that progressive loss of crankcase oil lubricity is not a serious problem for the use of sunflower oil as a diesel fuel, exclusive of the distribution

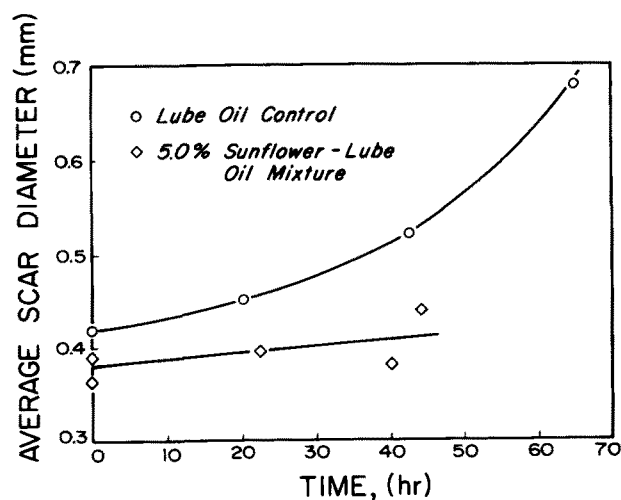


FIG. 2. ASTM D 4172 average scar dimension vs. time of exposure to simulated engine conditions.

issue. Even severely thickened and acidified sunflower-lube oil mixtures yield ASTM D 4172 wear values comparable to pure, unexposed lube oil. Interestingly, the lubricity of the pure lube oil control deteriorates more rapidly than the contaminated mixtures. A repeatability range of 0.12 mm average scar dimension is cited in ASTM D 4172. Duplicate testing of the original sunflower-lube oil mixture with no exposure gave a difference of only 0.03 mm as shown.

Improved crankcase oil lubricity with plant oil contamination is not altogether unexpected. It has been proposed (5) that the polar triglycerides adsorb as a monolayer on metal surfaces yielding reduced metal-to-metal friction. This phenomenon apparently continues as the sunflower oil polymerizes and acidifies over 45 hr of exposure to conditions simulating an engine crankcase.

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