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MECHANISMS OF RECOVERY OF RADIATION DAMAGED SILICATE-TREATED ZINC OXIDE THERMAL CONTROL COATINGS

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GSFC — GODDARD SPACE FLIGHT CENTER —
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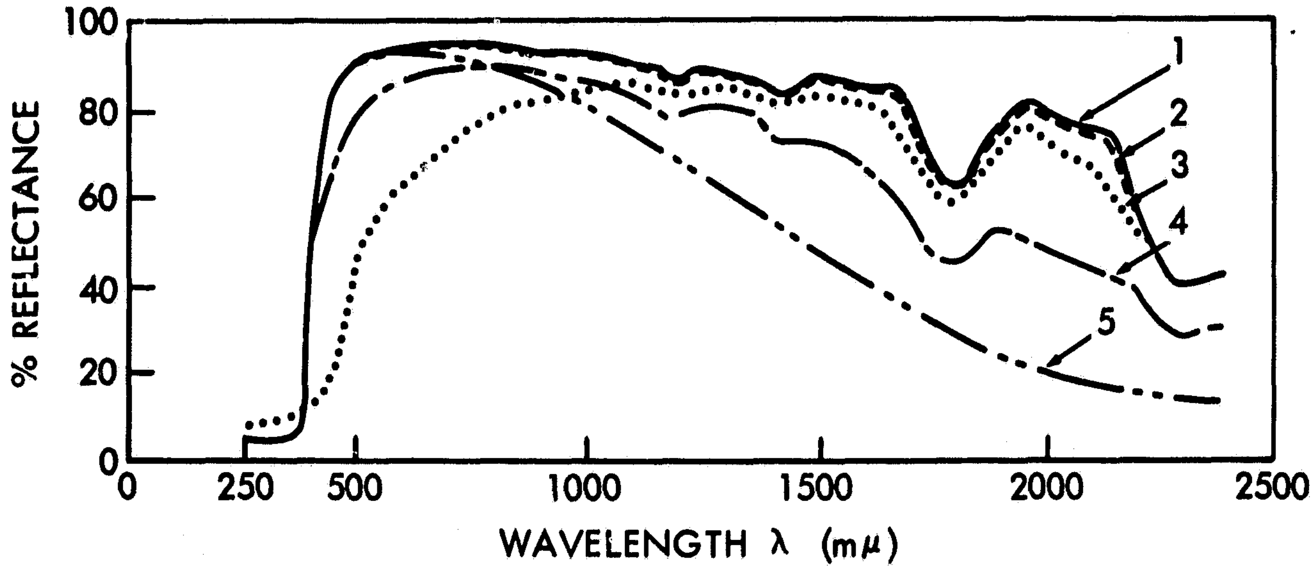
INTRODUCTION

The spectral reflectance of white pigmented coatings for thermal control surfaces of spacecraft suffers considerable damage due to the severe radiations of the space environment, namely, ultraviolet, electron, and proton radiations.[1,2,3] This instability has resulted in thermal design problems and compromises for years and has also spawned a great many searches for new and more stable materials.[4,5] However, the practical advantages of the pigmented coatings (ease of application to all types of substrate and geometric shapes as well as low cost) demand that every effort be made to create satisfactory space environment stability in these materials. This requires a basic research investigation of the mechanisms of damage to pigmented material. Unfortunately, few meaningful mechanism studies have been conducted due to the extreme complication of studies of surface phenomena on powders and to the lack of well developed methods for attacking this problem.

Probably the most prominently used and most widely studied pigment for thermal control coatings is zinc oxide.[6,7,8] Radiation damage to this material results in a considerable reduction of near infrared reflectance which is rapidly reversible if the sample is returned to an air environment. Morrison, by applying semiconductor theory of surface recombination centers for photo-induced charge carriers, has met with some success surface doping zinc oxide with ferro- and ferri-cyanide complexes.[9] Photo conductance measurements of doped and undoped single crystals are the basis for this success while radiation effects on the powders are still being determined. Bulk doping of zinc oxide with copper has been shown to be partially effective as a stabilizer by Greenberg but has the disadvantage of causing a considerable reduction in initial reflectance.[7] By far the largest volume of stabilization data has evolved from various potassium silicate surface treatments of zinc oxide but little has been done to elucidate the mechanism of this protection.[10,11] It has been shown that this stabilization, while effective against ultraviolet exposures, is overridden by the higher energy ionizing radiations such as electrons, x-rays, and gamma rays[11,12] (Figure 1). Thus, the questions of mechanisms of degradation or partial protection are still unresolved and the causes of effects of binders, doping, and formulation on pigment stability are unknown.

In an effort to obtain further insight into the nature of this degradation and silicate stabilization, an experimental study was made of the rates of bleaching (recovery of infrared reflectance) of such a coating (101)* as a function of



Curve Identification:

————————	#1	Initial reflectance
- - - - - - - - -	#2*	240 UV hrs, xenon lamp, "in situ" measurement
··················	#3*	10^{16} p/cm^2, 30 kev protons, air measurement
——— – ———	#4*	10^{16} e/cm^2, 30 kev electrons, air measurement
——— – – ———	#5	17 x 10^{16} kev/cm^2, x-ray dose, from copper target, "in situ" measurement

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*Test results from E. M. R. under contract No. NAS 5-9469

Figure 1. Effect of Various Radiations on Spectral Reflectance of Silicate-Treated ZnO Coating "101"

environmental atmosphere. The silicate-treated zinc oxide coating was chosen because of the slow bleaching rate (four hours instead of less than three seconds as with the untreated pigment) which allows a more careful analysis of subtle differences in rate due to variables of environment. Radiation damage similar to electron damage was provided by X-ray bombardment. A special apparatus was developed for X-irradiation of the sample in vacuum followed by exposure to near atmospheric pressures of various gases and with spectral reflectance measurements of damage and recovery being made at appropriate stages while maintaining the environment (in situ).

The bleaching rates of coating and of treated pigment alone were studied using both dry and water saturated gases. Simultaneous exposure with ultraviolet light during bleaching was also observed for each gas. Correlations between relative rates for the coating and for the pigment were made in order to determine the effect of the binder (silicone vehicle).

APPARATUS

The apparatus used for this work consists essentially of five associated systems. The heart of the system is the environmental cell in which the sample resides during x-irradiation in vacuum, recovery in various atmospheres, and all reflectance measurements. It is equipped with a five mil berylium window for admission of the x-ray beam, a supersil quartz window through which spectral reflectance measurements are made and a sample holder mounted on a translational feedthrough for appropriate positioning of the sample.

The vacuum system included a liquid nitrogen cooled sorption pump for roughing and a Varian 8 l/sec Vacion pump which provided a working pressure of 1×10^{-6} torr.

Spectral reflectance measurements of the sample from 0.30 to 2.4 microns were obtained using a Beckman DK-2A spectroreflectometer. The sample was first positioned flat against the inside of the quartz window. Then the entire environmental cell was positioned flat against the integrating sphere sample port. By using an equivalent quartz window at the reference port, this technique resulted in a reproducibility of measurement of ±1%. (See Figure 2.)

Gases were conducted from the cylinders to the environmental cell through the gas inlet system. This included a sorption pump bulb to remove initial air, a gas dissolver for saturating the gas with water when necessary, a manometer for measuring the final pressure and a microleak valve for admitting gas to the cell.

X-irradiation for producing damage in the sample was produced by a General Electric X-ray tube with a copper target operated at 45 kilovolts and 30 milliamps. The entire environmental cell was attached to the X-ray unit by a specially prepared clamping system during irradiation (Figure 3).

TESTS

The experimental technique required for a single run involved at least six phases. Initially the sample was attached to the sample holder and the cell

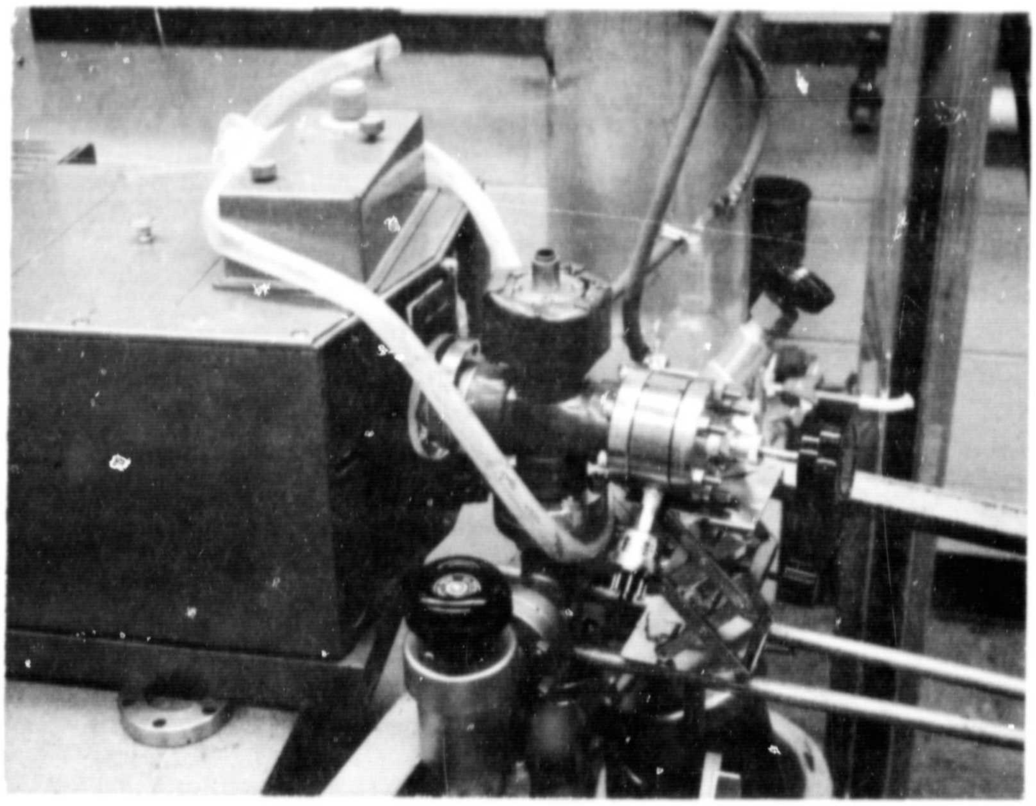

Figure 2. Apparatus for Spectral Reflectance Measurement of Samples

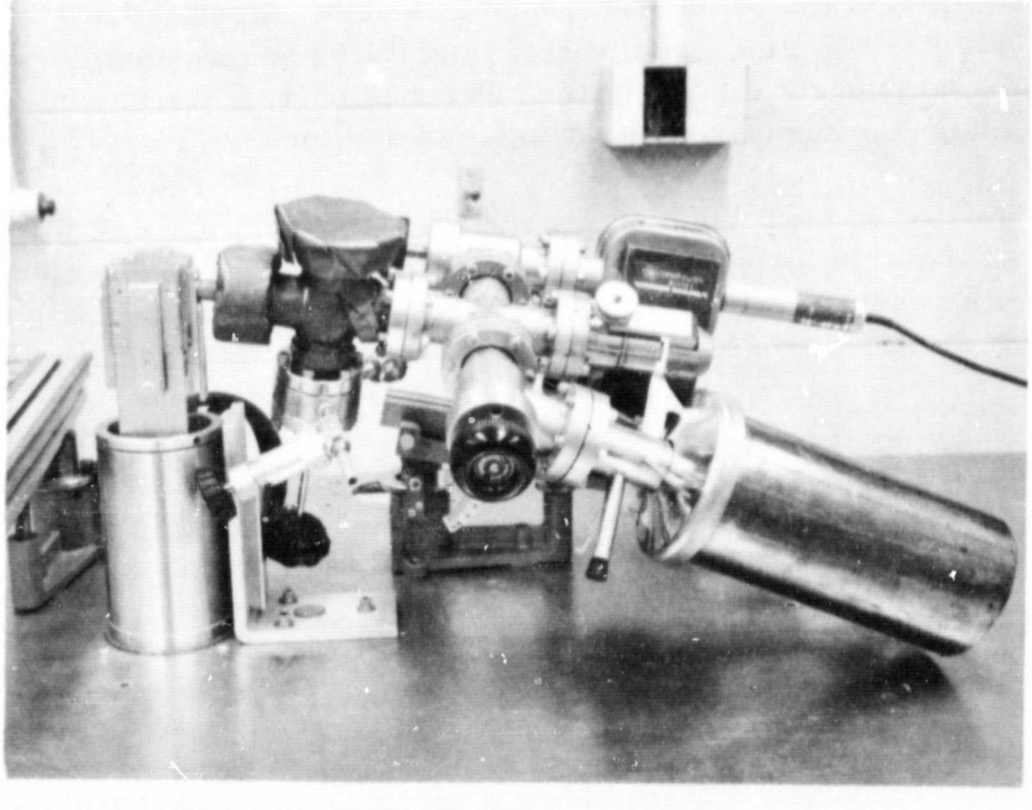

Figure 3. Apparatus for X-irradiation of Samples

evacuated to at least 10^{-6} torr. After the spectral reflectance had been recorded the system was moved to the X-ray unit and the sample irradiated overnight (17 hours). This was sufficient to achieve saturation of the infrared damage and represented an energy absorption of $1.7 \times 10^{17} \pm 0.2 \times 10^{17}$ kev per square centimeter as determined by a standard ferrous sulfate dosimeter technique[15]. The spectral reflectance was again obtained and the gas of interest allowed to flow into the cell. This was done after appropriate flushing of the inlet system to eliminate all residual air. At the moment of gas influx a time clock was started and the rate of bleaching determined. The wavelength of maximum damage (2.0 microns) was used in all rate measurements. The results of differences in recovery rates due to environmental conditions were then used to infer details of the mechanisms of degradation and recovery.

RESULTS AND DISCUSSION

The effect of X-irradiation on "101" coating is shown by the spectral reflectance curve in Figure 4. Included in this curve are bleaching points taken in an oxygen atmosphere and recorded at the wavelength of maximum damage. The bleaching curves discussed below are the result of plotting these bleaching points as a function of time. Saturation of X-ray damage is indicated by the degradation rate curve of Figure 5. As can be noted, little change occurs after fourteen hours, thus, an exposure time of 17 hours is sufficient to minimize errors due to individual differences in samples and sample positioning.

The effects of various atmospheres on the bleaching rate are shown in Figure 6. Rapid recovery is observed with oxygen whereas the other gases — nitrous oxide, nitrogen, and carbon dioxide — form a group exhibiting a slow but steady recovery rate. This residual recovery has been attributed to oxygen impurity in the gases, possible slight leaks in the gas inlet system, and oxygen retained in or adsorbed to the sample. This latter contribution is attested to by the fact that bleaching of four to seven percent has been observed in 18 hours while maintaining the vacuum environment (10^{-6} torr). Saturation of the gases with water vapor had a negligible effect on dark bleaching of the sample.

A comprehensive presentation of bleaching rate data with oxygen is given in Figure 7. The drastic increase in recovery rate due to heating the sample to 70°C has been attributed both to increased reaction rate of O_2 with the damaged surface and to increased diffusion rate through the silicone binder. The most dramatic effect shown by this data is the suppression of bleaching rate when the sample is irradiated with ultraviolet light during bleaching in dry oxygen. The ultraviolet source used here was an Hanovia 673A medium pressure mercury arc lamp which has emission lines down to wavelengths as short as 2170 angstroms. Since this suppression of rate is not observed when the coating sample

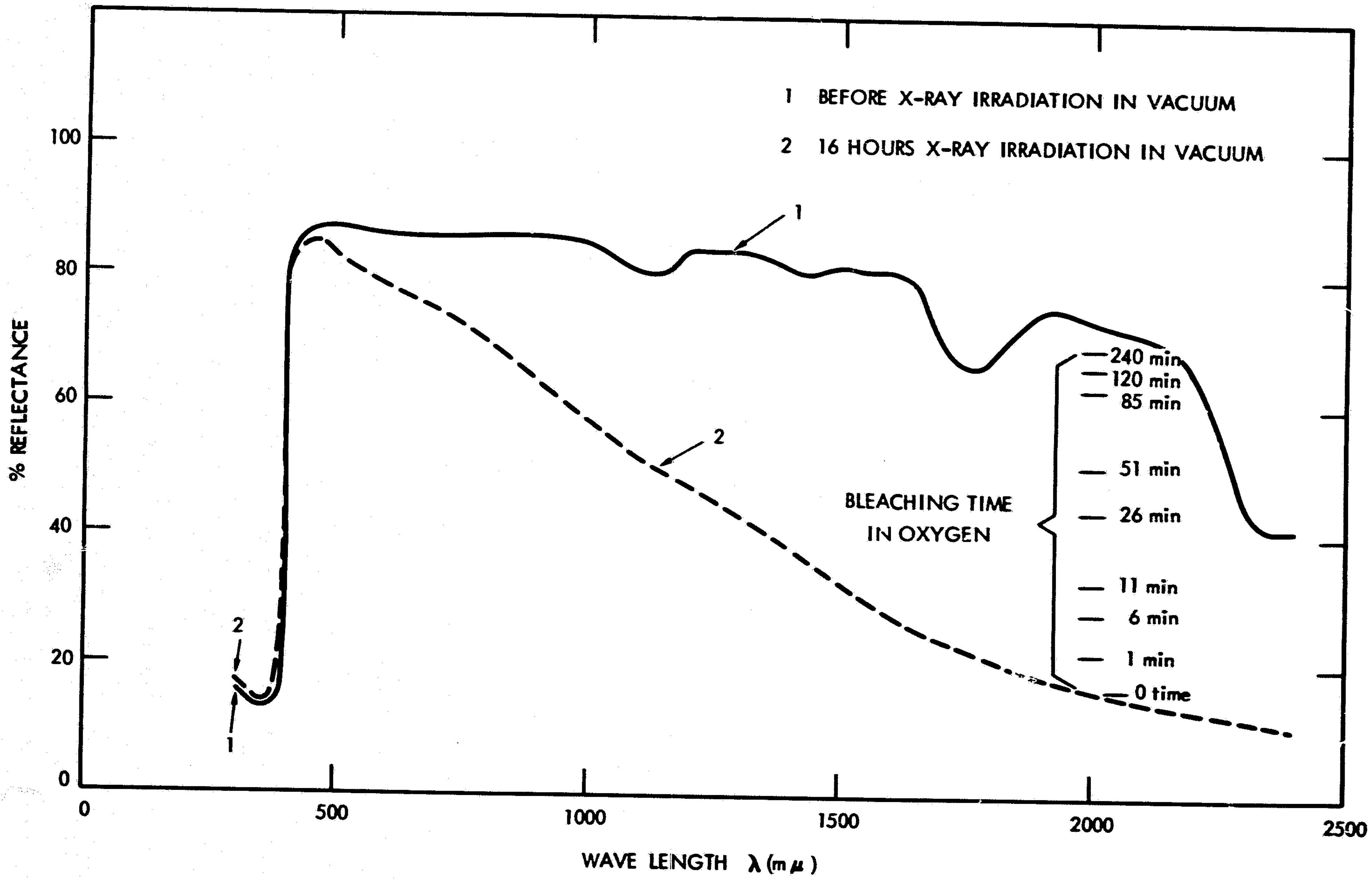

Figure 4. Spectral Curve of X-Ray Damage and Oxygen Bleaching

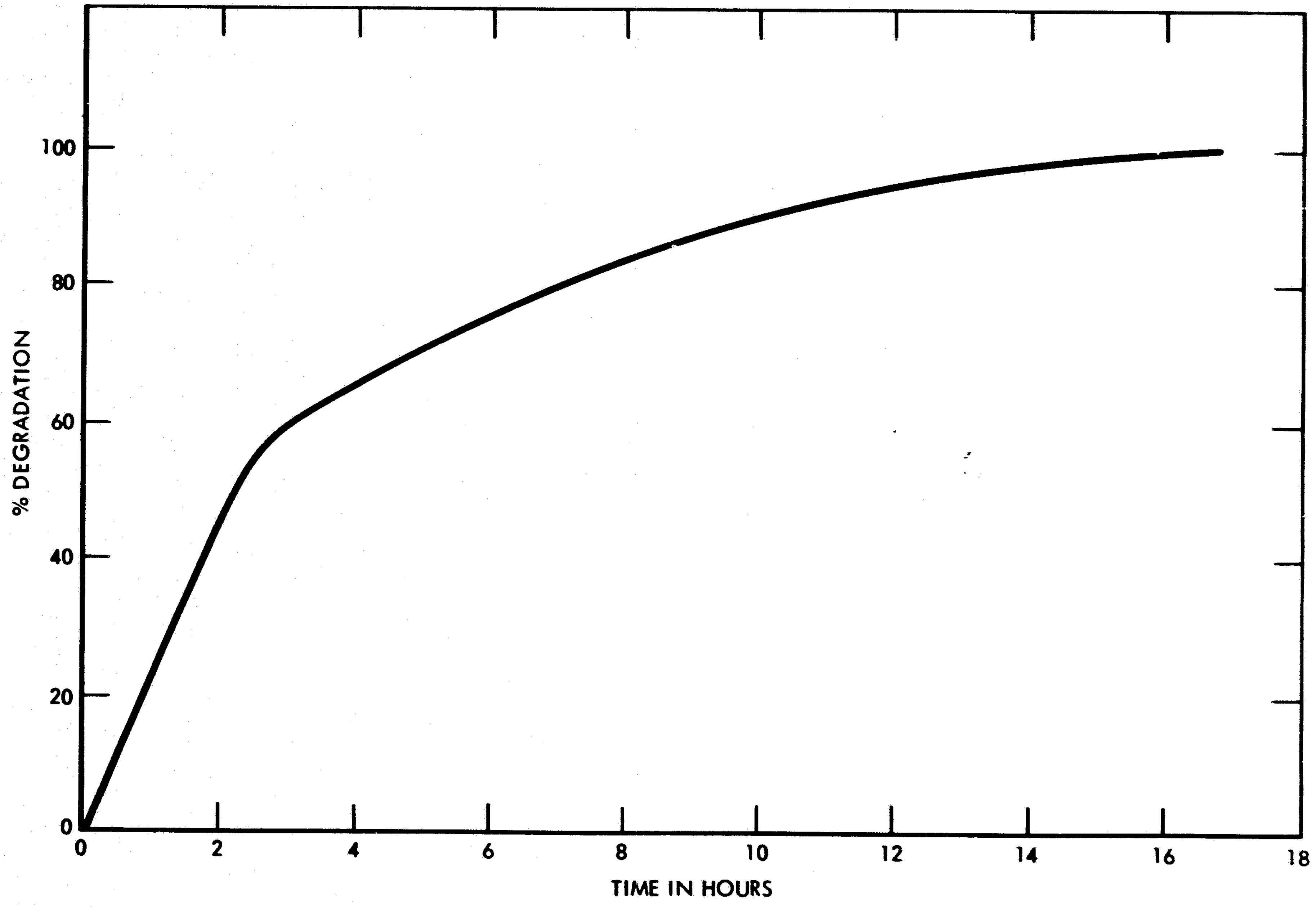

Figure 5. Paint Degradation Rate

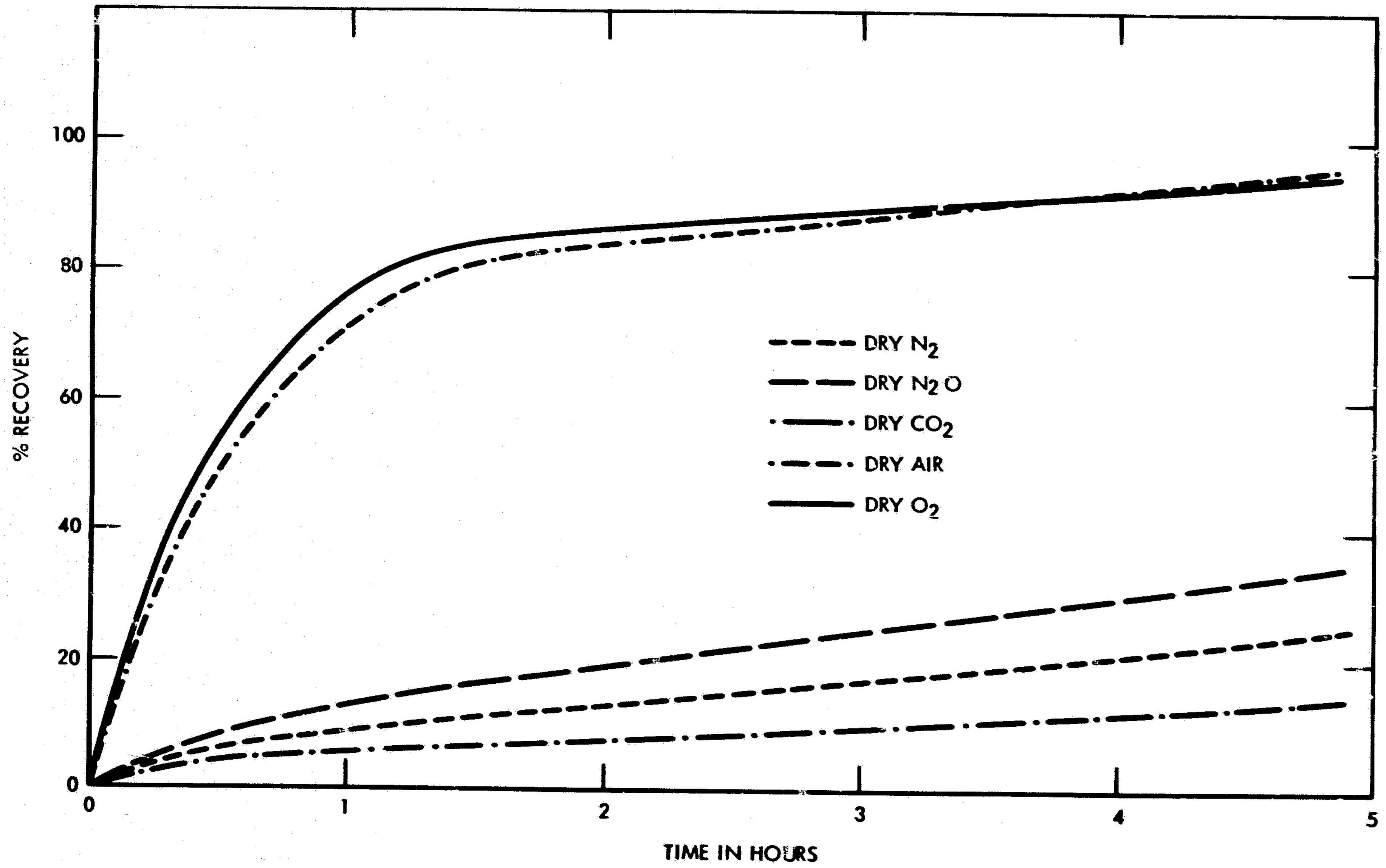

Figure 6. Paint Bleaching in Various Atmospheres

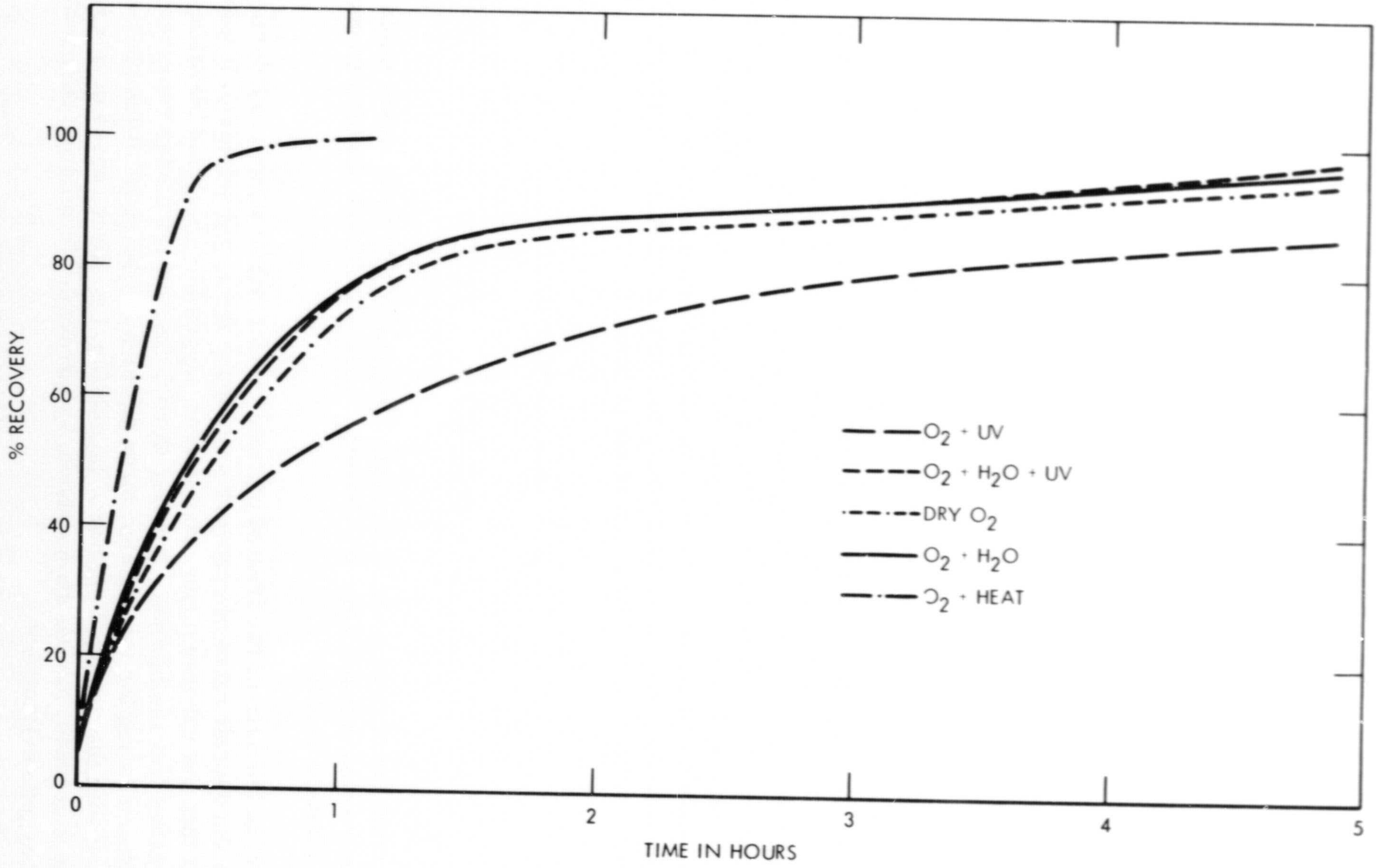

Figure 7. Paint Bleaching in Oxygen

is replaced with a sample of treated pigment only (Figure 8), it has been concluded that the mechanism of the suppression involves oxygen photolysis to yield oxygen free radicals which react with the silicone binder producing a barrier to oxygen diffusion

$$O_2 + h\nu \longrightarrow 2\,O\cdot$$

$$O\cdot + \text{Methyl Silicone} \longrightarrow \text{Oxygen Barrier}$$

The presence of water vapor, which nullifies the suppression of bleaching, indicates that water is a scavenger for oxygen free radicals, thus preventing the formation of the diffusion barrier.

Enhancement of the bleaching rates due to ultraviolet irradiation was observed with all other gases (N_2, CO_2, and N_2O) as shown by the synoptic graph of Figure 9. For nitrogen and carbon dioxide for which identical responses occurred, the increased recovery rate was attributed to heating of the sample by the long wavelength portion of the spectrum from the mercury lamp. As was shown above for oxygen bleaching, heating is extremely effective in increasing recovery rate, in this case due to oxygen impurity. Ultraviolet exposure during nitrous oxide bleaching caused a significantly greater enhancement of rate. Here the enhancement was considered to be due to photolysis of nitrous oxide to produce oxygen as well as to the effect of heat.

$$N_2O + h\nu \longrightarrow N_2 + O$$

$$O\cdot + O\cdot \longrightarrow O_2$$

The production of even a small amount of oxygen by this mechanism would result in considerable enhancement of recovery, especially if this photolysis occurred on the pigment surface.

Finally, in the case of the treated pigment alone (without silicone binder), although the overall rates of recovery were much faster (30 minutes), it was observed that the relative difference between oxygen bleaching and bleaching in other gases was maintained. In other words, the silicone binder represents a protective coating for the pigment through which oxygen must diffuse before reacting with the damaged pigment. In addition, the effectiveness of this barrier may be increased, as was shown above, by ultraviolet irradiation during bleaching in an oxygen environment.

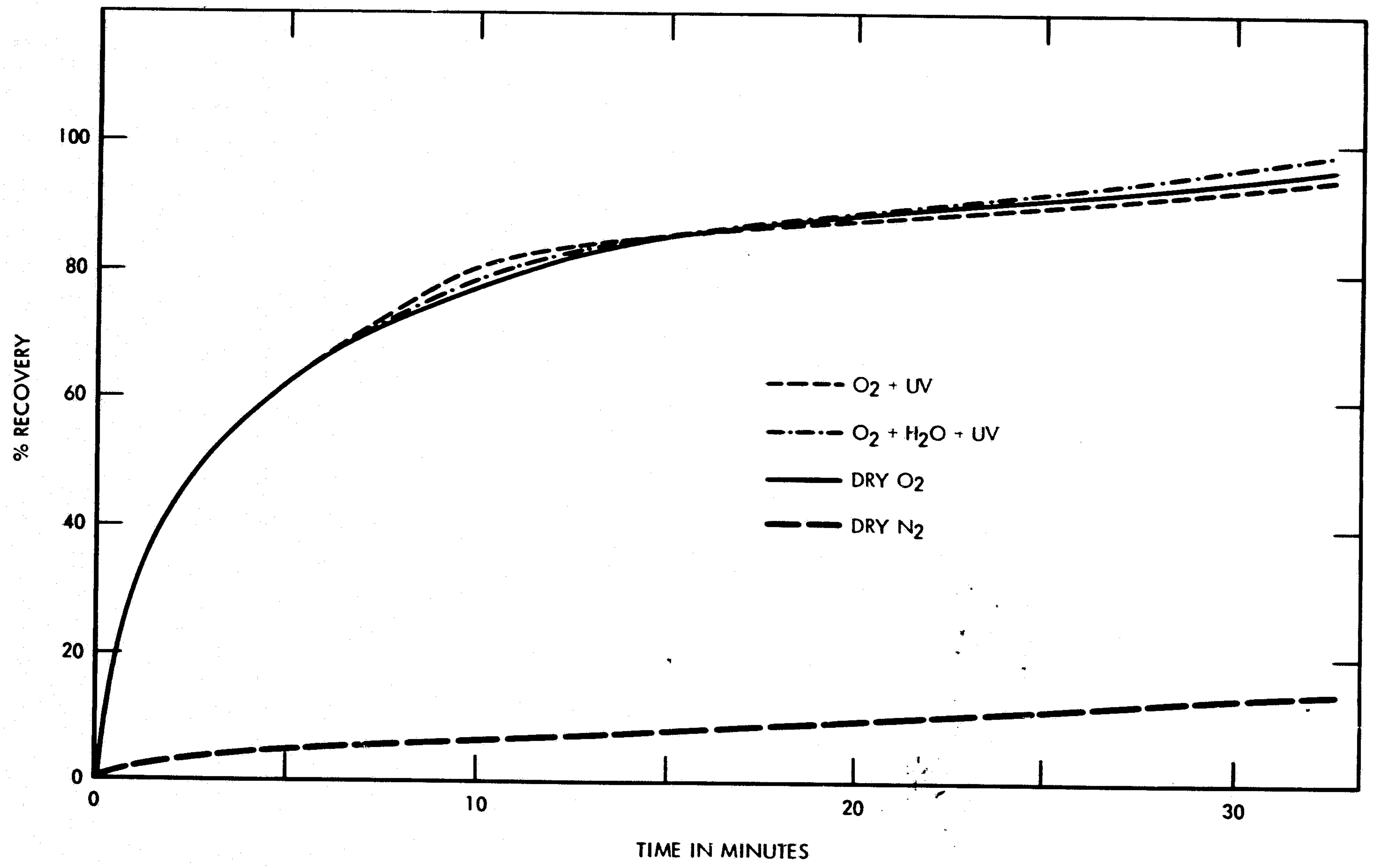

Figure 8. Pigment Only Bleaching in Various Atmospheres

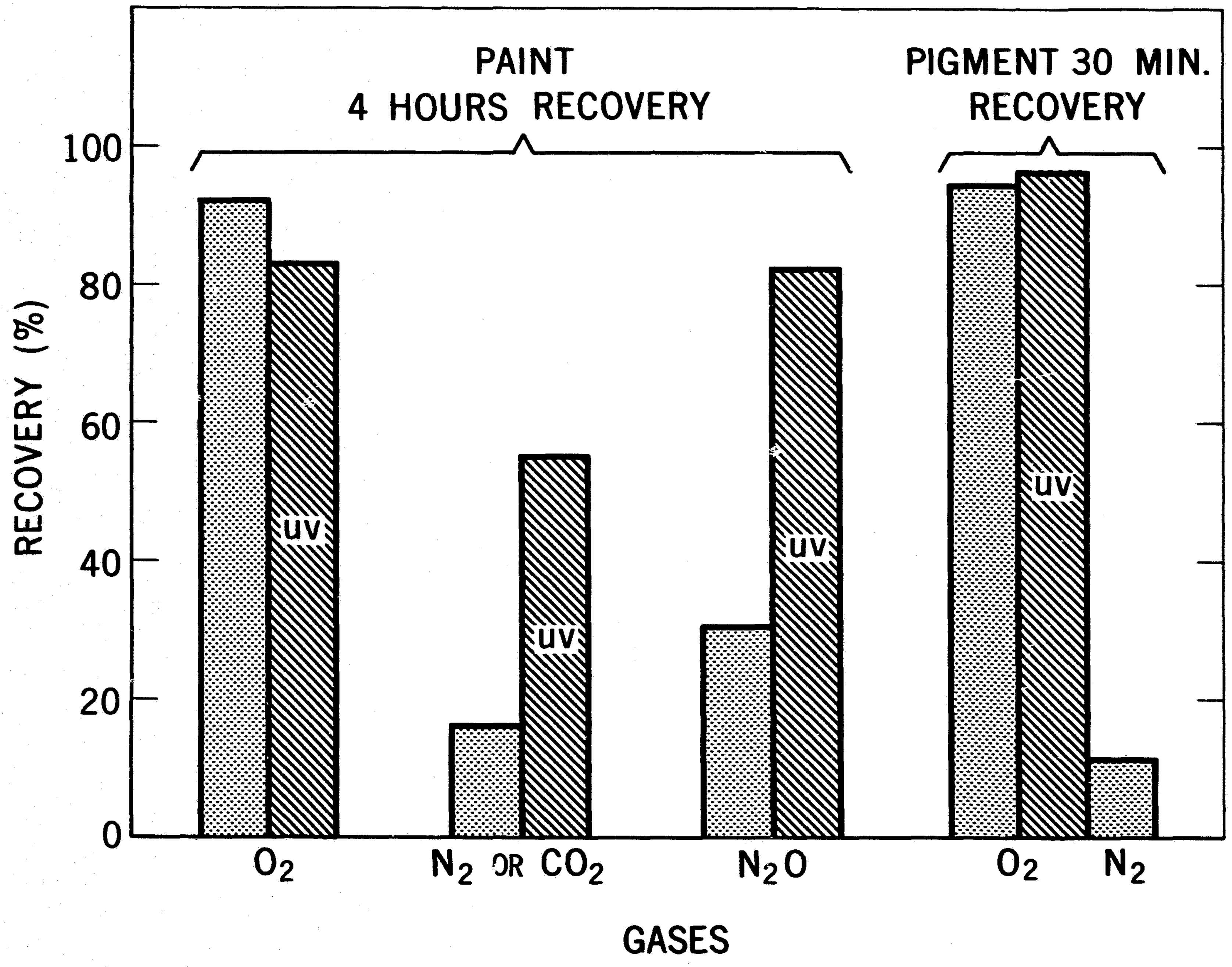

Figure 9. Recovery in Various Atmospheres

CONCLUSIONS

X-ray exposure of a silicate-treated zinc oxide coating results in a drastic reduction of near infrared reflectance. This damage is completely reversible upon exposure to an oxygen environment as is the case for ultraviolet induced damage in coatings made from untreated zinc oxide. Thus, damage in both cases is due to loss of oxygen from the zinc oxide crystals. The rapid increase in bleaching rate with increase in temperature is due to an accelerated diffusion rate of molecular oxygen through the silicone binder as well as to possible increased kinetics of reaction of oxygen molecules with damaged pigment.

Oxygen photolysis due to ultraviolet exposure during bleaching results in a suppression of bleaching rate. This is due to interaction of atomic oxygen with the methyl silicone binder which creates a barrier for diffusion of molecular oxygen.

Finally, comparisons between bleaching effects of the coating and of the treated pigment alone indicate consistent relative behavior as a function of environment. The mechanisms of damage and recovery, then, must be unaffected by the silicone binder.

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