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**CATALYTIC AGENT DEGRADATION ON OXIDE
FILMS AND IN MICROHETEROGENEOUS SOLUTION
SYSTEMS**

First Interim Report

by

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Experimental efforts related to Contract no. DAJA45-90-C-0007 entitled "Catalytic Agent Degradation on Oxide Films and in Microheterogeneous Solution Systems" is described in this first technical report (December 8, 1989 - February 8, 1990). Emphasis in the first two months of research has been placed on thermal degradations in aqueous dispersions of colloidal semiconductors (precisely, TiO_2) and on TiO_2 films containing CW simulants and strong oxidants. Catalytic agents were employed to enhance these decompositions. The experiments with dispersions are extensions of preliminary studies in this area.^{1,2} Thin film systems have likewise been examined.

As mentioned earlier¹ thermal decompositions of organophosphorous compounds were not witnessed in the presence of powerful oxidants such as hydrogen peroxide, periodate and bromate alone. Only $\text{K}_2\text{S}_2\text{O}_8$ had a high enough reactivity to allow thermal activated decomposition and enough oxidizing power to push forward these degradations without the adjunction of catalytic agents, e.g. AgNO_3 , although only at sufficiently elevated temperatures. (In presence of an adequate concentration of AgNO_3 the reaction could proceed at ambient temperature.)

Previous experiments likewise demonstrated the feasibility of using alternative redox catalysts such as Fe_2SO_4 , $\text{Co}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$, with only FeSO_4 yielding promising results. The relative success with FeSO_4 lead our experimental endeavors into testing $\text{Fe}_2(\text{SO}_4)_3$ as a possible catalytic agent.

Fe (III) ions catalyze efficiently the total oxidation of simulants by H_2O_2

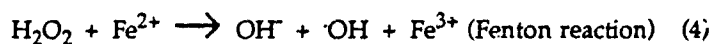
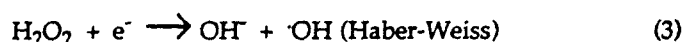
The usage of $\text{Fe}_2(\text{SO}_4)_3$ as a catalyst in these degradation reactions proved to be an important discovery. $\text{Fe}_2(\text{SO}_4)_3$ is a cheap and readily available compound which has no harmful effect on the environment. It was found to greatly accelerate the total oxidation of phosphate ester simulants in aqueous environment even at relatively low concentrations.

The catalytic effect of $\text{Fe}_2(\text{SO}_4)_3$ is demonstrated in Fig. I where the decomposition of 4-NPIPP (4-nitrophenylisopropylphenyl phosphinate) evaluated by CO_2 evolution as a function of catalyst concentration is depicted.

All aqueous dispersions were prepared by the following technique. The appropriate quantity of 10^{-1} M simulant solution (THF solvent) was injected onto the reaction vessels' walls and the solvent evaporated by heating until no traces of solvent were left. Subsequently, the simulant was redissolved in water. In Fig. 1, titanium dioxide (P25, Degussa, 5g/l) was also present. (The role of

As the organophosphate is subsequently oxidized Fe(IV) is regenerated into Fe(III) thus maintaining its catalytic status. Hydrogen peroxide is exhausted as a sacrificial oxidant.

At higher temperatures aqueous solutions of H_2O_2 may be rapidly decomposed into water and oxygen decreasing the prominence of this Fe (IV) reaction pathway and allowing the decomposition to occur via other pathways. Concentrations of $Fe_2(SO_4)_3$ and H_2O_2 and the reaction temperature have to be adjusted in order to optimize the Fe (IV) reaction pathway. The eventuality of a Haber-Weiss type reaction such as is believed to happen in presence of $FeSO_4$ (specifically a Fenton reaction):



with subsequent oxidation of the CW simulant by hydroxyl radicals cannot be discounted if Fe^{3+} is initially reduced by the organic moieties of the organophosphorous compounds. There is not enough energy available at the temperatures studied to allow the formation of hydroxyl radicals by simple thermal dissociation (-1 eV binding energy for H_2O_2), as is possible at elevated temperatures for persulfate.

Titanium dioxide sustains the oxidizing action of hydrogen peroxide by formation of surface peroxides

TiO_2 plays a stabilizing role in these experiments. This effect is shown in Figs. II and III at $70^\circ C$ and at constant concentration of $Fe_2(SO_4)_3$ (i.e. 10^{-3} M) where the decomposition of 4-NPIPP (CO_2 evolution) at various concentrations of H_2O_2 is illustrated. Without TiO_2 present (Fig. II) the lower concentrations of H_2O_2 are much less effective in the decomposition of 4-NPIPP than when TiO_2 is present at 5 gm/l (Fig. III). In TiO_2 containing solutions there is very little difference in degradation efficiency between 0.02 M and 1 M H_2O_2 . The surface of TiO_2 must therefore play a decisive role in sustaining the oxidative action of H_2O_2 . In TiO_2 -free solution the H_2O_2 decomposes by disproportionation into oxygen and water. This competes with the H_2O_2 reaction with agent explaining the incomplete nature of simulant degradation at the lower H_2O_2 concentration. In the presence of TiO_2 the H_2O_2 is bound to the surface forming titanium

peroxo complexes which do not undergo such disproportionation. The important role of TiO_2 which emerges from these studies is that it stabilizes the peroxide while maintaining its high oxidation power.

Preliminary experiments with thin films of TiO_2

The degradation of 4-NPDEP (paraoxon, 4-nitrophenyldiethylphosphate) on TiO_2 fractal electrodes was examined in presence of various catalytic agents. These electrodes had a surface area of 16 cm^2 and were prepared by thermal decomposition of titanium ethoxide $[\text{Ti}(\text{OC}_2\text{H}_5)_4]$ on the surface of Ti sheets (Siber Hegner Rohstoff AG, Zurich, Switzerland ASTM grade 2, thickness 0.05 cm). Exact experimental details of this preparation are described elsewhere.² We present here preliminary results where desorption of the agent at various reaction times and spectral analysis was used to monitor degradation. More detailed kinetic evaluation for the various systems is forthcoming. However, it is obvious from the spectra illustrated in Figs. IV, and V that degradation does take place and that this decomposition is enhanced in the presence of oxidants such as $\text{K}_2\text{S}_2\text{O}_8$ and H_2O_2 .

Pursuits in the immediate future involve the confirmation of these thermal degradation studies in order to optimize the reaction conditions. Other combinations of redox catalysts and strong oxidants will be tested and optimized. In addition to this experimentation, photoelectrochemical studies are underway in order to further elucidate the role of surface species (supposedly surface peroxos)³ in the mechanism of the oxidation of these CW simulants.

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1. M. Grätzel, "Agent Degradation via Catalytic and Photocatalytic Reactions on Surfaces and In Organized Assemblies", Final Technical Report, December 4, 1989 on US Army Contract No. DAJA 45-87-C-0005.
2. C.K. Grätzel, M. Jirousek and M. Grätzel, "Catalytic Agent Degradation on Oxide Films and in Microheterogeneous Solution Systems", Proceedings from the Chemical Defense Research Conference held in November 1989.
3. C.K. Grätzel, M. Jirousek and M. Grätzel, "Decomposition of Organophosphorous Compounds on Photoactivated TiO_2 Surfaces, J. Molec. Catalysis, in press.

FIGURE LEGENDS

- Fig. I Effect of $\text{Fe}_2(\text{SO}_4)_3$ Concentration on 4-NPIPP Thermal Degradation by H_2O_2 in Aqueous Colloidal TiO_2 Suspensions:
 $[\text{TiO}_2] = 5 \text{ gm/l}$, $[\text{H}_2\text{O}_2] = 3.10^{-1}\text{M}$
 $[4\text{-NPIPP}] = 6.5.10^{-4}\text{M}$; $\Delta [\text{Fe}_2(\text{SO}_4)_3] = 5.10^{-4}\text{M}$,
 $\diamond [\text{Fe}_2(\text{SO}_4)_3] = 10^{-3}\text{M}$, $\square [\text{Fe}_2(\text{SO}_4)_3] = 5.10^{-3}\text{M}$
 $* [\text{Fe}_2(\text{SO}_4)_3] = 10^{-2}\text{M}$, $\bullet [\text{Fe}_2(\text{SO}_4)_3] = 0$, $T = 50^\circ\text{C}$
- Fig. II Effect of H_2O_2 concentration on 4-NPIPP Thermal Degradation with $\text{Fe}_2(\text{SO}_4)_3$ Catalyst in Aqueous Colloidal TiO_2 Suspensions:
 $[\text{TiO}_2] = 5 \text{ gm/l}$, $[\text{Fe}_2(\text{SO}_4)_3] = 10^{-3}\text{M}$, $[4\text{-NPIPP}] = 6.5.10^{-4}\text{M}$;
 $\circ [\text{H}_2\text{O}_2] = 2.10^{-2}\text{M}$, $\Delta [\text{H}_2\text{O}_2] = 5.10^{-2}\text{M}$, $\diamond [\text{H}_2\text{O}_2] = 10^{-1}\text{M}$
 $\square [\text{H}_2\text{O}_2] = 3.10^{-1}\text{M}$, $* [\text{H}_2\text{O}_2] = 5.10^{-1}\text{M}$, $\star [\text{H}_2\text{C}_2] = 1\text{M}$,
 $T = 70^\circ\text{C}$
- Fig. III Effect of H_2O_2 Concentration on 4-NPIPP Thermal Degradation with $\text{Fe}_2(\text{SO}_4)_3$ Catalyst in Aqueous Solution:
 $[\text{Fe}_2(\text{SO}_4)_3] = 10^{-3}\text{M}$, $[4\text{-NPIPP}] = 6.5.10^{-4}\text{M}$, $[\text{H}_2\text{O}_2] = 2.10^{-2}\text{M}$,
 $\Delta [\text{H}_2\text{O}_2] = 5.10^{-2}\text{M}$, $\diamond [\text{H}_2\text{O}_2] = 10^{-1}\text{M}$,
 $\square [\text{H}_2\text{O}_2] = 3.10^{-1}\text{M}$ $* [\text{H}_2\text{O}_2] = 5.10^{-1}\text{M}$,
 $\star [\text{H}_2\text{O}_2] = 1\text{M}$, $\bullet [\text{H}_2\text{O}_2] = 0$, $T = 70^\circ\text{C}$.
- Fig. IV Photodecomposition of 4-NPDEP on Oxidant Coated TiO_2 Fractal Films: $[4\text{-NPDEP}] = 1 \text{ monolayer}$, $[\text{K}_2\text{S}_2\text{O}_8] = 20 \text{ monolayers}$, 16 cm^2 metal electrode, $\lambda \geq 350 \text{ nm}$ (solar simulator).
- Fig. V Photodecomposition of 4-NPDEP on Oxidant Coated TiO_2 Fractal Films: $[4\text{-NPDEP}] = 1 \text{ monolayer}$, dipped into H_2O_2 (2 M), 16 cm^2 metal electrode, $\lambda \geq 350 \text{ nm}$ (solar simulator).

FIGURE I

EFFECT OF Fe CONCENTRATION ON
4-NPIPP THERMAL DEGRADATION

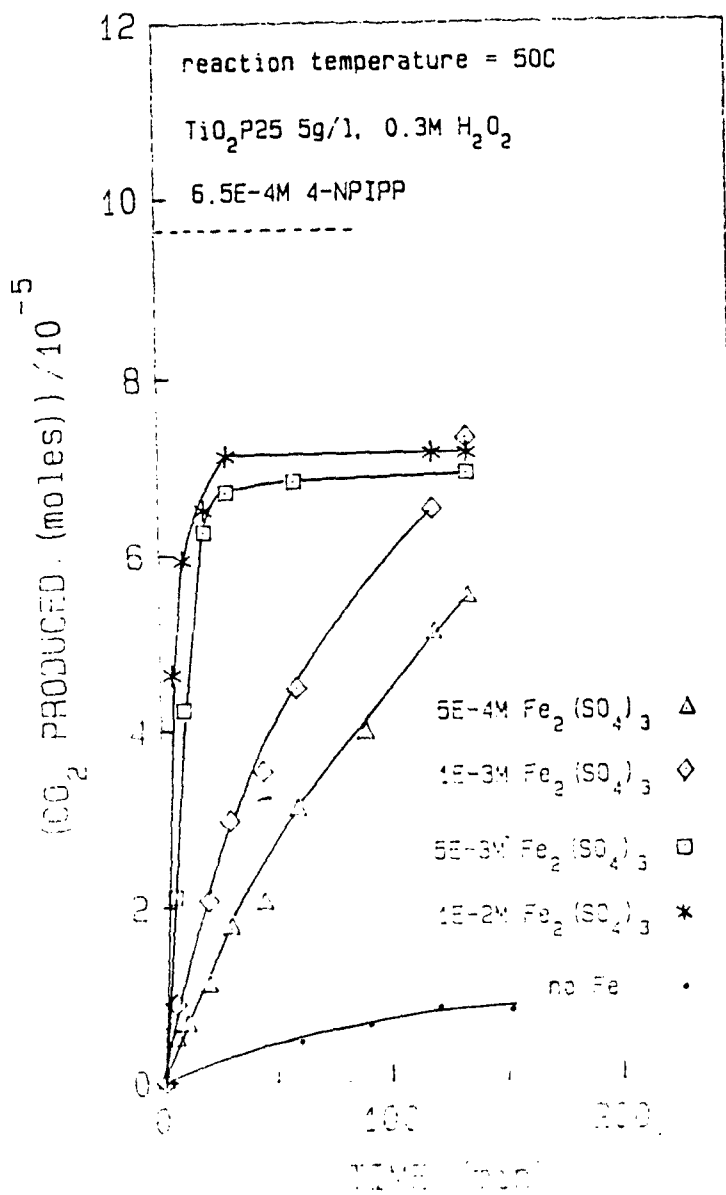


FIGURE II

EFFECT OF H_2O_2 CONCENTRATION ON
4-NPIPP THERMAL DEGRADATION

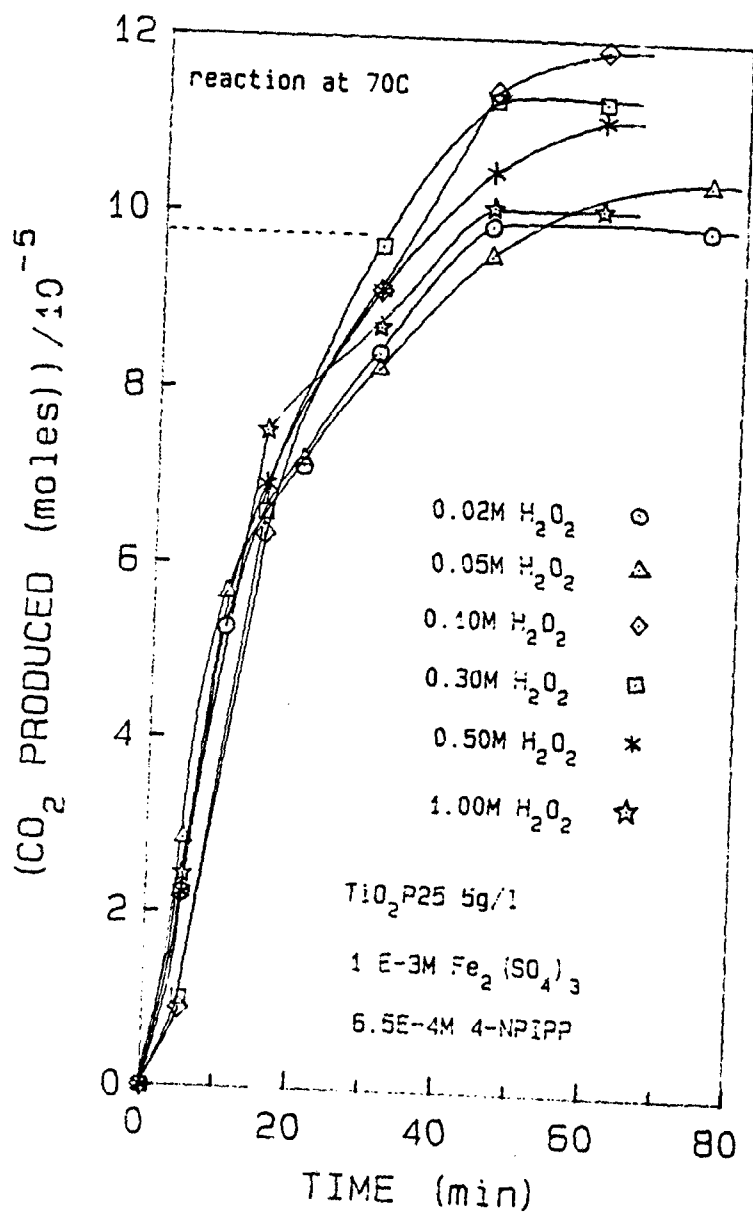
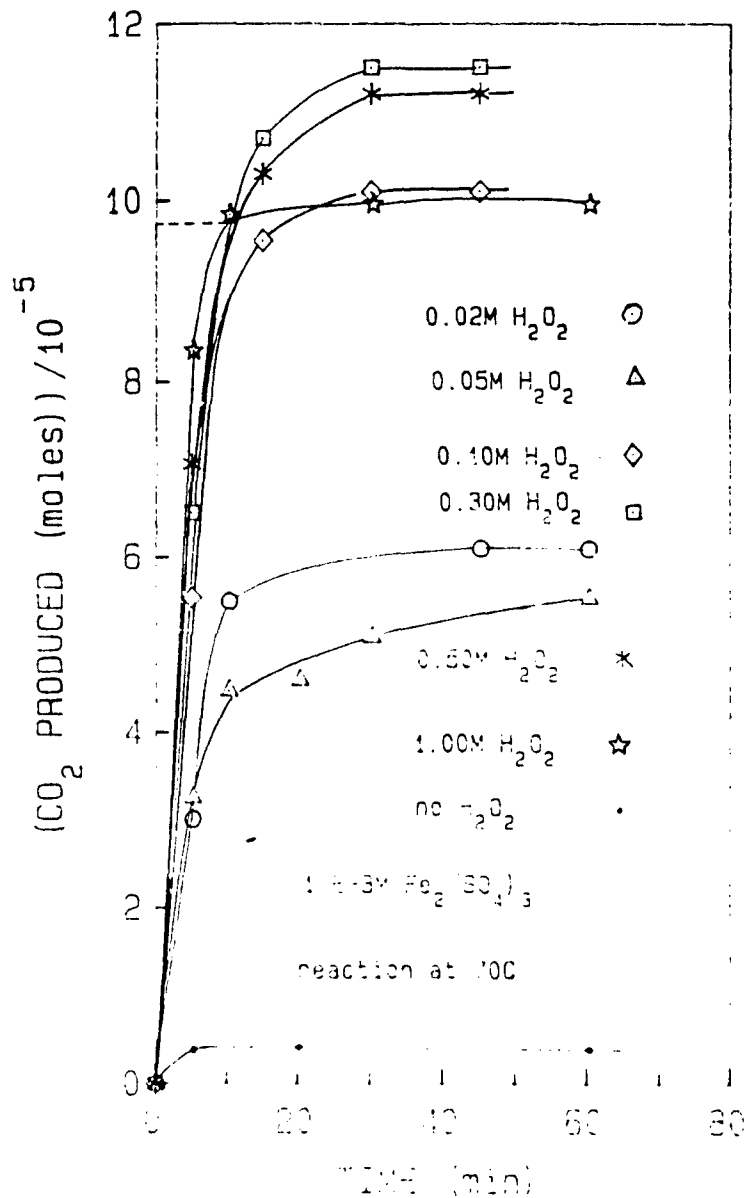


FIGURE III

EFFECT OF H_2O_2 CONCENTRATION ON
4-NPIPP THERMAL DEGRADATION



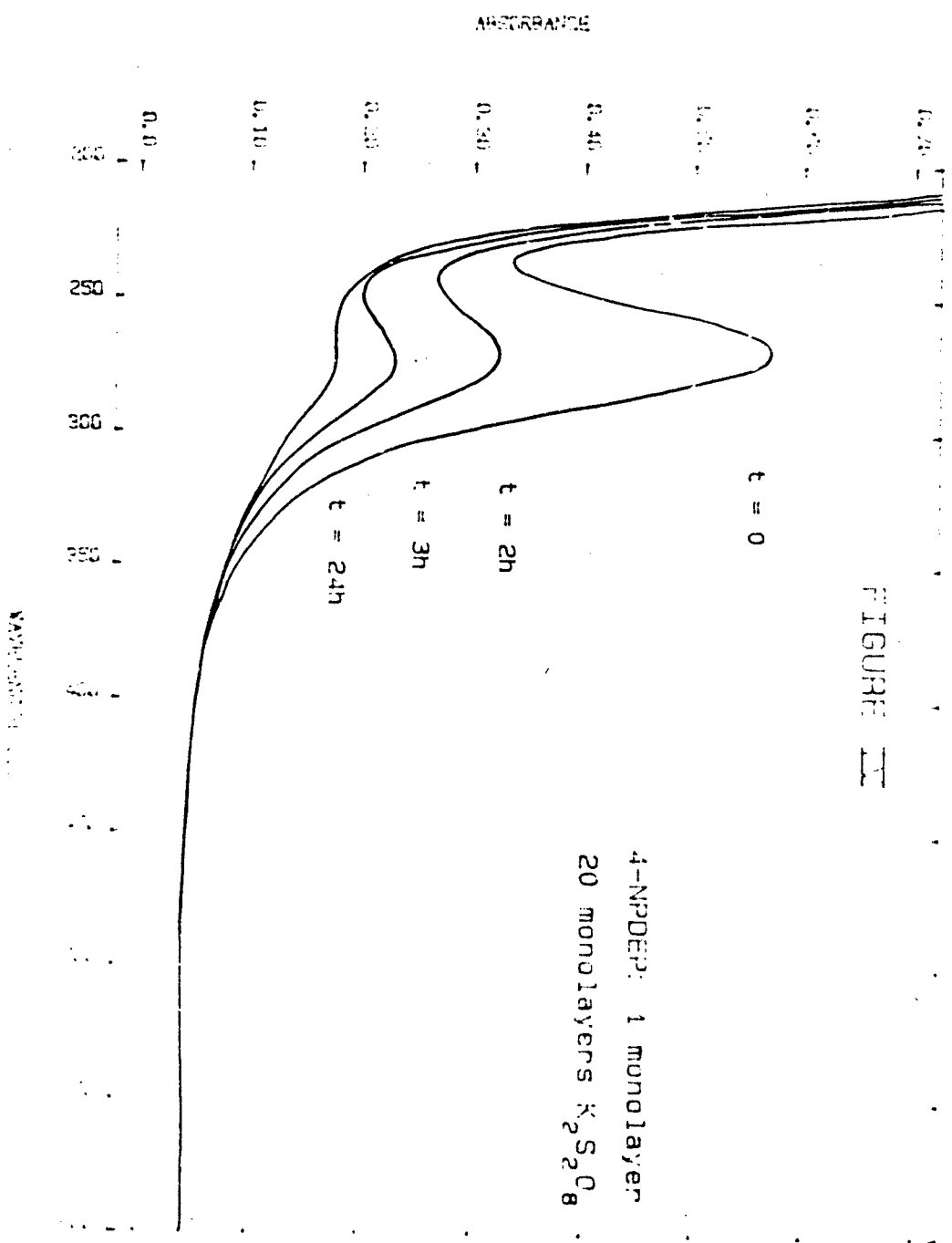


FIGURE III

4-NPDEP: 1 monolayer
 20 monolayers $K_2S_2O_8$

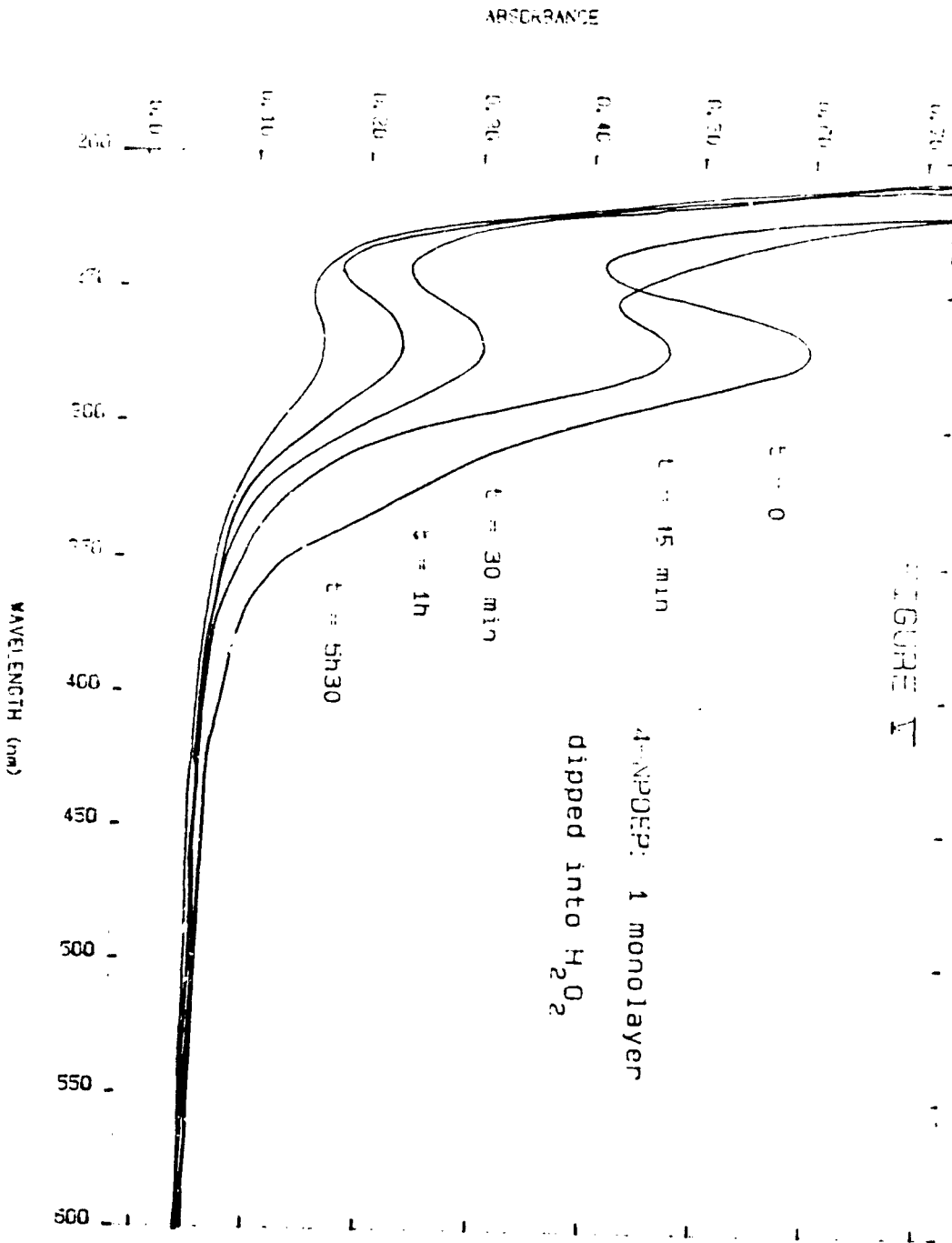


FIGURE V

4-NPDEP: 1 monolayer
dipped into H₂O₂