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PHOTOASSISTED OXIDATION OF OIL FILMS ON WATER

Progress Report

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PROJECT OUTLINE AND OBJECTIVES:

The objective of the project is to develop a method for the solar assisted oxidation of oil slicks. A semiconducting photocatalyst, titanium dioxide, is used. Upon absorbing a photon, an electron-hole pair is generated in the TiO_2 microcrystal. The electron reacts with surface-adsorbed oxygen, reducing it to hydrogen peroxide; the hole directly oxidizes adsorbed organic compounds. Titanium dioxide is denser than either oil or seawater; the density of its anatase phase is 3.8 and that of its rutile phase is 4.3. In order to keep the titanium dioxide at the air/oil interface, it is attached to a low density, floating material. The particles of the latter are sufficiently small to make the system economical. Specifically, the photocatalyst particles are attached to inexpensive hollow glass microbeads of about 100μm diameter. Those areas of the microbeads that are not covered by photocatalyst are made oleophilic, so that the microbeads will follow the oil slick and not migrate to either the air/water or the water/oil interface.

To enhance cost effectiveness, each microbead harvests light from an area substantially exceeding the area of its cross section. Light concentration in the microbeads derives from the oil films' index of refraction of 1.50 exceeding those that of seawater (1.34) and air (1.00). The oil film thus acts as a lightguide; unless lost to absorption, internally generated photons propagate in the film through multiple total internal reflection. In order to achieve such propagation, it is necessary, however, to generate the photons in the film, i.e. it is of essence either to have sunlight scattering particles or bubbles in the film, or use the films' normal fluorescent constituents.

PROGRESS:

Methods for quantitatively assaying the photoactivity of TiO_2 particles in the oxidation of model organic compounds were developed. In a survey of TiO_2 samples from the U.S., the Federal Republic of Germany and Japan, made by 11 manufacturers, it was found that two of the German manufacturers supply particularly efficient photocatalysts. Their samples, of particle sizes as small as 30nm and as large as 1800nm, have alcohol-photooxidation quantum efficiencies of ~60%. The price of the TiO_2 is about 80¢/lb.

Hollow glass microbeads of varying chemical composition have been obtained from PQ Corporation in Conshohocken, Pennsylvania. Their densities are of .2 to .7 and their cost is of about 50 ¢/lb.

Three methods of attaching TiO_2 to glass microbeads have been explored. In the first, a sol-gel is generated on the surface of the microbead by controlled hydrolysis of a silicon tri- or tetraalkoxide. The crystallites are bound to the nascent silicon oxide during the hydrolytic process. In the second process, the microbeads are suspended in a fluidized bed reactor in a stream of humidified titanium tetrachloride with an inert carrier gas. At a controlled pressure of water vapor and of $TiCl_4$, TiO_2 crystals grow on the beads at 400-600°C. In the third process, microbeads are partially coated with an electrostatically adhering layer of TiO_2 particles, then brought to a temperature where the particles are bound to their surface. The yield of the coated particles is highest when the particles are made by the third method, as extensive fracturing occurs in the first two processes. It was found that high sodium or high alkaline earth glasses lose with time their TiO_2 particles because of slow dissolution, resulting in undercutting. In contrast, the higher melting and stronger aluminosilicate glasses retain the bound particles.

The glass microbeads have been successfully coated with oleophilic films using octadecylsilane. The coated microbeads follow, as expected, oil films on water.

Lightguiding, i.e. the propagation of light in oil films on the surface of water through multiple total internal reflection has been confirmed experimentally, (see Fig. 1) as has the concentration of light in the floating glass microbeads.

will be optimized to maximize the quantum efficiency of photooxidation of oil.

2. Acceleration of electron transfer to molecular oxygen.

Calculations show that at high solar concentration by lightguiding to the particles (over 100), the rate of electron transfer will not keep up with either the rate of diffusion of oxygen to the particles or with the rate of hole transfer to the adsorbed oil. Anticipating such a problem, we shall develop catalysts for the acceleration of electron transfer to oxygen and methods for depositing such catalysts on the TiO_2 particles.

3. Coupling of Sunlight into the Oil Films:

The mathematical physics of coupling sunlight into oil films through light scattering solid particles that are commonly found in the crude oil slicks will be developed. Specifically, the dependence of sunlight coupling on the shape and amplitude of the waves in the sea and on the angle of incidence of sunlight will be calculated for scattering particles and air bubbles of different size.

4. Analysis of Photooxidation Products:

The analysis of photooxidation products, first of model aliphatic hydrocarbons, then of aromatic hydrocarbons, and finally of heavy crude oil, will be undertaken. The purpose of this study will be to determine whether the photoassisted oxidation process results in chemicals that are potentially toxic.

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