RADIATION EFFECTS ON ORGANIC SCINTILLATORS:
STUDIES OF COLOR CENTER ANNEALING

R. L. Clough and J. S. Wallace
Sandia National Laboratories

Abstract

The interaction of ionizing radiation with organic, polymer-based scintillators results in the discoloration of the material, which reduces the scintillation efficiency. This phenomenon can be described in terms of two types of color centers: annealable and nonannealable. For many common materials, at doses of a few Mrad, the annealable color centers account for a large fraction of the observed radiation-induced absorption. We are conducting studies to understand the mechanisms and kinetics of the annealing process. By conducting experiments on polystyrene in which polymerization of the monomer, γ-irradiation, and post-irradiation annealing were all carried out in a sealed, degassed tube, we have been able to resolve the question of whether annealing can occur in the absence of oxygen. We find that annealing does indeed occur under inert conditions. The rate of inert annealing at room temperature is drastically slower than oxygen-mediated annealing, whereas the rates for the two processes is only slightly different at 80°C. We have measured the annealing rate of color centers in γ-irradiated polystyrene in air over the temperature range of 30 to 90°C, and find a large increase in annealing rate with increasing temperature. Arrhenius plots of the annealing data show strong non-linearity, which can be ascribed to two different annealing mechanisms of very different activation energy: presumably oxidative and nonoxidative. Ongoing work involves deconvolution of the two annealing processes, and construction of a model for long-term annealing kinetics in these materials.

Introduction

Scope of Sandia Program

We have initiated a program to address the radiation stability of optical polymers and luminescent dyes used in scintillator fabrication. Primary goals include: identification of radiation-degradation mechanisms in scintillators, development of radiation-resistant systems, implementation of effective annealing schemes for scintillator recovery, and demonstration of predictive aging techniques for evaluating material lifetimes under low-level radiation conditions. Work carried out to date includes: 1) A survey of the radiation-induced color center formation in 21 different optical polymers, 2) an evaluation of radiation effects on the major classes of scintillator dyes, both in terms of their decomposition and their discoloration in a polystyrene matrix, 3) evaluation and synthesis of new red-shifted scintillator dyes, and 4) a detailed investigation of temperature and oxygen effects in the annealing of color centers in irradiated polystyrene. This report covers the results and conclusions to date on the annealing studies in polystyrene (number 4 above). Results on the other topics all involve extensive tables and discussion, and will be published elsewhere.

Major Issues in Color Center Annealing

There have been conflicting reports circulating on whether oxygen plays a beneficial or detrimental role in the radiation-induced changes in polymer-based scintillators [1]. The answer to this question can be expected to be complex, and will likely be affected by the particular polymers, dyes, environmental conditions and timescales involved. This issue is fundamental to the choice of the gaseous environment which will surround the scintillator media in future detectors, and is also crucial in the design of rad-hard scintillator materials. Another important materials issue is the ability to model the kinetics of color center annealing, for the purpose of

predicting long-term effects of radiation exposure. This implies understanding the interrelationship of time and temperature in the annealing phenomenon. To address these primary annealing issues, we have conducted post-irradiation annealing experiments over a range of temperatures in vacuum and under air.

Results and Discussion

Annealing in the Absence of Oxygen

The concentration of annealable color centers which gives rise to the radiation-induced absorption is unknown; they may be very small in number. If so, then a tiny amount of oxygen contamination could potentially cause significant annealing. Thus, an "inert atmosphere" study which had even minimal oxygen exposure, and which revealed annealing at a rate slower than that found in air, would be open to the question: would the results actually represent oxygen annealing at a partial pressure lower than that of air? Because of this concern, we carried out experiments in which styrene monomer was subjected to repeated freeze-thaw degassing, and the glass tube in which it was contained was sealed under vacuum using a torch. This allowed for efficient and rapid deoxygenation, compared to what would be possible using polystyrene polymer, due to the extremely slow rate for gaseous permeation in the solid matrix [2]. All of the following operations were carried on the sealed-tube sample: polymerization of the styrene monomer, γ-irradiation, and postirradiation annealing. Each absorption spectrum run was obtained using a separate sample which was open to the air immediately prior to the measurement.

Figure 1 presents data for the time-dependent change in absorbance, at 400 nm, for γ-irradiated polystyrene samples (15 Mrad dose under vacuum) which were subsequently annealed near room temperature under inert and air atmospheres. The samples held under vacuum do exhibit a slow, steady decrease in absorbance. This amounts to less than 10% after 40 days, and occurs more than an order of magnitude slower than annealing in the presence of air. Figure 2 presents data for annealing at 80°C under vacuum and air atmospheres. Substantial annealing is seen under both atmospheres, with the vacuum annealing occurring only moderately slower. In all cases, the annealing asymptotically approaches a lower residual value, corresponding to color centers which are permanent, and/or which at least have much longer annealing times.

From these data, it is clear that color center annealing does occur in the absence of oxygen. The difference in oxygen-mediated annealing and non-oxygen-mediated annealing is further apparent upon visual examination of samples. In the case of oxygen annealing, a distinct bleaching front moves through the samples with time, corresponding to the permeation of oxygen through the material. Thus, in a partially annealed sample, distinct colored regions remain in the interior of the specimen, while the edge regions appear nearly colorless. In the case of inert-atmosphere annealing, the sample coloration appears homogeneous throughout the annealing process.

It is likely that the annealable color centers involve reactive species (such as radicals, radical ions, trapped electrons, or similar) which are immobilized in the glassy polymer matrix. (A strong ESR signal is in fact observed for polystyrene samples subjected to γ-irradiation, and we are using the ESR technique to study the annealing phenomenon. This will not be discussed further in this report). The annealing mechanism in air must correspond to reaction with molecular oxygen to yield colorless (or less colored) products. Rapid reaction of oxygen with all of the species listed above would be expected. The annealing mechanism under inert atmosphere must correspond to mobility of the reactive species themselves within the matrix, leading to recombination reactions with other reactive species (i.e., radical-radical recombination; radical cation-radical anion recombination). Both the diffusion of oxygen and the diffusion of reactive species (including reactive sites on the macromolecules) can be expected to increase with increasing temperature, as is seen with the data. Thus, as the polystyrene is heated toward its glass transition temperature (~105°C), the mobility of species within the matrix is greatly increased. Under these conditions of

low matrix rigidity, the annealable color centers have very short lifetimes.

An implication of these data is that elevated temperature may be useful for eliminating annealable color centers. Since oxygen may have an undesirable degrading effect on polymers [3] (possibly leading to higher concentrations of permanent color centers) and also on dyes (leading to oxidative degradation) [4], it may be desirable to utilize inert annealing processes. Clearly, even at room temperature, color centers diminish with time. Further kinetic studies should lead to predictions of decay time of the color centers under a given set of operating conditions (temperature, atmosphere, etc.), and should allow estimation of steady-state concentrations of annealable color centers under particular long-term operating conditions (dose rate, temperature) as irradiation is in progress.

Temperature-Dependence Plots

Figure 3 presents time-dependent decay curves for the radiation-induced absorbance of polystyrene at 400 nm, obtained in air atmosphere at temperatures ranging from 30 to 90°C. Progressively more rapid decay is seen at higher experimental temperatures. Figure 4 presents an Arrhenius plot for the data of Fig. 3, showing the time for recovery to three different extents of annealing as a function of reciprocal temperature. The three curves follow very much the same trend, and exhibit a strong non-linearity. Linearity in such a plot would be characteristic of a process having a single rate-determining step [5]. The curvature observed indicates the occurrence of two or more rate-limiting processes having substantially different activation energies. Such behavior would result from the competition of the two annealing mechanisms described earlier (oxygen-diffusion annealing, and inert-atmosphere recombination annealing), if these two process made proportionately different contributions at different temperatures. Comparison of the data in Figs. 1 and 2 would indicate that this is so. We are presently carrying out annealing experiments under both vacuum and air at a number of additional temperatures, from which we will construct Arrhenius plots for both annealing process. Deconvolution of the the two annealing processes will be carried out with the goal of utilizing the Arrhenius approach for modeling time-dependent annealing under both atmospheres. In addition, extensive experiments are currently being initiated to irradiate samples under various combinations of temperatures and low dose rates for construction of further long-term aging models utilizing the time-temperature-dose rate superposition approach which has been applied previously to the radiation-degradation of mechanical properties of polymers [5,6].

References

[1] H. Schonbacher, "Review of Radiation Damage Studies on Scintillating Materials Used in High Energy Physics Experiments," in Radiation Effects at the SSC, M. G. D. Gilchriese, ed., SSC-SR-1035 (June, 1988), p. 215.

[2] K. T. Gillen and R. L. Clough, "Techniques for Monitoring Heterogeneous Oxidation of Polymers," in Handbook of Polymer Science and Technology, Vol. 2, N.P. Cheremisinoff, ed., Marcell Dekker, New York (1989) p. 167.

[3] R. L. Clough and K. T. Gillen, "γ-Radiation-Induced Oxidation and Mechanisms of its Inhibition," in Oxidation Inhibition in Organic Materials, Vol. II, J. Pospisil and P. P. Klemchuk, eds., CRC Press, Boca Raton (1990) p. 191.

[4] R. L. Clough, "γ-Radiation-Oxidation of Polycyclic Aromatic Hydrocarbons: Involvement of Singlet Oxygen," J. Amer. Chem. Soc., 102, 5242 (1980).

[5] K. T. Gillen and R. L. Clough, "Time-Temperature-Dose Rate Superposition: a Methodology for extrapolating Accelerated Radiation Aging Data to Low Dose Rate Conditions," Polym. Deg. and Stab., 24, 137 (1989).

[6] K. T. Gillen and R. L. Clough, "A Kinetic Model for Predicting Oxidative Degradation Rates in Combined Radiation-Thermal Environments," J. Polym. Sci., Polym. Chem. Ed. 23, 2683 (1985).

FIGURE CAPTIONS

Figure 1. Air and vacuum annealing at 30°C of color centers in polystyrene after γ-irradiation in vacuum to 15 Mrad. Samples were polished disks 0.25 in (0.635 cm) thick and 0.612 in (1.55 cm) in diameter.

Figure 2. Air and vacuum annealing of radiation-induced color centers in polystyrene at 30°C. Irradiation and sample size as in Figure 1.

Figure 3. Temperature dependence of air annealed color centers. Irradiation and sample size as in Figure 1.

Figure 4. Arrhenius plot of the decrease in the initial post-irradiation concentration of color centers as a function of 1/T. Concentration decreases shown are 25%, 50%, and 75%.
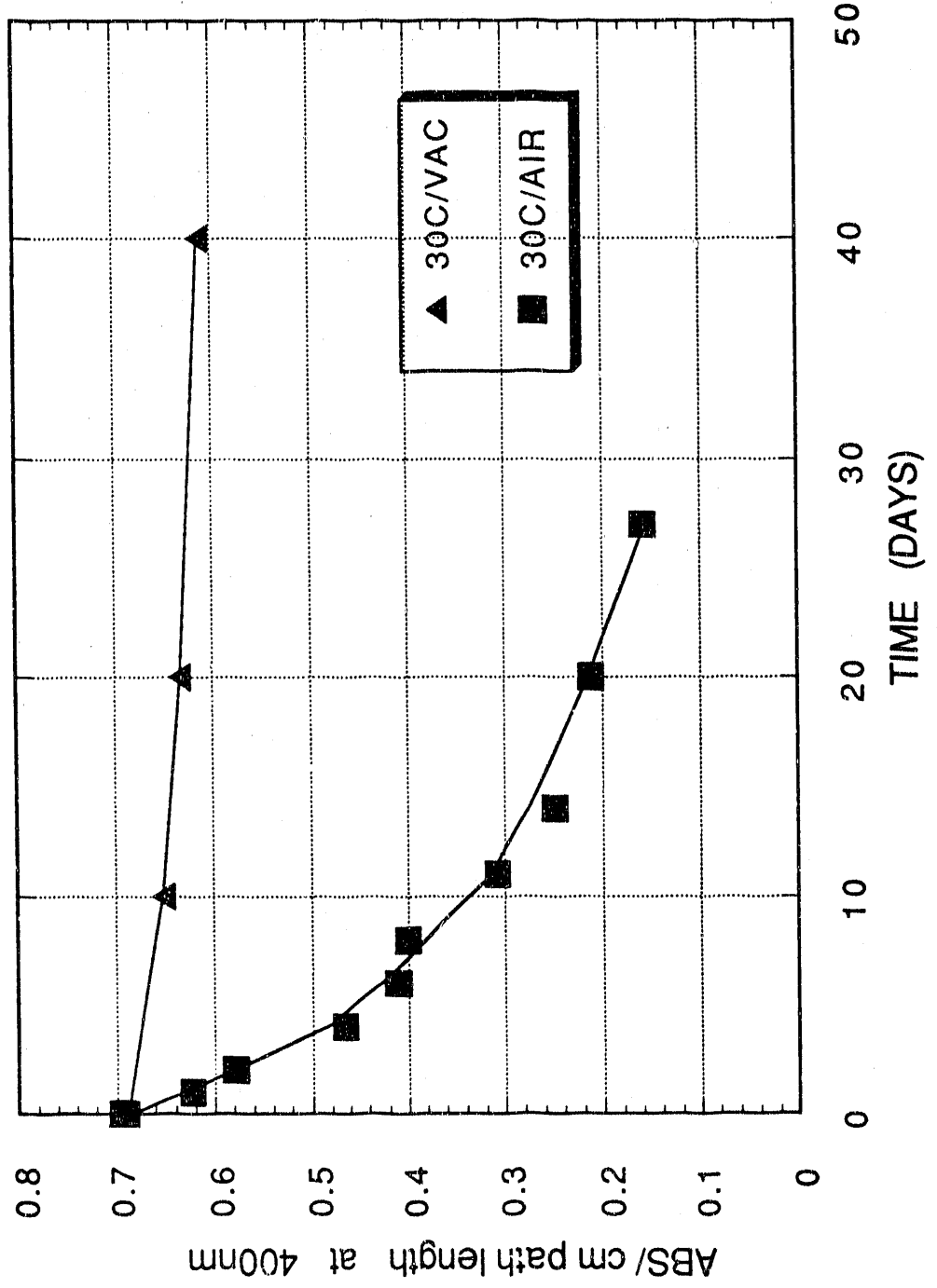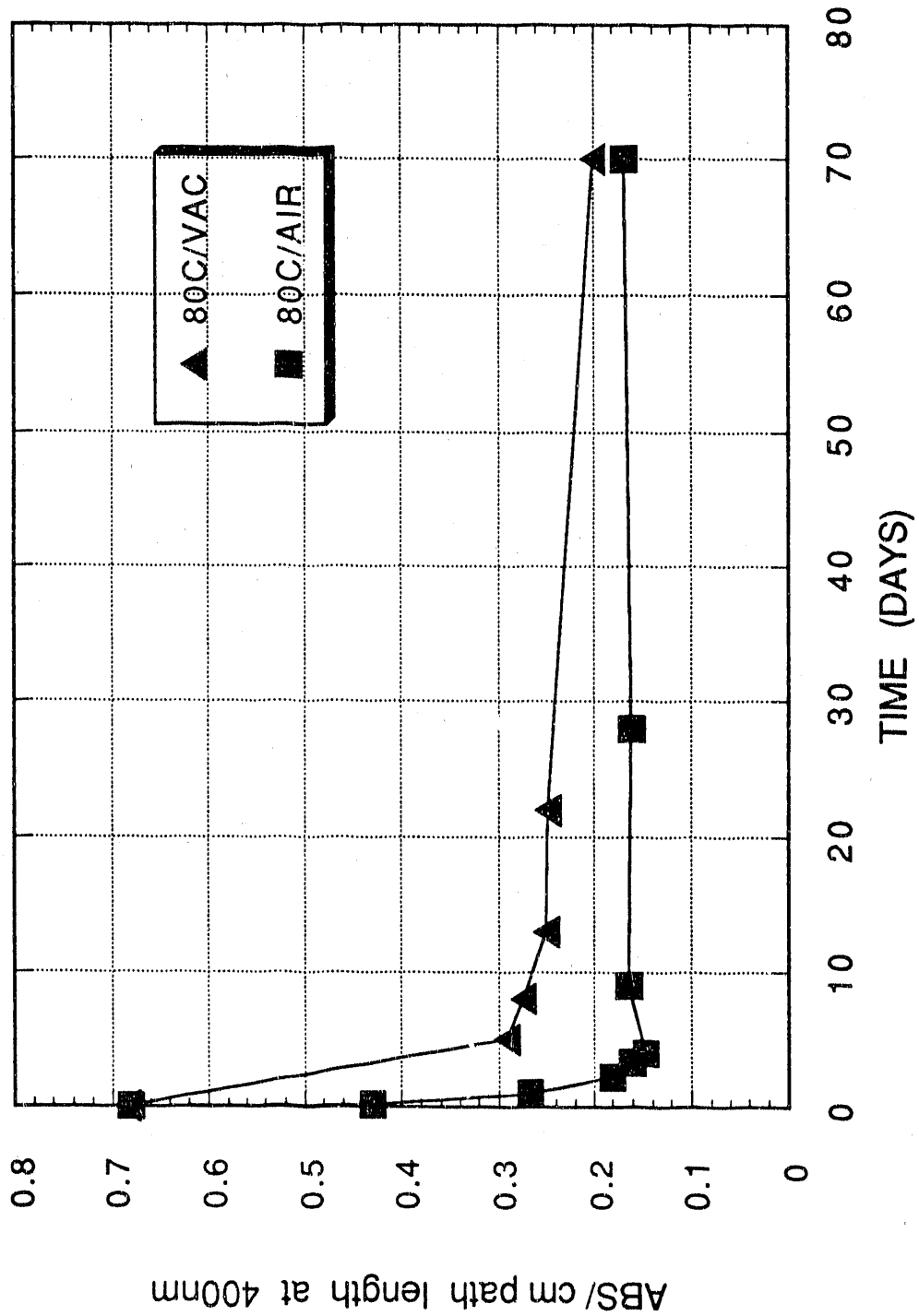
Figure 1

Figure 2

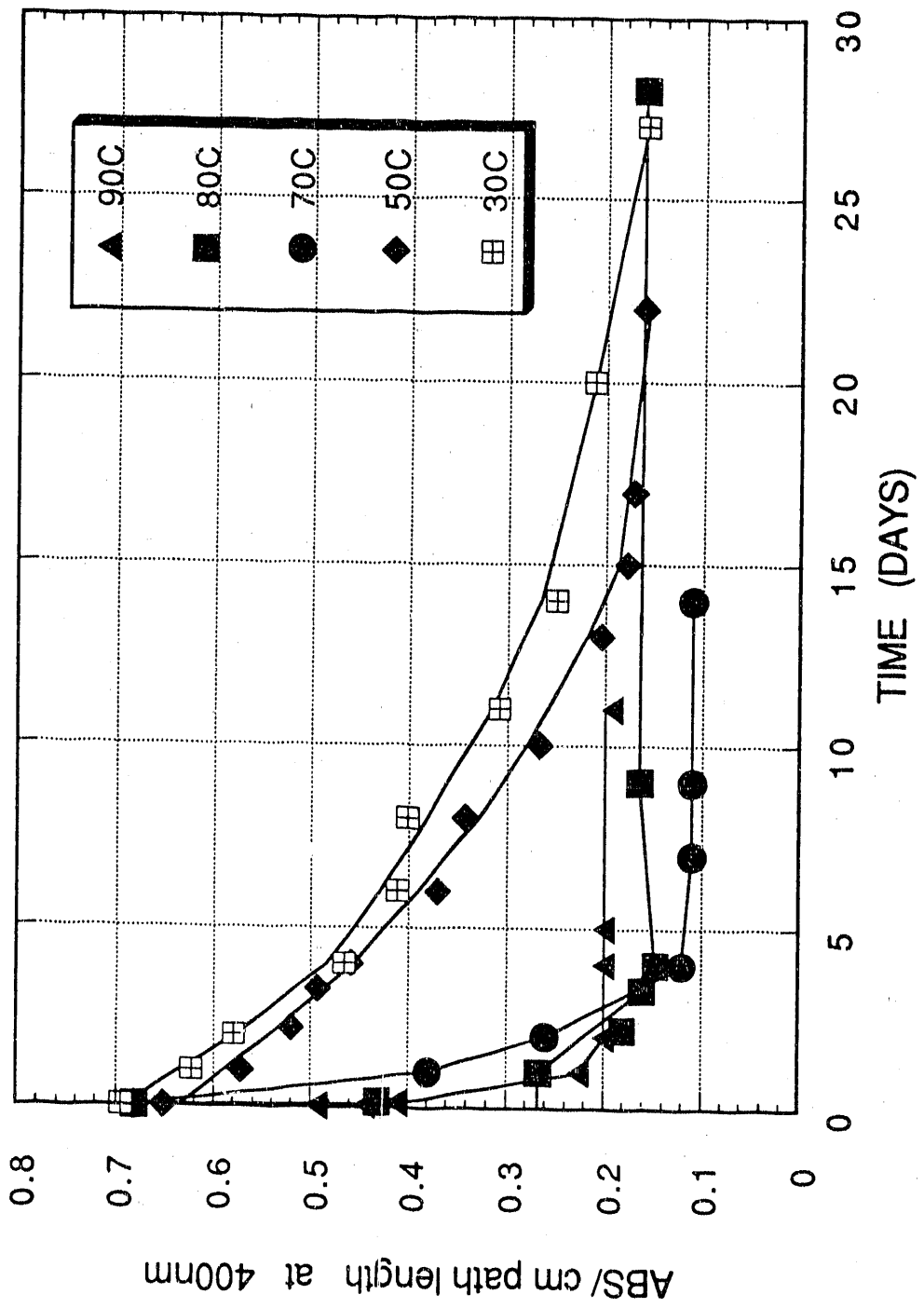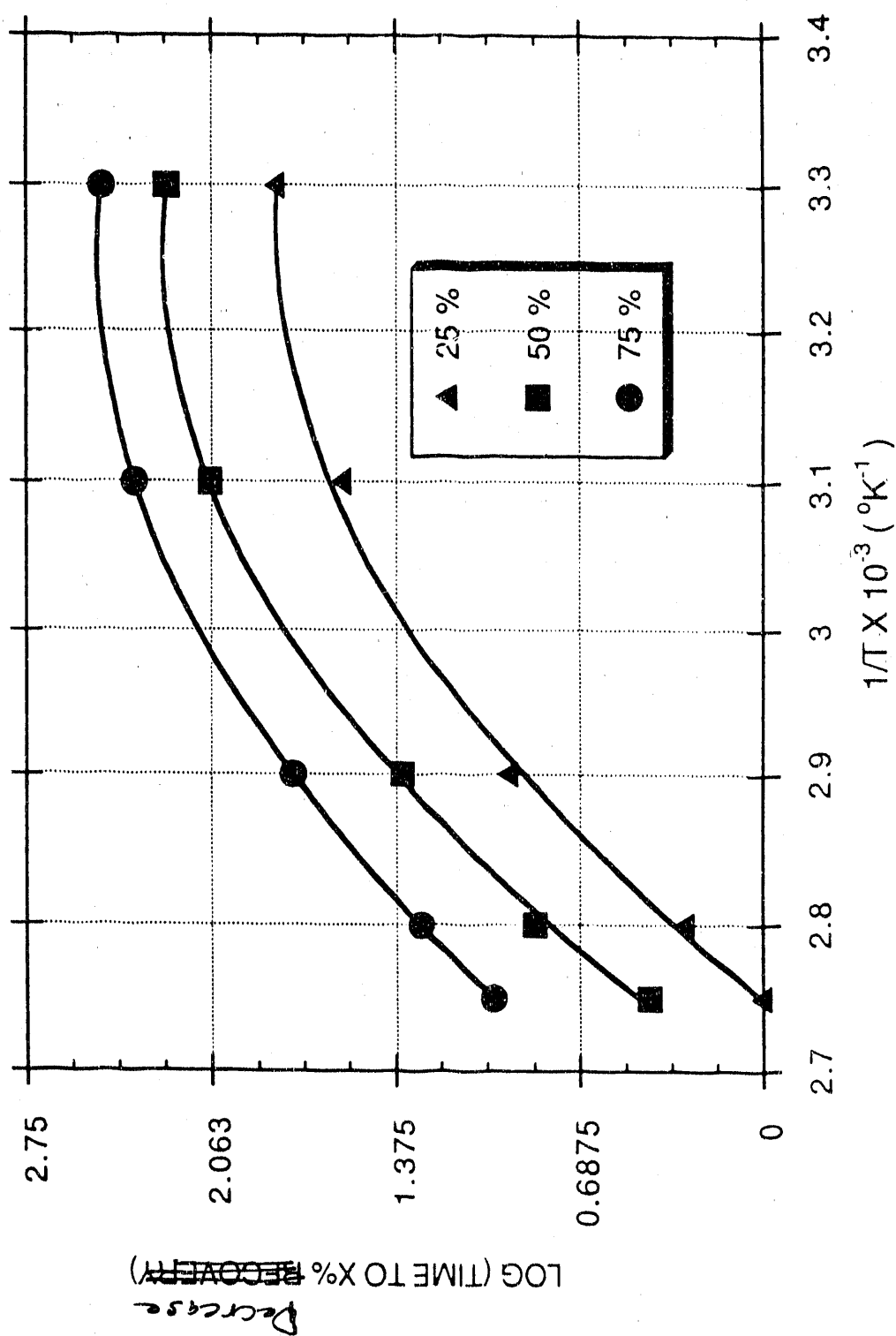ABS/ cm path length at 400nm

TIME (DAYS)

▲ 80C/VAC.
■ 80C/AIR

Figure 3

Figure 3

Y-axis: ABS/ cm path length at 400nm (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8)

X-axis: TIME (DAYS) (0, 5, 10, 15, 20, 25, 30)

Legend:
- 90C ▲
- 80C ■
- 70C ●
- 50C ◆
- 30C ⊞

Figure 4

END

DATE FILMED

12 / 03 / 90