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PHOTOASSISTED OXIDATION OF OIL FILMS ON WATER

FINAL PERFORMANCE REPORT

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Introduction:

The objective of the project has been the development of a technology for cleaning up oil spills on water through their photocatalytic oxidation. The photocatalyst used was titanium dioxide. Nanocrystalline TiO_2 , of anatase or anatase/rutile phase, was bound to hollow ceramic microspheres of sufficiently low density to be buoyant on water. In the presence of these, under sunlight, oil films were photocatalytically oxidized by dissolved oxygen.

Materials:

The preparation of the titanium dioxide hollow glass microspheres is described in the enclosed publication "Attachment of TiO_2 Powders to Hollow Glass Microbeads: Activity of the TiO_2 -Coated Beads in the Photoassisted Oxidation of Ethanol to Acetaldehyde", N. B. Jackson, C. M. Wang, Z. Luo, J. Schwitzgebel, J. G. Ekerdt, J. R. Brock and A. Heller, *J. Electrochem. Soc.* 138, 3660-3664 (1991).

Optics of the photocatalyst-coated hollow glass microspheres:

The enclosed publication "Collection Optics of TiO_2 Photocatalyst on Hollow Glass Microbeads Floating on Oil Slicks", I. Rosenberg, J. R.

Brock and A. Heller, J.Phys.Chem. 96, 3423-3428 (1992), describes the dependence of the collection efficiency of near ultraviolet solar flux by the photocatalyst when attached to hollow glass microbeads floating at the air/oil interface. Controlling parameters are the buoyancy of the microbeads, and thickness and distribution of the TiO_2 particles on the microbead surface. In general microbeads that are deeply immersed in the oil film are less effective in accelerating the oxidation reaction than microbeads that are sufficiently buoyant for half of the bead to be above the air/oil interface. The efficiency of collection increases with TiO_2 coverage until approximately 60-70% of the bead surface is covered with titanium dioxide then levels off. Because the microbeads are spherical, the collection efficiency is independent of the angle of the sun with respect to zenith. However when the sunlight is filtered by a thinner layer of air, i.e. when the sun is closer to zenith, a greater fraction of the near solar ultraviolet photons are transmitted by the atmosphere and reaches the catalyst coatings.

Rate limiting factors:

The rate of photoassisted oxidation of oil spills can be limited, when the near UV flux is low, by irradiance. When oxygen mass transport is inadequate, it is limited by the flux of oxygen to the surface of the microbubbles. When both the near UV irradiance and oxygen mass

transport are adequate, the rate depends on the kinetics of the photocatalytic coatings. The kinetics of the coatings can be limited by the rate of depolarization of photogenerated electrons on the titanium dioxide semiconducting particles, i.e. the slow reaction step can be that of stripping of electrons from the TiO₂ particles' surface by oxygen. When this is the case, co-catalysts, such as palladium, enhance the photoassisted oxidation reaction (see enclosed paper on "Palladium Catalysis of O₂ Reduction by Electrons Accumulated on TiO₂ Particles during Photoassisted Oxidation of Organic Compounds", C.-M. Wang, A. Heller and H. Gerischer, *J.Am.Chem.Soc.* *114*, 5230-5234 (1992)).

The transport of oxygen to the semiconductor particle surface can also be rate limiting, particularly when the system is quiescent. (see enclosed papers on "The Role of Oxygen in Photooxidation of Organic Molecules on Semiconductor Particles, H. Gerischer and A. Heller, *J.Phys.Chem.* *95*, 5261-5267 (1991); "Photocatalytic Oxidation of Organic Molecules at TiO₂ Particles by Sunlight in Aerated Water", H. Gerischer and A. Heller, *J.Electrochem.Soc.* *139*, 113-118 (1992)).

It was found that the rate of photoassisted oxidation of oil is oxygen mass transport limited in the absence of agitation at a near UV flux of 46W m⁻², just above the AM1 solar near UV flux at sea level. However, in a well agitated system, i.e. in the presence of "waves", the rate was not oxygen mass transport limited.

Chemistry of Photoassisted Oxidation:

Although it was initially thought that the oxidation products of crude oil will be water soluble oxygenated organic reaction products of the hydrocarbons, it was found that the dominant reaction products were actually carbon dioxide and water, even in the initial phase of the reaction, i.e. when more than 95% of the original oil was still intact. The photoassisted oxidation of n-octane was studied in detail. Other than carbon dioxide and water, the major oil soluble product was a mixture of the three octanone isomers. Traces of other, lower molecular weight, carbonyl compounds were also observed, and the aqueous phase contained traces of low molecular weights carboxylic acids. Photoassisted oxidation of the aromatic components of crude oils produced phenols in amounts that were well below those produced upon the natural weathering of the oil. (see enclosed papers Photoassisted Oxidation of Oil and Organic Spills on Water, A. Heller, M. Nair, L. Davidson, Z. Luo, J. Schwitzgebel, J. Norrell, J. R. Brock, S.-E. Lindquist, and J. G. Ekerdt, Chapter in "Photocatalytic Purification and Treatment of Water and Air", D. F. Ollis and H. Al-Ekabi, Editors, Elsevier Publishers, 139-153 (1993); Accelerated Photooxidative Dissolution of Oil Spills, A. Heller and J. R. Brock, Aquatic and Surface Photochemistry, G. R. Helz, R. G. Zepp, and D. G. Crosby, Editors, 427-436, ACS Symposium Series (1994)).

Actual and Projected Cleanup Rates:

The actual cleanup rates are summarized in the enclosed paper "Rates of Photocatalytic Oxidation of Crude Oil on Salt Water on Buoyant, Cenosphere-Attached Titanium Dioxide, M. Nair, Z. Luo and A. Heller, I&EC Research, 2318-2323 (1993)" for TiO_2 coated cenospheres of 0.7g cm^{-2} density.

The rates did not depend substantially on irradiance in direct sunlight, nor did they depend substantially on the type of oil that was used. It was estimated that with highly buoyant glass microbubbles, completely spread to harvest the maximum solar flux in the presence of waves, and in direct sunlight, one barrel of oil could be cleaned up in one to two weeks by 100 lbs of photocatalyst coated $50\mu\text{m}$ diameter microbubbles of 0.37g cm^{-3} density.

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