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**ANALYTICAL STUDY OF A SOLAR DEGRADATION MODEL  
FOR THERMAL CONTROL MATERIALS  
AND SOME RAMIFICATIONS FOR ACCELERATED  
SOLAR RADIATION TESTING**

**A. M. Smith and A. Y. Lee  
ARO, Inc.**

**September 1968**

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## FOREWORD

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## ABSTRACT

A photoreaction-diffusion model for the solar degradation of thermal control materials is mathematically formulated and analyzed. The governing differential equation for the concentration of defect specie created in the material by radiation is derived, and an analytical solution is obtained for appropriate boundary conditions. From this solution for the concentration  $N_i$  of the  $i$ th-type defects, an analytical expression is derived for the number  $Q_i$  of the  $i$ th-type defects present in a material layer of depth  $x$  and unit irradiated area. These analytical relations are used to predict the radiation-induced increase in the absorption coefficient and absorption optical thickness of a hypothetical thermal control material exposed to damaging ultraviolet irradiance equal to that of the sun. The solutions for  $N_i$  and  $Q_i$  are also used to better define the environmental parameters which must be controlled during solar radiation testing of thermal control coatings. For example, the time-irradiance reciprocity principle often employed in accelerated solar testing is investigated by use of the aforementioned solutions and is found to be invalid for materials which degrade according to the photoreaction-diffusion model.

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## NOMENCLATURE

|            |                                                                                        |
|------------|----------------------------------------------------------------------------------------|
| D          | Diffusion coefficient                                                                  |
| erfc       | Complementary error function                                                           |
| $F_{-1}$   | Function defined in Eq. (8)                                                            |
| $G_{-1}$   | Function defined in Eq. (13)                                                           |
| I          | Radiant energy flux in photons/sec-cm <sup>2</sup>                                     |
| k          | Quantum yield, net number of defects created per absorbed photon                       |
| N          | Defect concentration                                                                   |
| n          | Number of different types of defect specie                                             |
| P          | Pressure                                                                               |
| Q          | Number of given type of defects present in a layer of depth x and unit irradiated area |
| R          | Reflectance                                                                            |
| T          | Temperature                                                                            |
| t          | Irradiation time                                                                       |
| x          | Local depth in material (see Fig. 1)                                                   |
| $\alpha$   | Absorptance                                                                            |
| $\gamma$   | Wavelength of damaging radiation                                                       |
| $\Delta$   | Change in an associated quantity                                                       |
| $\epsilon$ | Absorption coefficient                                                                 |
| $\lambda$  | Wavelength of radiation                                                                |
| $\sigma_a$ | Absorption cross section                                                               |
| $\tau$     | Absorption optical thickness                                                           |

## SUBSCRIPTS

|   |                        |
|---|------------------------|
| i | ith-type defect specie |
| o | Conditions at surface  |
| r | Reference value        |

|                     |                               |
|---------------------|-------------------------------|
| s                   | Solar value                   |
| x                   | Conditions at depth x         |
| $\gamma$            | Value at wavelength $\gamma$  |
| $\frac{d}{d\gamma}$ |                               |
| $\lambda$           | Value at wavelength $\lambda$ |

## SECTION I INTRODUCTION

In several previous studies of solar ultraviolet radiation effects on the zinc oxide (ZnO) pigments of thermal control coatings (Refs. 1 through 3), the investigators postulated that a photoreaction-diffusion damage mechanism causes the changes induced in the optical properties of the zinc oxide. They also suggested that the same type of mechanism causes the ultraviolet (UV)-induced damage observed for similar thermal control materials such as titanium dioxide (TiO<sub>2</sub>) and tin oxide (SnO<sub>2</sub>). In the work presented here, a photoreaction-diffusion model for the solar degradation of thermal control materials of this type is mathematically formulated and analyzed. That was the main objective of this study. There were several secondary objectives. One was to deduce a mathematical model which, when completely formulated, might permit the theoretical prediction of solar absorptance change of spacecraft thermal control surfaces as a function of irradiation time, irradiance level, and surface temperature. An example application of this model is given and used to predict the induced absorption coefficient and the increase in absorption optical thickness (Ref. 4) of a hypothetical thermal control material exposed to damaging UV irradiance equal to that of the sun. Another objective was to mathematically define the space environment conditions which should be simulated in laboratory tests of solar degradation effects on thermal control coatings. Among the environmental effects considered are the magnitude and spectral distribution of the damaging irradiance. For example, a theoretical investigation was made of the time-irradiance reciprocity principle used in accelerated solar radiation testing.

## SECTION II FORMULATION OF MATHEMATICAL MODEL FOR PHOTOREACTION- DIFFUSION DAMAGE MECHANISM

### 2.1 PHYSICAL MODEL OF DAMAGE MECHANISM

The photoreaction-diffusion damage mechanism postulated for the solar degradation of thermal control materials basically assumes that ultraviolet photons absorbed near the surface of the material possess sufficient energy to produce defects by photochemical reaction. The defects are created within the penetration depth of the damaging irradiation and then diffuse into the material bulk as the generation process continues at a decreasing rate near the surface. These defects will

absorb radiation in a spectrally dependent manner and hence may cause a significant increase in the parent material absorption properties at wavelengths in the visible and infrared. It is assumed that the change in monochromatic absorptance at these wavelengths is a function of the defect concentration in the parent material.

## 2.2 MATHEMATICAL MODEL AND DERIVATION OF GOVERNING EQUATIONS

A mathematical model for the UV degradation of thermal control materials may be formulated in the following manner. The material is assumed to be in a low pressure vacuum environment. Its surface, as shown in Fig. 1 (Appendix), is exposed to damaging irradiation of wavelengths lying within the differential wavelength interval  $d\gamma$ . The spectral irradiance at wavelength  $\gamma$  lying within  $d\gamma$  is denoted by  $I_{0,\gamma}$  and the total irradiance with  $d\gamma$  is given by  $I_{0,\gamma}d\gamma$ . Most of this incident radiant energy flux will be absorbed by the material within a depth of less than 0.1 micron from the surface and there generate by photoreaction  $k_{i,\gamma}$   $i$ th-type defects per absorbed photon. Figure 1 shows a cross section of this region of the material with a differential element  $dx$  located at a distance  $x$  from the surface ( $x = 0$ ). The concentration of the  $i$ th defect specie produced by damaging irradiation of wavelength  $\gamma$  and now present in  $dx$  at time  $t$  is denoted by  $N_{i,\gamma}d\gamma$ . Hence, the symbol  $N_{i,\gamma}$  can be interpreted as the concentration of the  $i$ th-type defects created per wavelength interval  $d\gamma$  by damaging radiation of wavelength  $\gamma$ . The net radiant energy flux downward at depth  $x$  is shown in Fig. 1 and denoted by  $I_{x,\gamma}d\gamma$ . Figure 1 also shows the diffusion fluxes  $-D_i \frac{\partial N_{i,\gamma}}{\partial x} d\gamma$  which exist in the material because of the presence of specie  $i$ . The symbol  $D_i$  denotes the diffusion coefficient of the  $i$ th defect specie in the parent material. It is assumed that there are no interactions between defects.

To derive the governing differential equations for the defect species concentrations, the law of mass conservation is assumed for the  $i$ th defect specie present in the differential element  $dx$  shown in Fig. 1. This yields the following partial differential equation

$$\frac{\partial N_{i,\gamma}}{\partial t} = -k_{i,\gamma} \frac{\partial I_{x,\gamma}}{\partial x} + \frac{\partial}{\partial x} \left( D_i \frac{\partial N_{i,\gamma}}{\partial x} \right) \quad (1)$$

where  $k_{i,\gamma}$  is designated as the  $i$ th defect quantum yield (Ref. 5) of the material for damaging radiation of wavelength  $\gamma$ . From this equation it can be seen that an analytical expression for  $I_{x,\gamma}$  is needed. For a

collimated radiant flux incident normally on the surface as shown in Fig. 1,\* the analytical relation for  $I_{x,\gamma}$ , assuming internal scattering to be negligible at wavelength  $\gamma$ , is

$$I_{x,\gamma} = (1 - R_\gamma) I_{0,\gamma} \exp(-\epsilon_\gamma x) \quad (2)$$

Hence,

$$\frac{\partial I_{x,\gamma}}{\partial x} = -(1 - R_\gamma) \epsilon_\gamma I_{0,\gamma} \exp(-\epsilon_\gamma x) \quad (3)$$

where  $R_\gamma$  and  $\epsilon_\gamma$  are, respectively, the reflectance and linear absorption coefficient for the parent material at the wavelength of the damaging radiation. Thus, from Eq. (1) with  $D_i$  independent of  $x$  and Eq. (3), the governing differential equation for the concentration of defect specie  $i$  is

$$\frac{\partial N_{i,\gamma}}{\partial t} = k_{i\gamma}(1 - R_\gamma) \epsilon_\gamma I_{0,\gamma} \exp(-\epsilon_\gamma x) + D_i \frac{\partial^2 N_{i,\gamma}}{\partial x^2} \quad (4)$$

If  $n$  different types of noninteracting defect specie are generated by damaging radiation of wavelength  $\gamma$ , there will be  $n$  different equations of the form of Eq. (4).

### 2.3 FACTORS POTENTIALLY INFLUENCING PHYSICAL

#### PARAMETERS $I_{0,\gamma}$ , $D_i$ , $\epsilon_\gamma$ , $R_\gamma$ , AND $k_{i\gamma}$

As noted by the subscript  $\gamma$ , the physical parameters  $I_{0,\gamma}$ ,  $\epsilon_\gamma$ ,  $R_\gamma$ , and  $k_{i\gamma}$  appearing in Eq. (4) can all be a function of the wavelength of the damaging radiation. These parameters along with  $D_i$  may also be a function of other factors. For example, the spectral irradiance  $I_{0,\gamma}$  might be a function of time,  $t$ . Potentially influencing factors for the other parameters are described below.

First, consider  $D_i$ , the diffusion coefficient of the  $i$ th defect specie. In general,  $D_i$  can depend on the temperature of the parent material, the concentration of the  $i$ th-type specie, and also the concentrations of any other types of specie which may be present. However, the dependence of  $D_i$  on concentration is usually negligible except at very high concentration levels (Ref. 6).

Next, consider the absorption coefficient and reflectance of the parent material at the wavelength of the damaging radiation,  $\epsilon_\gamma$  and  $R_\gamma$ , respectively. In general, it is felt that  $\epsilon_\gamma$  will not vary greatly with

---

\*In Fig. 1, it is assumed that the penetration depth of the damaging irradiation is much less than the material thickness.

location in the thermal control material and hence can be considered a constant with respect to  $x$ . This assumption is employed throughout the analysis. In addition, it is assumed that  $\epsilon_\gamma$  is not a function of time,  $t$ . This assumption physically means that although defects generated by damaging irradiation of wavelength  $\gamma$  can absorb radiation at that same wavelength, the resulting increase in absorption at  $\gamma$  is negligible relative to the initial absorption at  $\gamma$ . An illustrative problem presented later in the text will prove that this assumption is definitely valid. As for  $R_\gamma$ , the reflectance of the material at the wavelength of the damaging radiation, it also is assumed constant with respect to time,  $t$ .

Finally, it is necessary to consider  $k_{i\gamma}$ , the  $i$ th defect quantum yield. As noted earlier,  $k_{i\gamma}$  is a function of the wavelength of the damaging radiation (Ref. 5). It also can be a function of the radiant exposure of the surface. For thermal control materials of the type mentioned previously,  $k_{i\gamma}$  is likely to decrease rapidly as the radiant exposure of the surface increases (Ref. 7). It is speculated that  $k_{i\gamma}$  is also a function of the irradiance level of the damaging radiation (Ref. 8). In addition, the temperature of the material can affect  $k_{i\gamma}$  through its influence on secondary chemical processes taking place in the medium (Ref. 8). It is also possible that the pressure of the vacuum environment in which the material is located could affect  $k_{i\gamma}$ . This would happen if the pressure were not maintained at a low enough level to ensure that the concentration of any gases present was insufficient to influence the secondary chemical processes occurring in the material and on its surface (Ref. 7).

### SECTION III

#### AN ANALYTICAL EXPRESSION FOR THE CONCENTRATION OF $i$ th-TYPE DEFECT SPECIE

An analytical solution has been derived to Eq. (4) for  $I_0, \gamma$  constant with time and  $D_i$  independent of concentration. This solution was obtained under the following assumptions: (1) Initially there are no radiation-induced defects present in the material, (2) once the irradiation begins, none of the defects created by it will be lost through the irradiated surface ( $x = 0$ ), and (3) none of the radiation-induced defects will penetrate to the material boundary opposite the irradiated surface. Mathematically, these assumptions may be expressed as the following initial and boundary conditions on Eq. (4):

$$t = 0, N_{i,\gamma} = 0 \text{ for } x \geq 0$$

$$t > 0, \begin{cases} \left. \frac{\partial N_{i,\gamma}}{\partial x} \right|_{x=0} = 0 \\ N_{i,\gamma} \rightarrow 0 \text{ as } x \rightarrow \infty \end{cases} \quad (5)$$

The solution to Eq. (4), subject to the conditions stated in Eq. (5), has been obtained by operational techniques for  $k_{i\gamma}$  being the following function\* of radiant exposure,

$$k_{i\gamma} = k_{i\gamma r} \left( \frac{I_{0,\gamma} t}{I_{r,\gamma} t_r} \right)^{-1/2} \quad (6)$$

This solution to Eqs. (4), (5), and (6) takes the form

$$N_{i,\gamma} = \left( \frac{m_r}{D_i} \right)^{1/2} (1 - R_v) k_{i\gamma r} (I_{r,\gamma} I_{0,\gamma})^{1/2} F_{-1} \left[ 2\epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right] \quad (7)$$

where, noting  $\epsilon_\gamma x = 2\epsilon_\gamma (D_i t)^{1/2} \cdot \frac{x}{2(D_i t)^{1/2}}$

$$\begin{aligned} F_{-1} \left[ 2\epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right] &= \operatorname{erfc} \left[ \frac{x}{2(D_i t)^{1/2}} \right] \\ &- \exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \operatorname{erfc} [\epsilon_\gamma (D_i t)^{1/2}] \\ &+ \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \operatorname{erfc} \left[ \epsilon_\gamma (D_i t)^{1/2} - \frac{x}{2(D_i t)^{1/2}} \right] \\ &- \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t + \epsilon_\gamma x) \cdot \operatorname{erfc} \left[ \epsilon_\gamma (D_i t)^{1/2} + \frac{x}{2(D_i t)^{1/2}} \right] \end{aligned} \quad (8)$$

Figure 2 presents this solution for  $N_{i,\gamma}$  in the dimensionless form  $F_{-1}$  with  $\frac{x}{2(D_i t)^{1/2}}$  taken as the independent variable and  $2\epsilon_\gamma (D_i t)^{1/2}$  as a parameter. Note that  $F_{-1}$  is essentially the same for all values of  $2\epsilon_\gamma (D_i t)^{1/2} \geq 10$ .

An analysis of Eq. (7) indicates that it can be used to predict analytically the  $x$ -distribution of  $N_{i,\gamma}$  as a function of time,  $t$ , and the spectral irradiance,  $I_{0,\gamma}$ . Thus,  $N_{i,\gamma} d\gamma$ , the concentration of the  $i$ th defect specie generated by damaging radiation lying within the small wavelength interval  $d\gamma$ , can be predicted as a function of the same variables. For the case

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\*The subscript  $r$  on the symbols in Eq. (6) denotes reference values of the associated physical quantities.

where the material is irradiated with total radiation, the concentration of the  $i$ th defect specie,  $N_i$ , must be obtained by integrating  $N_i, \gamma$  of Eq. (7) over all damaging wavelengths since photons at other wavelengths besides  $\gamma$  may also produce defect specie of type  $i$ . The resulting expression for  $N_i$  is

$$N_i = \left( \frac{\pi I_r}{D_i} \right)^{\frac{1}{2}} \int_0^{\gamma_i(T)} (1 - R_\gamma) k_{i\gamma r} (I_{r,\gamma} I_{o,\gamma})^{\frac{1}{2}} F_{-1} \left[ 2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, \frac{x}{2 (D_i t)^{\frac{1}{2}}} \right] d\gamma \quad (9)$$

where  $\gamma_i$  is the largest wavelength at which incident photons will produce defect specie of type  $i$ . It is indicated that  $\gamma_i$  can be a function of the material temperature,  $T$ . This is because the wavelength at which the material absorption edge occurs may shift with temperature (Ref. 3). Note that the concentration of defects at the surface can be obtained directly from Eq. (9) and is

$$N_{i0} = \left( \frac{\pi I_r}{D_i} \right)^{\frac{1}{2}} \int_0^{\gamma_i} (1 - R_\gamma) k_{i\gamma r} (I_{r,\gamma} I_{o,\gamma})^{\frac{1}{2}} F_{-1} [2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, 0] d\gamma \quad (10)$$

$$F_{-1} [2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, 0] = 1 - \exp(\epsilon_\gamma^2 D_i t) \operatorname{erfc} [\epsilon_\gamma (D_i t)^{\frac{1}{2}}]$$

An analysis of Eq. (9) indicates that it can be used to predict the concentration distribution of  $i$ th-type defects created in the irradiated material by radiation of wavelengths lying within the wavelength interval  $(0, \gamma_i)$ . This can be done as a function of irradiation time and the magnitude and spectral distribution of the damaging irradiance. Such an expression is useful because the concentration  $N_i$  determines the increase in the spectral absorption coefficient of the material caused by the presence of  $i$ th-type defect specie.

#### SECTION IV NUMBER OF $i$ th-TYPE DEFECTS PRESENT IN A LAYER OF DEPTH $x$ AND UNIT IRRADIATED AREA

The number  $Q_i$  of  $i$ th-type defects present in a layer of depth  $x$  and unit irradiated area is mathematically related to the specie concentration  $N_i$  by the expression

$$Q_i = \int_0^x N_i dx' \quad (11)$$

Thus,  $Q_i$  is the integral of the specie concentration over depth  $x$  into the material. This integral has been evaluated for  $N_i$  given by Eq. (9) and the resulting expression is

$$Q_i = \left( \frac{\pi I_r}{D_i} \right)^{1/2} \int_0^{y_i(T)} \frac{(1 - R_\gamma) k_{i\gamma r} (I_{r,\gamma} I_{o,\gamma})^{1/2} G_{-1} \left[ 2\epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right]}{\epsilon_\gamma} dy \quad (12)$$

where

$$\begin{aligned} G_{-1} \left[ 2\epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right] = & \exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \operatorname{erfc} [\epsilon_\gamma (D_i t)^{1/2}] \\ & + 2\epsilon_\gamma (D_i t/\pi)^{1/2} \left( 1 - \exp\left(-\frac{x^2}{4 D_i t}\right) \right) + \epsilon_\gamma x \operatorname{erfc} \left[ \frac{x}{2 (D_i t)^{1/2}} \right] \\ & - \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \operatorname{erfc} \left[ \epsilon_\gamma (D_i t)^{1/2} - \frac{x}{2(D_i t)^{1/2}} \right] \\ & - \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t + \epsilon_\gamma x) \cdot \operatorname{erfc} \left[ \epsilon_\gamma (D_i t)^{1/2} + \frac{x}{2(D_i t)^{1/2}} \right] \quad (13) \end{aligned}$$

The function  $G_{-1}$  is displayed in Fig. 3 with  $\frac{x}{2(D_i t)^{1/2}}$  as the independent variable and  $2\epsilon_\gamma (D_i t)^{1/2}$  taken as a parameter. Note that  $G_{-1}$  can also be interpreted as

$$\begin{aligned} Q_{i,\gamma} / \left( \frac{\pi I_r}{D_i} \right)^{1/2} (1 - R_\gamma) k_{i\gamma r} (I_{r,\gamma} I_{o,\gamma})^{1/2} & \\ Q_{i,\gamma} \equiv \int_0^x N_{i,\gamma} dx & \quad (14) \end{aligned}$$

Equation (12) for  $Q_i$  can be used to predict the number of  $i$ th defects present in a material layer of depth  $x$  and unit irradiated area as a function of irradiation time and the magnitude and spectral distribution of the damaging irradiance. Such an expression is particularly useful since  $Q_i$  strongly influences the increase in absorption optical thickness resulting from the presence of  $i$ th-type defects. This increase in absorption optical thickness is one of the most important parameters governing the induced spectral absorptance of thermal control materials.

## SECTION V

### RELATION OF $N_i$ AND $Q_i$ TO THEORETICAL PREDICTIONS OF SOLAR ABSORPTANCE CHANGE

#### 5.1 GENERAL DISCUSSION OF MATHEMATICAL MODEL

In a mathematical model for predicting the solar absorptance change of spacecraft thermal control surfaces as a function of irradiation time and irradiance level, it is assumed that defects are generated in thermal control materials by absorption of high energy photons. If the defect concentration,  $N_i$ , and the number,  $Q_i$ , of  $i$ th-type defects per unit irradiated area could be predicted, then knowledge of the basic absorption properties of the defect would allow predictions of the increase in the material spectral absorption coefficient and absorption optical thickness. With the increases in absorption coefficient and absorption optical thickness determined, one would then solve the radiative transport equation with these variables present. The resulting solutions for the intensity and radiant flux could be used to predict the change in the material spectral absorptance as a function of irradiation time and irradiance level.

Obtaining analytical relations between the irradiation time and  $N_i$  and  $Q_i$  would be an important step in any model used for theoretically predicting the change in solar absorptance of thermal control materials. Another important step would be to develop an analytical relation between  $N_i$ ,  $Q_i$  and the spectral absorptance increase of these materials.

#### 5.2 ASSUMED RELATIONS BETWEEN $N_i$ , $Q_i$ AND THE INDUCED ABSORPTION PROPERTIES OF THERMAL CONTROL MATERIALS

Any attempt to develop analytical relations between  $N_i$ ,  $Q_i$  and the increase in spectral absorptance of thermal control materials will first require that theoretical expressions be established between the induced absorption properties of the material and  $N_i$  and  $Q_i$ . This study assumes that a linear relation exists between the induced absorption coefficient and the defect specie concentration. Thus, the increase in the monochromatic absorption coefficient of the parent material caused by the presence of  $i$ th-type defect specie,  $\Delta\epsilon_{\lambda i}$ , is the product of  $N_i$  and the absorption cross section for the  $i$ th defect specie at wavelength  $\lambda$ ,  $\sigma_{ai\lambda}$ .

$$\Delta\epsilon_{\lambda i} = \sigma_{ai\lambda} N_i \quad (15)$$

where  $\Delta\epsilon_{\lambda i}$  will be referred to, for conciseness, as the induced monochromatic absorption coefficient of the material for type  $i$  defect specie.

When  $n$  different types of defect specie are present, the total induced absorption coefficient of the material, at wavelength  $\lambda$ ,  $\Delta\epsilon_\lambda$ , is assumed to be the linear sum of the effect of each type of specie, or

$$\Delta\epsilon_\lambda = \sum_{j=1}^n \Delta\epsilon_{\lambda j} = \sum_{j=1}^n \sigma_{ai\lambda} N_i \quad (16)$$

This equation and the assumption on which it is based ignore any interaction effects that might occur between different defect species.

Once a relation between  $\Delta\epsilon_\lambda$  and  $N_i$  is specified, it is possible to establish a connection between the increase in monochromatic absorption optical thickness,  $\Delta\tau_\lambda$ , and  $N_i$ . For conciseness,  $\Delta\tau_\lambda$  will be referred to as the induced absorption optical thickness of the material at wavelength  $\lambda$ . An analytical expression between  $\Delta\tau_\lambda$  and  $N_i$  is obtained from Eq. (16) and the definition of  $\Delta\tau_\lambda$ ,

$$\Delta\tau_\lambda = \int_0^x \Delta\epsilon_\lambda dx = \sum_{j=1}^n \sigma_{ai\lambda} \int_0^x N_i dx' = \sum_{j=1}^n \sigma_{ai\lambda} Q_i \quad (17)$$

Equation (17) illustrates the relation between  $\Delta\tau_\lambda$  and  $N_i$ , or  $Q_i$ . This relation, of course, implicitly contains the assumptions on which Eqs. (15) and (16) were based. Note that the induced absorption optical thickness resulting from the presence of an  $i$ th-type defect specie,  $\Delta\tau_{\lambda i}$ , is given by the expression

$$\Delta\tau_{\lambda i} = \int_0^x \Delta\epsilon_{\lambda i} dx' = \sigma_{ai\lambda} \int_0^x N_i dx' = \sigma_{ai\lambda} Q_i \quad (18)$$

## SECTION VI

### THEORETICAL PREDICTIONS FOR THE SOLAR-INDUCED ABSORPTION PROPERTIES OF A HYPOTHETICAL THERMAL CONTROL MATERIAL

A simple example will now be given to illustrate the application of the mathematical model just described. Assume a hypothetical material to be exposed to a UV irradiance whose magnitude and spectral distribution is equal to that of the sun at one astronomical unit (Ref. 9). During this exposure the material is located in a high vacuum and maintained at a constant temperature of approximately 300°K. The spectral (ultraviolet and visible) absorption coefficient of this material prior to exposure is assumed to be identical to the one shown in Fig. 4. Note that  $\epsilon_\gamma$ , the absorption coefficient in the damaging wavelength interval ( $0 \leq \gamma \leq 385$  nm) is taken constant at a value of  $3 \times 10^5 \text{ cm}^{-1}$ . In turn,

$R_\gamma$ , the spectral reflectance of the material in this interval, is assumed constant at a value of 0.07.

## 6.1 CONCENTRATION OF THE $i$ th DEFECT SPECIE, $N_i$

Equation (9) is used to calculate the concentration distribution of the  $i$ th defect specie. This specie is assumed to have a diffusion coefficient in the parent material of  $D_i = 1.5 \times 10^{-13} \text{ cm}^2/\text{sec}$ . The reference UV spectral irradiance in Eq. (9),  $I_r, \gamma$ , is taken to be that of the sun,  $I_s, \gamma$ , and the reference irradiation time,  $t_r$ , is chosen as one second. For these reference conditions, the spectrally weighted (for solar irradiance  $I_s, \gamma$ )  $i$ th defect quantum yield

$$\bar{k}_{is} = \int_0^{\gamma_i} k_{i\gamma r} I_{s,\gamma} d\gamma / \int_0^{\gamma_i} I_{s,\gamma} d\gamma \quad (19)$$

is assumed to be  $10^{-4}$  defects per photon. Figure 5 presents the defect concentration distribution in the parent material with irradiation time shown as a parameter. It is seen that adjacent to the surface of the material there is a layer of high and essentially uniform concentration. As a result of diffusion, the width of this layer increases slowly with time. Note that the defect concentration increases rapidly with irradiation time until a limiting value is reached.

Figure 6 presents the time dependence of the defect concentration at various depths in the material. The curve labeled  $x = 0$  is the defect surface concentration,  $N_{i0}$ , as given by Eq. (10). Note how rapidly the surface concentration increases during the early stages of irradiation. After this large initial increase, the surface concentration is essentially constant with time. Similar behavior is observed for the defect concentration at a depth of 1.0 micron. At a depth of 10 microns, the rate of defect concentration increase is much less during the initial stages of radiation. However, after this initial radiation stage, the rate of concentration increase at 10 microns is greater than that of the depths closer to the surface ( $x = 0, 1.0\mu$ ). Hence, the defect concentration at all three depths will eventually become equal.

## 6.2 NUMBER OF $i$ th DEFECT SPECIE PER UNIT IRRADIATED AREA

In Fig. 7, the number of  $i$ th-type defects,  $Q_i$ , present per unit irradiated area from the surface to depth  $x$  is displayed as a function of depth into the material with irradiation time as a parameter. This figure shows that for a given irradiation time,  $Q_i$  increases sharply

with depth into the material until a certain depth is reached. At this depth,  $Q_i$  becomes constant and remains so for greater depths. This constant value of  $Q_i$  represents the total number of  $i$ th-type defects created in the material per unit irradiated area during the specified irradiation time. The depth at which this constant value of  $Q_i$  is achieved increases with irradiation time because of defect diffusion. Note that for a layer of given depth,  $Q_i$  increases sharply with irradiation time until some limiting or saturation value is attained.

### 6.3 INDUCED ABSORPTION COEFFICIENT, $\Delta\epsilon_{\lambda i}$

Figure 8 presents the increase in the absorption coefficient of the parent material at a depth of one micron caused by the presence of  $i$ th-type defects. Irradiation time is shown as a parameter, and the absorption coefficient of the material prior to irradiation is also indicated. In computing  $\Delta\epsilon_{\lambda i}$ , Eqs. (9) and (15) were used. For illustrative purposes, the  $i$ th-specie absorption cross section,  $\sigma_{ai\lambda}$ , was taken as  $2 \times 10^{-17} \text{ cm}^2$  and assumed to be independent of wavelength. From Fig. 8, it is seen that the induced absorption coefficient,  $\Delta\epsilon_{\lambda i}$ , increases rapidly with irradiation time and at approximately 10 hr equals the initial absorption coefficient of the parent material in the visible wavelength range,  $2 \times 10^1 \text{ cm}^{-1}$ . At about 2000 hr, the induced absorption coefficient reaches a saturation value of approximately 10 times the visible absorption coefficient of the parent material prior to irradiation. However, in the damaging wavelength interval (0, 385 nm), the induced absorption coefficient is less than 1/1000 of the absorption coefficient of the parent material prior to irradiation. Thus,  $\Delta\epsilon_{\gamma i}/\epsilon_{\gamma}$  is negligible and the change in the absorption coefficient of the parent material in the damaging wavelength range can be ignored. This, of course, validates the assumption made previously about  $\epsilon_{\gamma}$  not varying with irradiation time.

### 6.4 INDUCED ABSORPTION OPTICAL THICKNESS, $\Delta\tau_{\lambda i}$

Figure 9 displays  $\Delta\tau_{\lambda i}$ , the increase in absorption optical thickness of the parent material caused by the presence of  $i$ th-type defect specie. It is presented as a function of irradiation time, with depth into the material taken as a parameter. Equations (12) and (18) were used in evaluating  $\Delta\tau_{\lambda i}$ . As shown in Fig. 9,  $\Delta\tau_{\lambda i}$  increases very rapidly during the first few hours of irradiation. After this period,  $\Delta\tau_{\lambda i}$  continues to increase with irradiation time but at a much slower rate. Most all of the induced absorption optical thickness  $\Delta\tau_{\lambda i}$  occurs within

50 microns of the surface. For irradiation times of 2000 hr and greater, this value of  $\Delta\tau_{\lambda i}$  is approximately 0.2.

## SECTION VII

### USE OF THE $N_i$ RELATION TO MATHEMATICALLY DEFINE THE ENVIRONMENTAL PARAMETERS INVOLVED IN SOLAR RADIATION TESTING OF THERMAL CONTROL COATINGS

As mentioned in the introduction, one of the objectives of this study is to mathematically define the space environment conditions which should be simulated in laboratory tests of solar radiation effects on thermal control coatings. Since the solar-induced optical properties ( $\Delta\epsilon_\lambda$ ,  $\Delta\tau_\lambda$ ,  $\Delta\alpha_\lambda$ )\* are ultimately a function of

$$N_i(Q_i = \int_0^x N_i dx)$$

Eq. (9) will be used to accomplish this objective. Thus, with  $I_{r,\gamma}$  taken as the UV spectral irradiance of the sun,  $I_{s,\gamma}$  and  $t_r$  as some reference solar irradiation time,  $t_s$ ,

$$N_i = \left( \frac{\pi t_s}{D_i(T)} \right)^{\frac{1}{2}} \int_0^{\gamma_i(T)} [1 - R_\gamma] k_{i\gamma s}(P, T) [I_{s,\gamma} I_{o,\gamma}]^{\frac{1}{2}} F_{-1} \left[ 2\epsilon_\gamma (D_{it})^{\frac{1}{2}}, \frac{x}{2(D_{it})^{\frac{1}{2}}} \right] d\gamma \quad (20)$$

where  $k_{i\gamma s}$  is the value of  $k_{i\gamma r}$  for the condition  $I_{r,\gamma} = I_{s,\gamma}$ ,  $t_r = t_s$ .

From Eq. (20), it can be seen that  $k_{i\gamma s}$ ,  $R_\gamma$ , and  $\epsilon_\gamma$  can all depend on the wavelength of the damaging irradiation and each influences the value of  $N_i$ . Thus, in laboratory tests of solar degradation effects on thermal control coatings, the spectral distribution of the irradiance on the surface,  $I_{o,\gamma}$ , should closely simulate that of the sun for the wavelength range  $(0, \gamma_i)$ . This means that the resultant spectral distribution of the energy source and the intervening optics (e. g., windows and filters) between it and the test surface should closely approximate that of the sun over the interval  $(0, \gamma_i)$ .

It is also seen in Eq. (20) that the magnitude of the spectral irradiance  $I_{o,\gamma}$  influences the value of  $N_i$ . Thus, for solar radiation testing of thermal control coatings, both the magnitude and spectral distribution of the irradiance on the surface should be nearly equal to that of the

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\* $\Delta\alpha_\lambda$  is defined as the induced spectral absorptance of the parent material.

sun in the wavelength interval  $(0, \gamma_i)$ . The ramifications of this conclusion for accelerated solar radiation testing are discussed in the next section.

Equation (20) also shows that  $N_i$  can depend on the temperature of the material during irradiation because  $D_i$ ,  $k_{i\gamma_s}$ , and the wavelength at which the material absorption edge occurs,  $\gamma_i$ , all vary with temperature. Thus, the material temperature should be controlled during a solar radiation test and maintained at a value near that expected in flight.

Finally, it is seen that  $N_i$  of Eq. (20) can also be influenced by the pressure of the vacuum environment in which it is located. As was discussed earlier, this is because of the potential dependence of  $k_{i\gamma}$  on the concentration level of gases in the surrounding environment. Thus, solar radiation testing of thermal control coatings must be performed in a high vacuum and measurements of  $\Delta\epsilon_\lambda$ ,  $\Delta\tau_\lambda$ , and  $\Delta\alpha_\lambda$  must be made in place.

#### SECTION VIII VALIDITY OF THE TIME-IRRADIANCE RECIPROCITY PRINCIPLE USED IN ACCELERATED SOLAR RADIATION TESTING

The discussion in the previous section on solar radiation testing of thermal control coatings indicates that to obtain reliable data for  $\Delta\alpha_\lambda$ , both the magnitude and spectral distribution of the irradiance on the surface should closely approximate that of the sun in the wavelength interval  $(0, \gamma_i)$ . This conclusion, of course, questions the reliability of data obtained in accelerated solar radiation testing where, to save time, it is assumed that the same test results for  $\Delta\alpha_\lambda$  can be obtained by substituting high-intensity UV source irradiance for irradiation time. The validity of this time-irradiance reciprocity principle is investigated in the following paragraphs by use of the equations developed earlier in the study.

Since the induced spectral absorptance of the parent material caused by the presence of defect specie  $i$ ,  $\Delta\alpha_{\lambda i}$ , is a function of the induced absorption coefficient  $\Delta\epsilon_{\lambda i} = f(N_i)$  and the induced absorption optical thickness  $\Delta\tau_{\lambda i} = f(Q_i)$ , Eqs. (15), (9), (18), and (12) will be used to accomplish the aforementioned investigation. It will be assumed that if the reciprocity principle does not hold for  $\Delta\epsilon_{\lambda i}(N_i)$  and  $\Delta\tau_{\lambda i}(Q_i)$ , it will not hold for  $\Delta\alpha_{\lambda i}$ . The properties of the parent material and the  $i$ th defect specie will be taken the same as those used in the previous

illustrative example. Ultraviolet irradiance levels of 1 and 10 "Suns" will be used. The spectral distribution of both irradiances in the wavelength interval ( $0, \gamma_i = 385 \text{ nm}$ ) is assumed to be that of the sun (Ref. 9). Figure 10 presents the surface ( $x = 0$ ) value of the induced absorption coefficient  $\Delta\epsilon_{\lambda_i}$  as a function of radiant exposure in Equivalent Sun Hours (ESH) with UV irradiance level in "Suns" shown as a parameter. For a given radiant exposure,  $\Delta\epsilon_{\lambda_i}$  is seen to be significantly greater at an irradiance of 10 "Suns" than at 1 "Sun" irradiance. If the time-irradiance reciprocity principle held, there would be no effect of irradiance level on  $\Delta\epsilon_{\lambda_i}$ , and only a single curve equal to the one "Sun" value of  $\Delta\epsilon_{\lambda_i}$  would appear in Fig. 10.

Figure 11 displays the value of  $\Delta\epsilon_{\lambda_i}$  at a depth of 1 micron in the material. It is seen that for a radiant exposure less than 60 ESH,  $\Delta\epsilon_{\lambda_i}$  at 1 "Sun" irradiance is greater than  $\Delta\epsilon_{\lambda_i}$  at a UV irradiance level of 10 "Suns." However, for a radiant exposure greater than 60 ESH,  $\Delta\epsilon_{\lambda_i}$  at 10 "Suns" exceeds  $\Delta\epsilon_{\lambda_i}$  at 1 "Sun", which was the expected result for all values of ESH. This weird behavior of  $\Delta\epsilon_{\lambda_i}$  with irradiance and radiant exposure in ESH is a result of defect diffusion. It can be explained by noting that for an equivalent number of sun hours of radiant exposure a defect generated by 1 "Sun" irradiance can diffuse into the material 10 times as long as a defect created by an irradiance of 10 "Suns." Thus, for depths in the material which are somewhat greater than the penetration depth of the damaging irradiation, the defect concentration  $N_i$  and hence  $\Delta\epsilon_{\lambda_i}$  will be larger for the lower irradiance level until some particular ESH of radiant exposure is reached.

In Fig. 12, the induced absorption optical thickness  $\Delta\tau_{\lambda_i}$  for a layer of 10 microns depth is presented as a function of radiant exposure in ESH. The results for UV irradiance levels of 1 and 10 "Suns" are presented. It is seen that  $\Delta\tau_{\lambda_i}$  is larger at the 10 "Sun" irradiance for values of ESH  $> 200$ . For ESH  $< 200$ ,  $\Delta\tau_{\lambda_i}$  is the same for both irradiance levels. The results shown in this figure, Fig. 12, in conjunction with those presented in Figs. 10 and 11, indicate that the time-irradiance reciprocity principle does not hold for materials with optical properties that change according to the photoreaction-diffusion model of solar degradation.

## SECTION IX CONCLUSIONS

A partial differential equation has been derived for the concentration of the  $i$ th defect specie generated in thermal control materials by a photoreaction-diffusion mechanism of solar degradation. This equation

has been solved to yield an analytical solution for the defect specie concentration,  $N_i$ . An analytical expression has also been obtained for the number  $Q_i$  of  $i$ th-type defects present in a layer of arbitrary depth and unit irradiated area. Thus, a theoretical model for solar degradation of thermal control materials can be formulated in mathematical terms and analytical solutions can be obtained for both the concentration and number of  $i$ th defects generated by solar UV radiation. These solutions may be used to calculate both the concentration and number of defects created in thermal control materials as a function of irradiation time and spectral irradiance. This is a significant step toward theoretically predicting the solar-induced optical absorptance change of spacecraft surfaces as a function of time since the induced absorptance change is ultimately a function of defect concentration.

The solutions for  $N_i$  and  $Q_i$  can also be used to better define the environmental parameters that must be controlled during solar radiation testing of thermal control coatings. For example, the equations for  $N_i$  and  $Q_i$  show that both the magnitude and spectral distribution of the solar simulator irradiance on the coating surface should be nearly equal to that of the sun in the wavelength interval  $(0, \gamma_i)$ . In addition, these equations indicate that the temperature of the irradiated material should be controlled during a solar radiation test and maintained at a value near that expected in flight. Also, the relations for  $N_i$  and  $Q_i$  show that solar radiation testing of thermal control coatings must be performed in a high vacuum, and measurement of radiative properties should be made in place. Finally, these solutions indicate that the time-irradiance reciprocity principle used in accelerated solar testing is invalid for materials which degrade according to the photoreaction-diffusion model.

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**APPENDIX  
ILLUSTRATIONS**

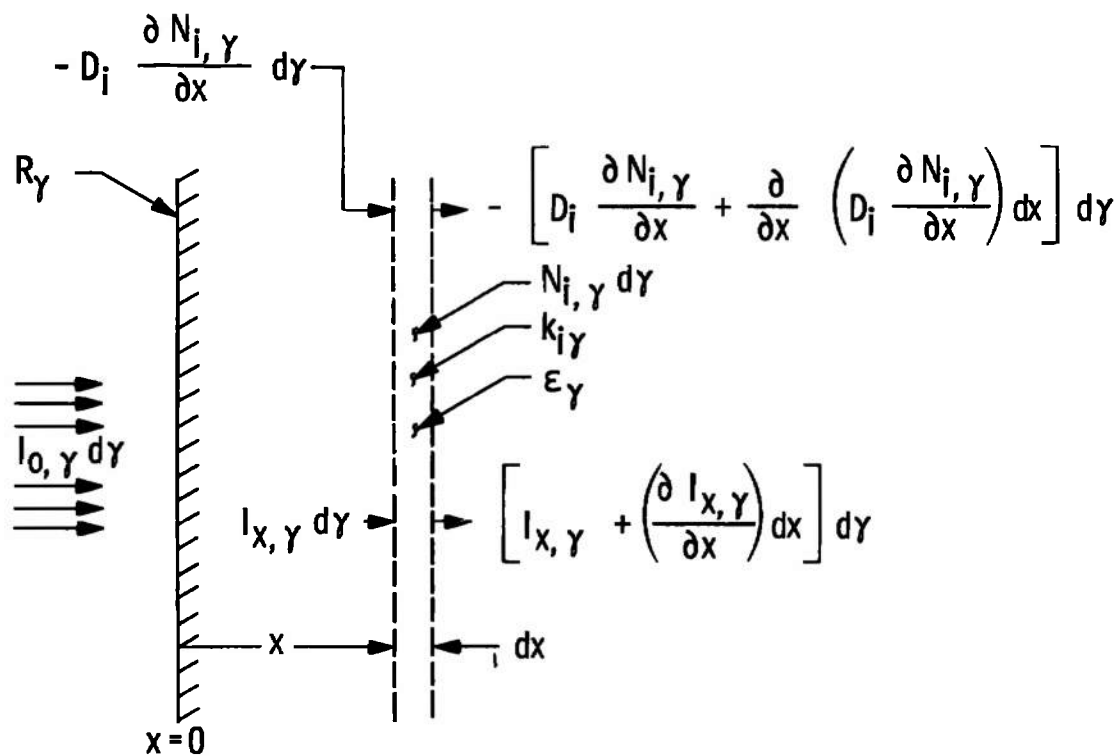


Fig. 1 Mathematical Model for Solar Degradation of Thermal Control Materials  
by Photoreaction-Diffusion Damage Mechanism

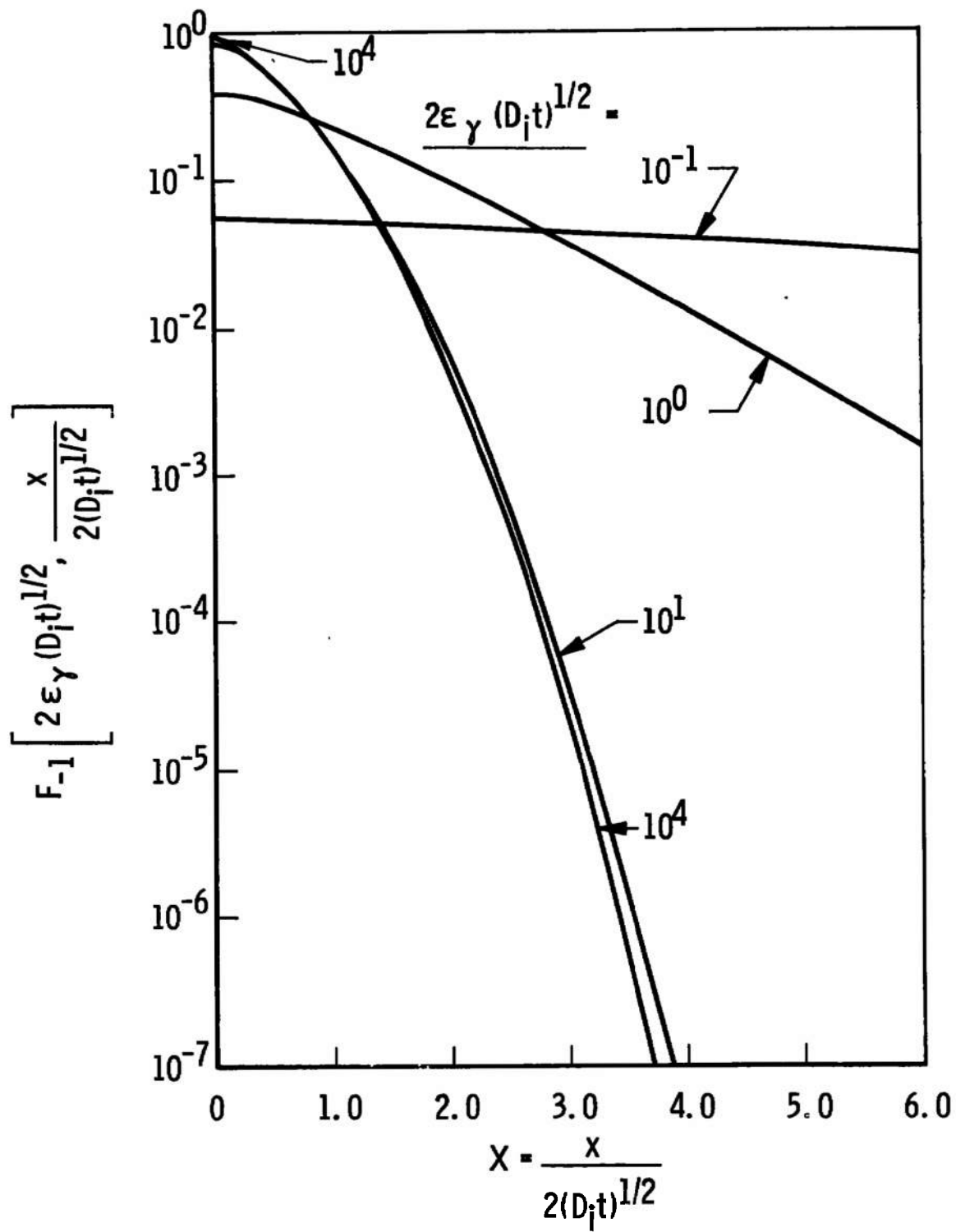


Fig. 2 Dimensionless Function  $F_{-1} \left[ 2\epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right]$

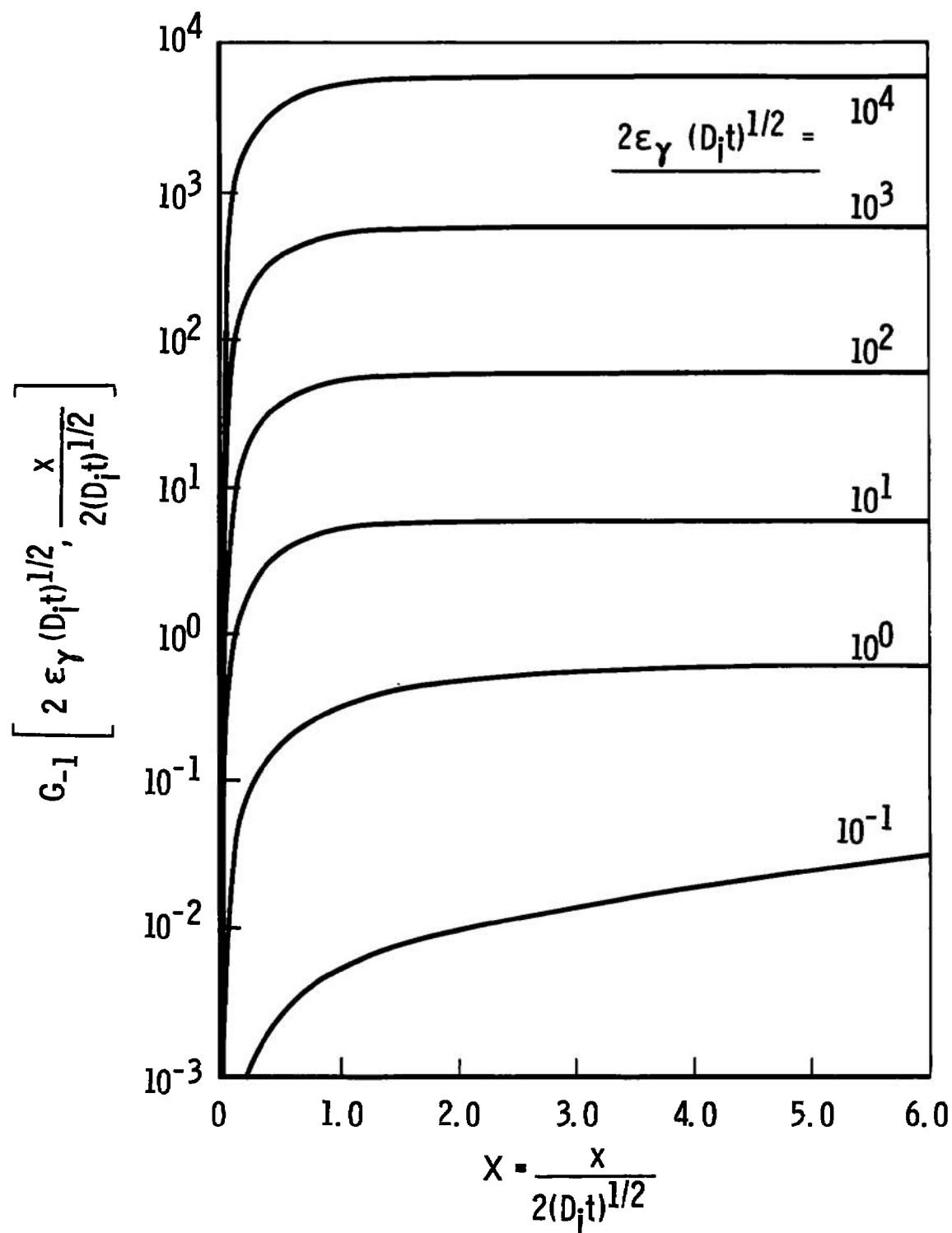


Fig. 3 Dimensionless Function  $G_{-1} \left[ 2 \epsilon_\gamma (D_i t)^{1/2}, \frac{x}{2(D_i t)^{1/2}} \right]$

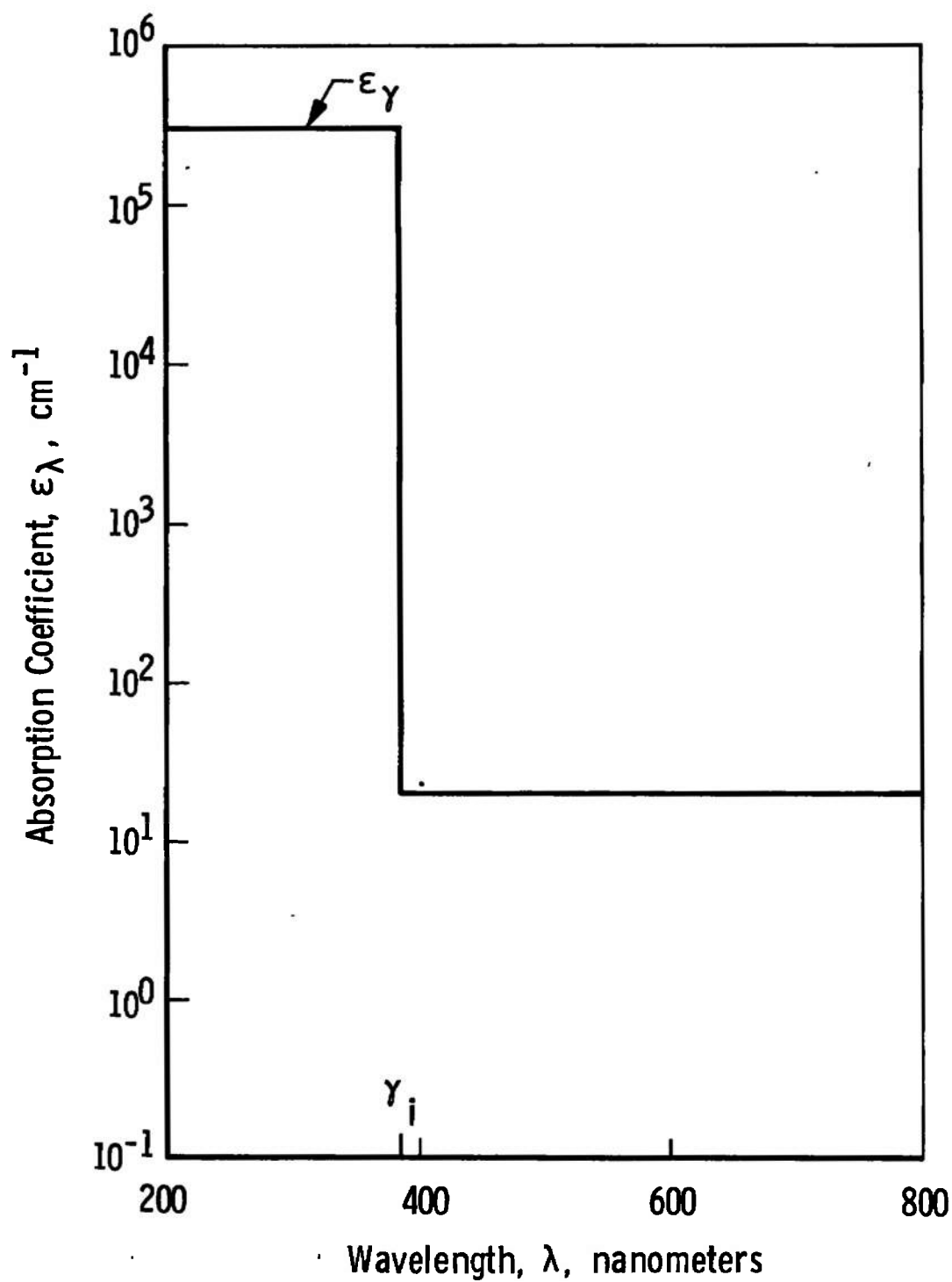


Fig. 4 Spectral (Ultraviolet and Visible) Absorption Coefficient of Parent Material prior to Irradiation

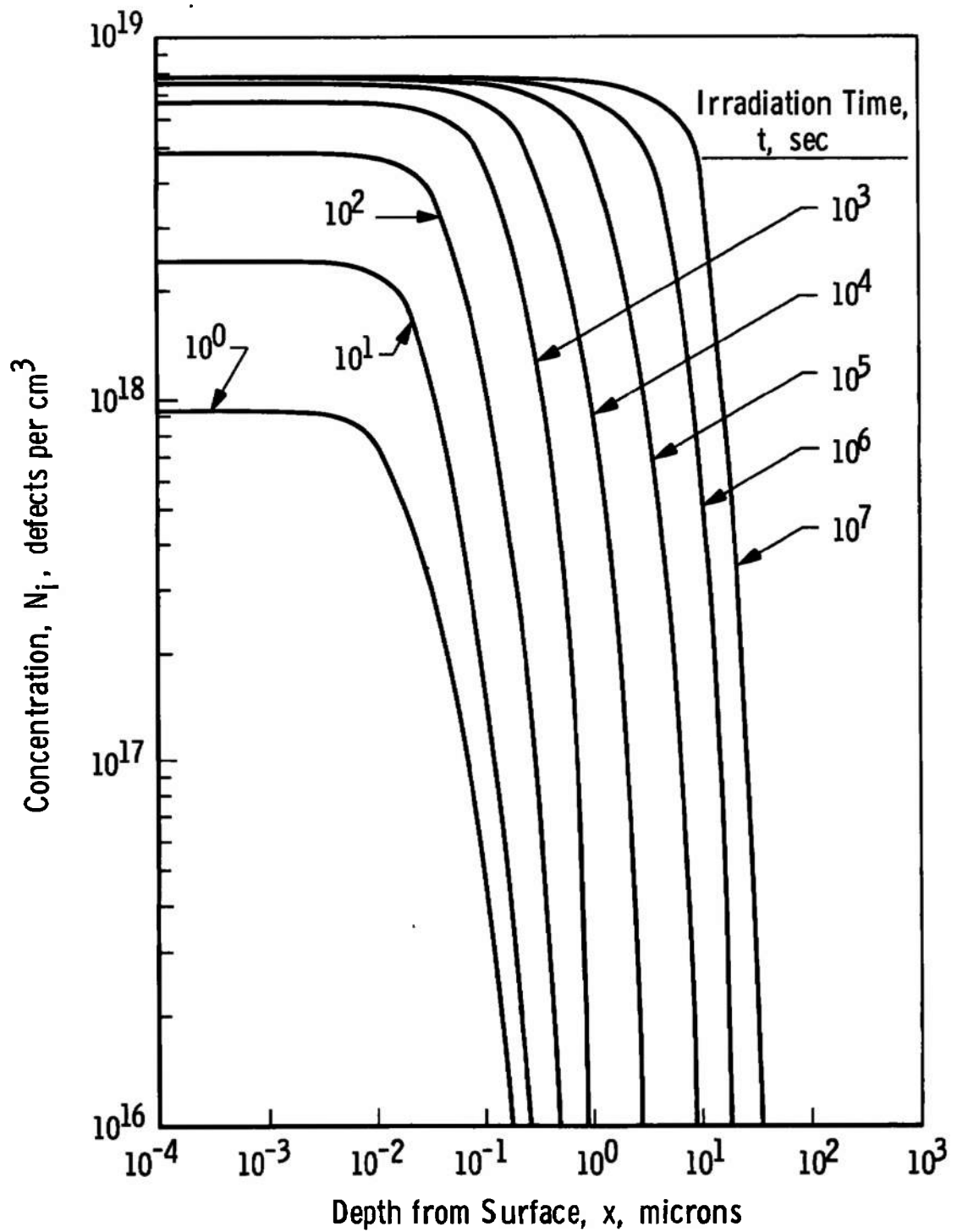


Fig. 5 Concentration Distribution of ith-Type Defects in Parent Material for an Ultraviolet Irradiance equal to that of the Sun

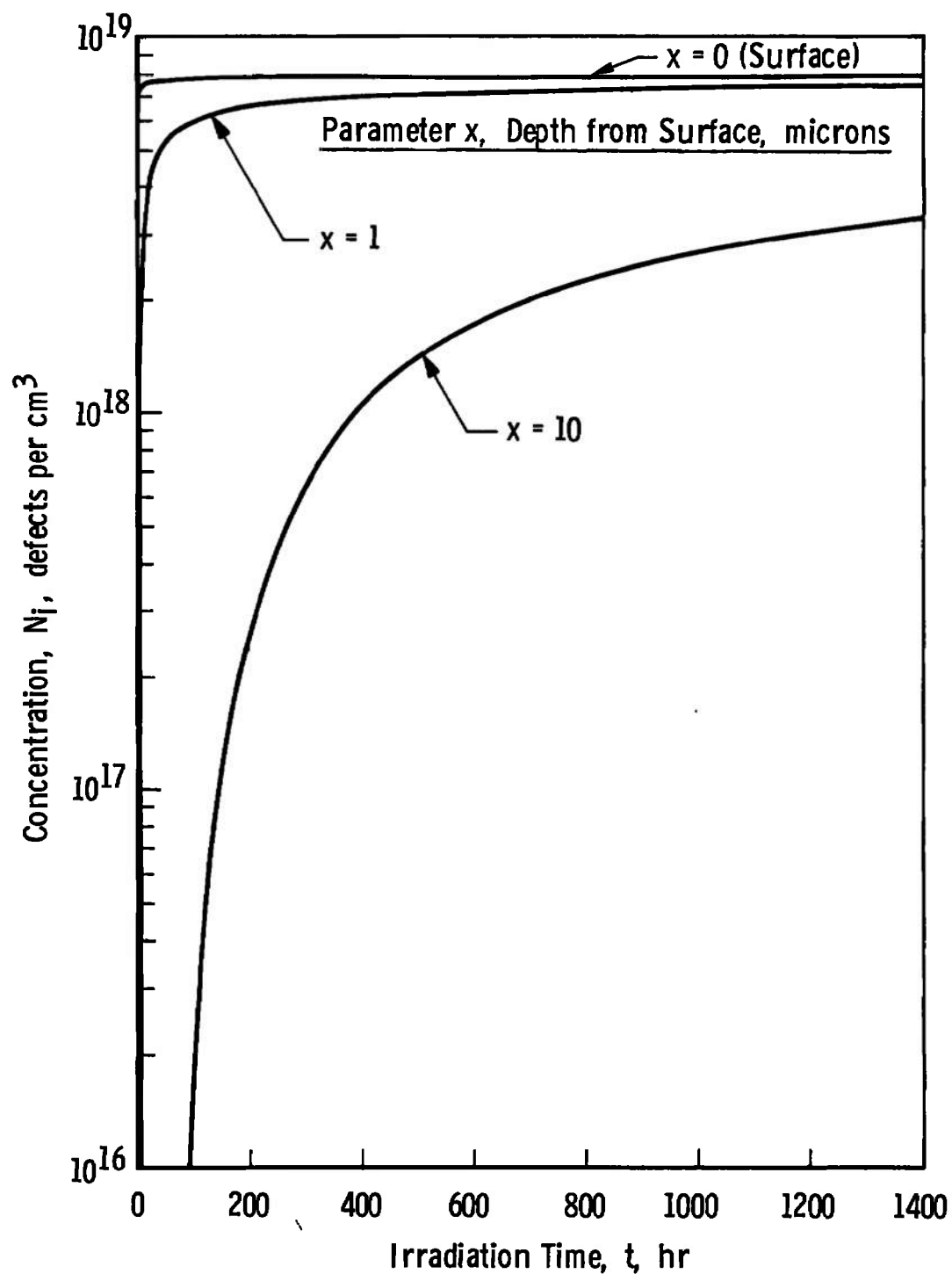


Fig. 6 Concentration of ith-Type Defects as a Function of Time Parent Material is Exposed to an Ultraviolet Irradiance equal to that of the Sun

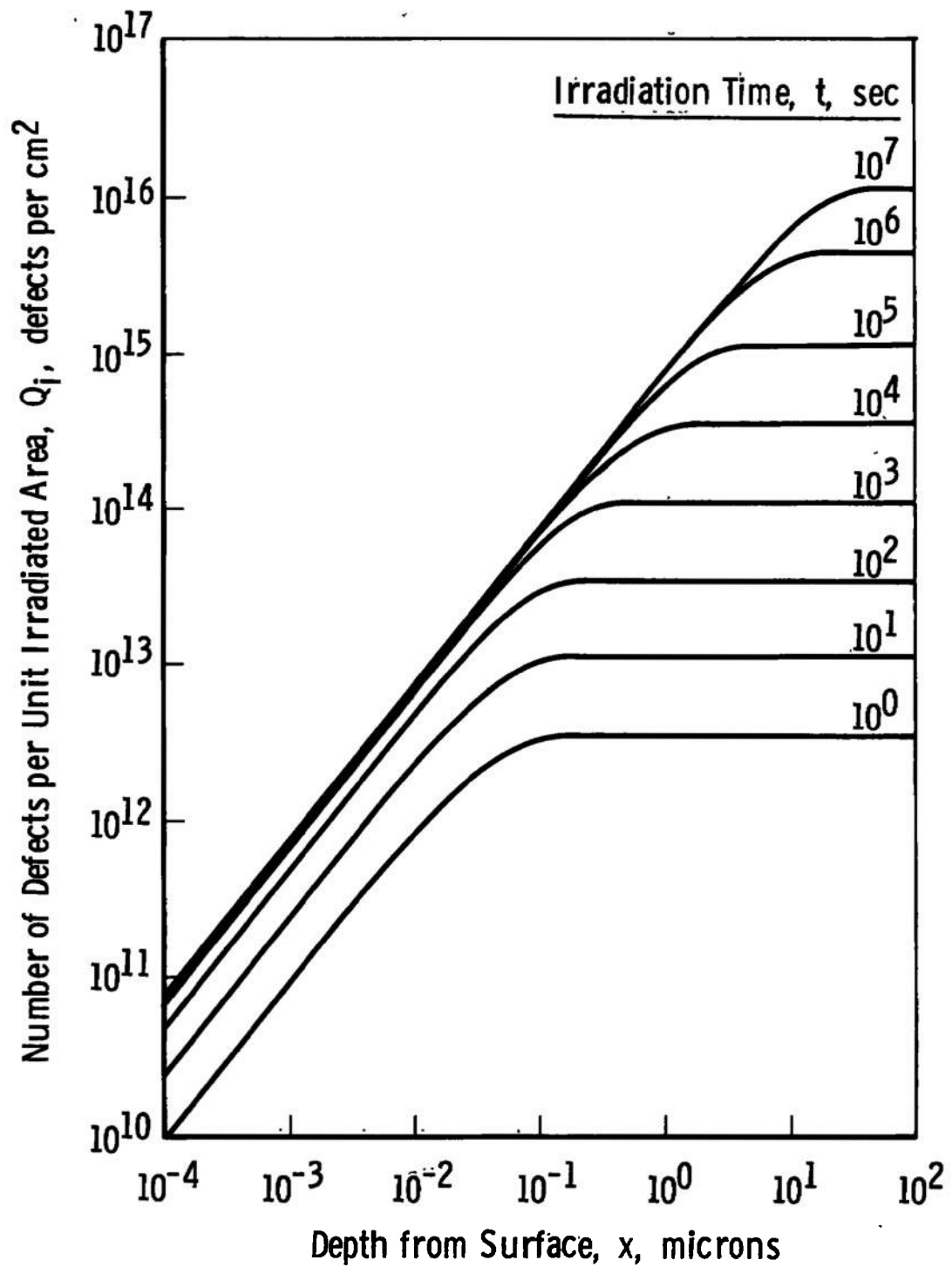


Fig. 7 Number of  $i$ th-Type Defects Present in Depth  $x$  of Parent Material for an Ultraviolet Irradiance equal to that of the Sun

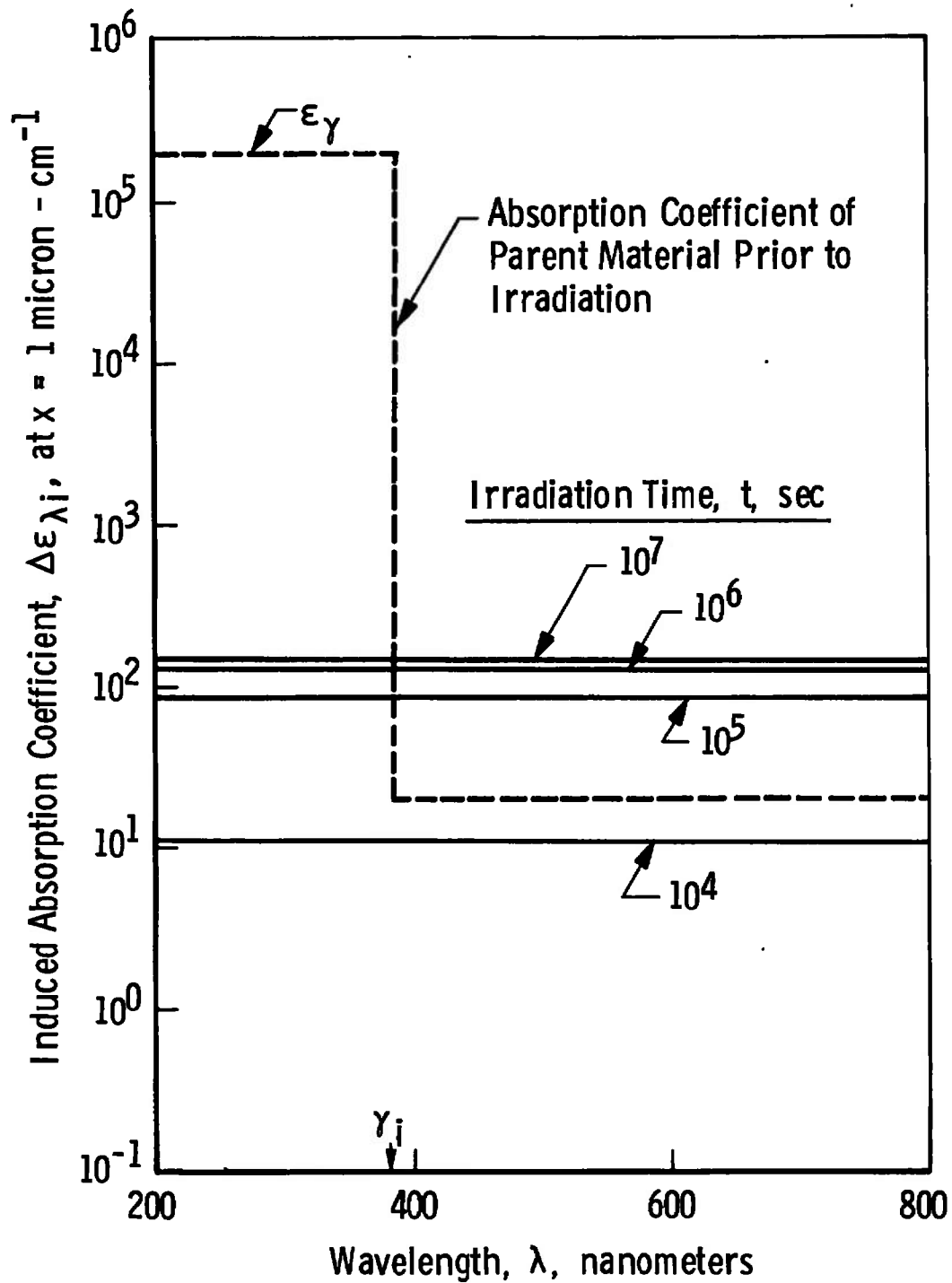


Fig. 8 Change in Parent Material Absorption Coefficient at  $x = 1.0 \text{ Micron}$  for an Ultraviolet Irradiance equal to that of the Sun

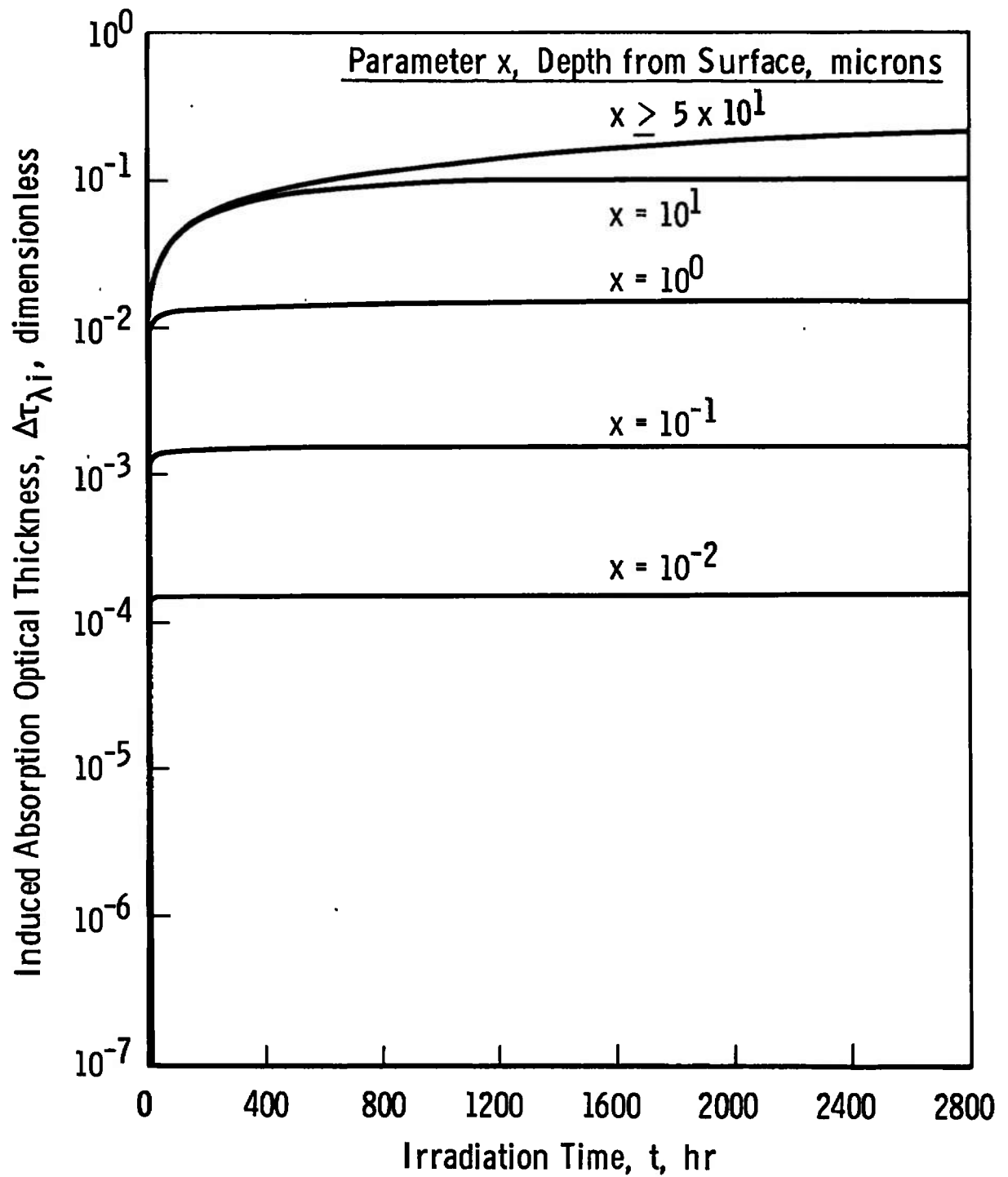


Fig. 9 Change in Parent Material Absorption Optical Thickness for an Ultraviolet Irradiance Equal to that of the Sun

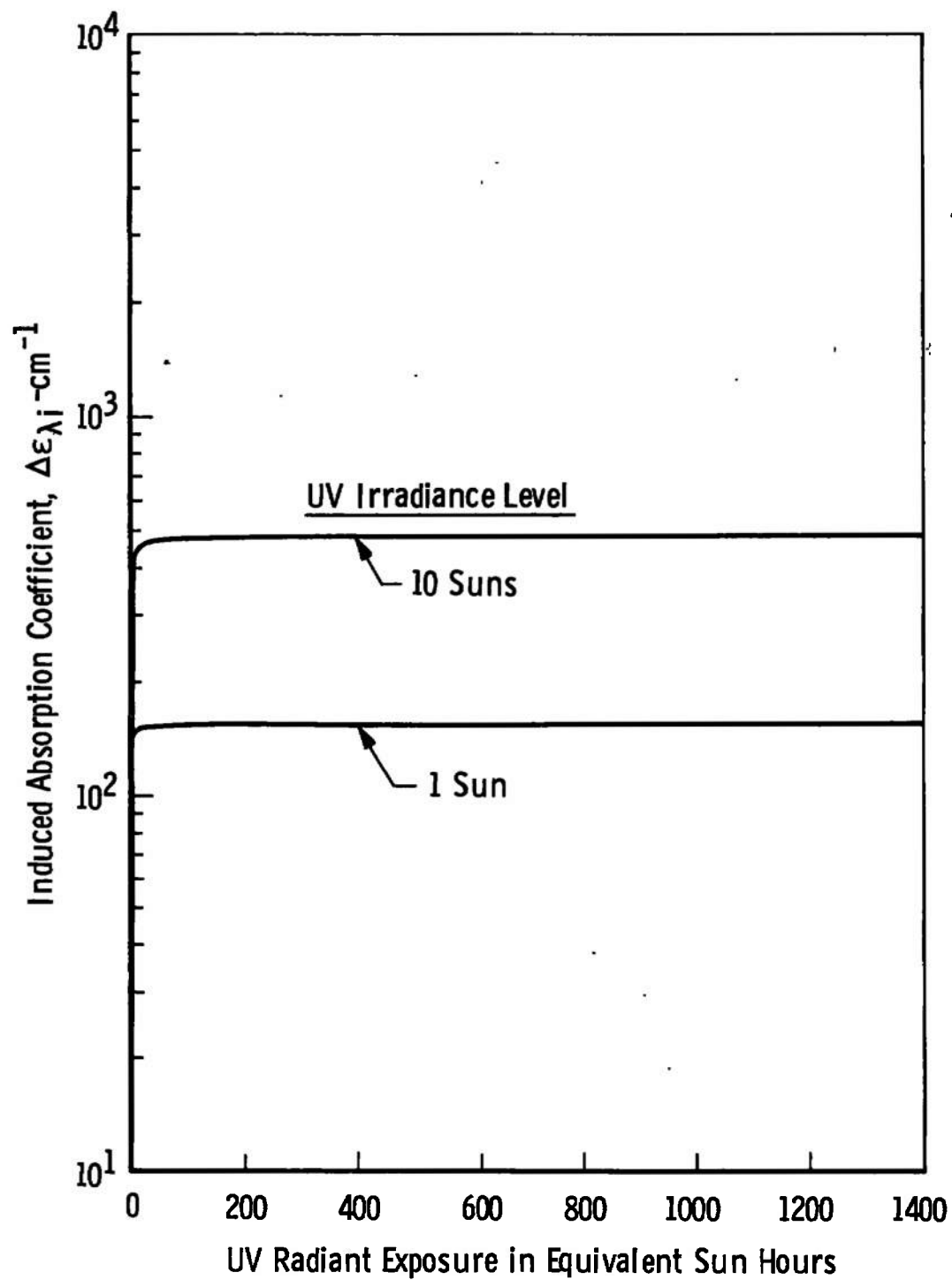


Fig. 10 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material Absorption Coefficient at the Surface,  $\Delta\epsilon_{\lambda i}(x = 0)$

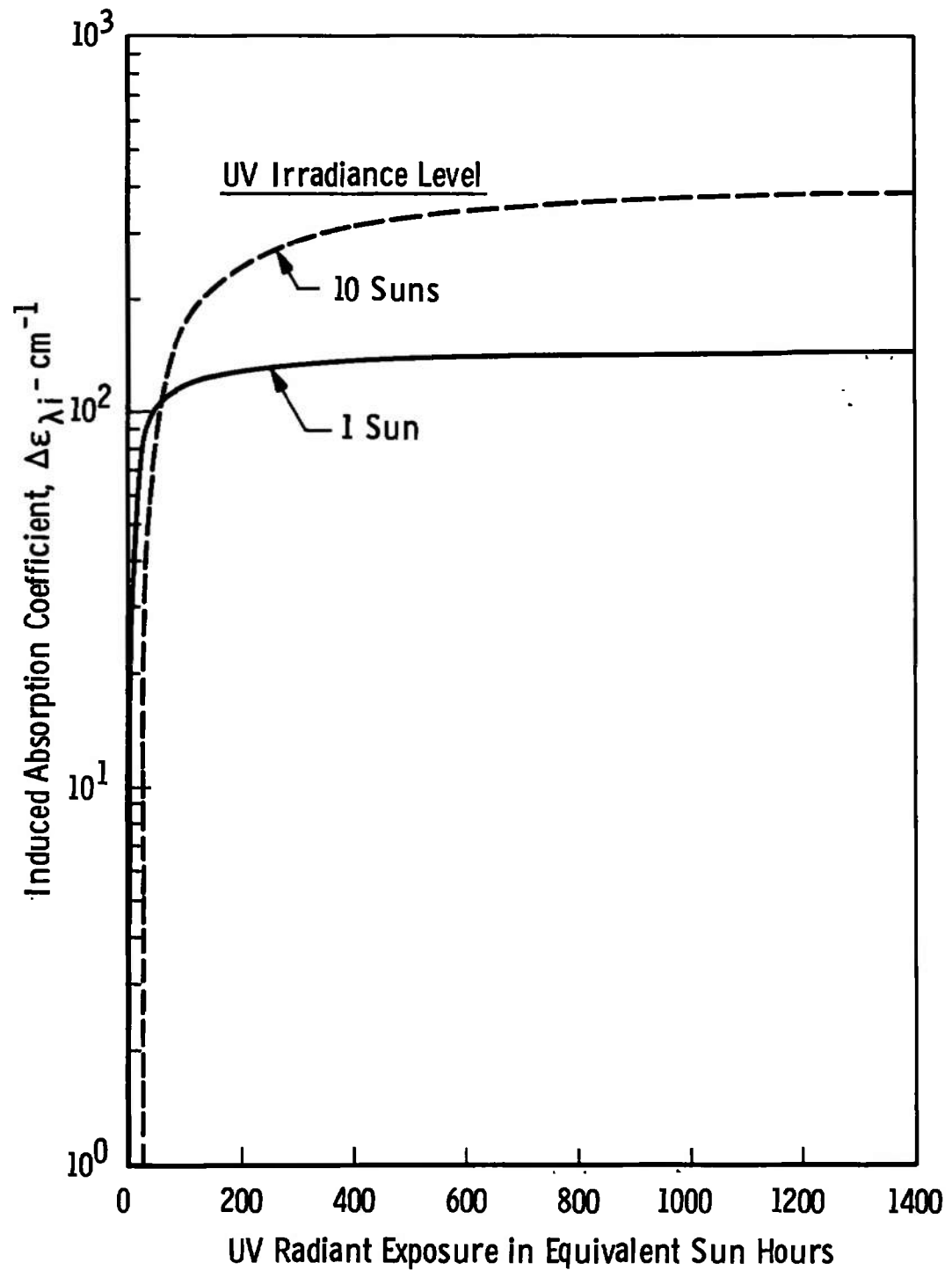


Fig. 11 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material Absorption Coefficient at a Depth of 1.0 Micron,  $\Delta\epsilon_{\lambda i} (x = 1\mu)$

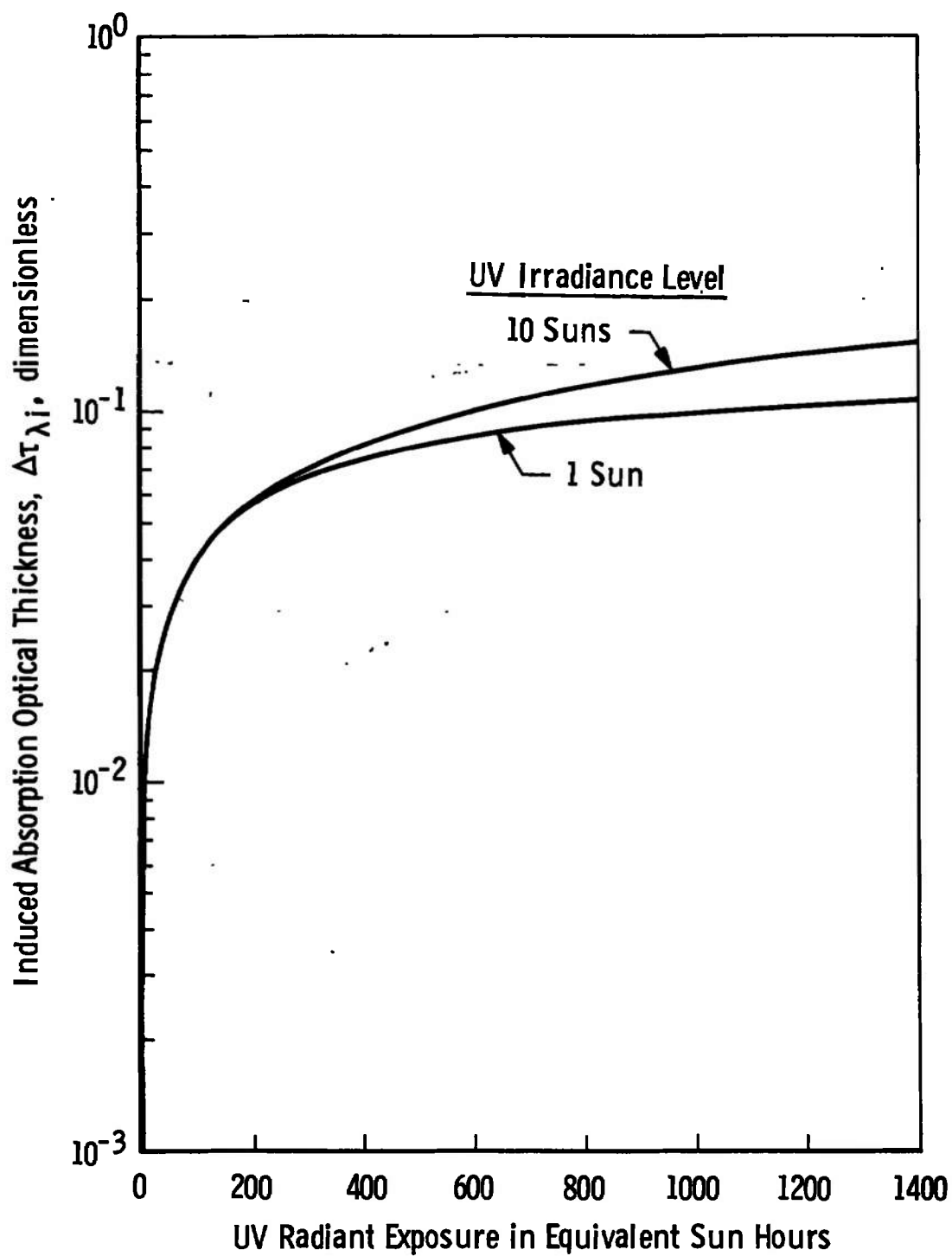


Fig. 12 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material Absorption Optical Thickness at a Depth of 10 Microns,  $\Delta\tau_{\lambda i}$  ( $x = 10\mu$ )

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Security Classification

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| c.<br>d.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)<br>N/A                                          |                      |
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| 11. SUPPLEMENTARY NOTES<br>Available in DDC.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  | 12. SPONSORING MILITARY ACTIVITY<br>Arnold Engineering Development Center (AETS), Arnold Air Force Station, Tennessee 37389 |                      |
| 13. ABSTRACT<br>A photoreaction-diffusion model for the solar degradation of thermal control materials is mathematically formulated and analyzed. The governing differential equation for the concentration of defect specie created in the material by radiation is derived, and an analytical solution is obtained for appropriate boundary conditions. From this solution for the concentration $N_i$ of the $i$ th-type defects, an analytical expression is derived for the number $Q_i$ of $i$ th-type defects present in a material layer of depth $x$ and unit irradiated area. These analytical relations are used to predict the radiation-induced increase in the absorption coefficient and absorption optical thickness of a hypothetical thermal control material exposed to damaging ultraviolet irradiance equal to that of the sun. The solutions for $N_i$ and $Q_i$ are also used to better define the environmental parameters which must be controlled during solar radiation testing of thermal control coatings. For example, the time-irradiance reciprocity principle often employed in accelerated solar testing is investigated by use of the aforementioned solutions and is found to be invalid for materials which degrade according to the photoreaction-diffusion model. |  |                                                                                                                             |                      |

| 14. KEY WORDS                                                                                                                                                                   | LINK A |    | LINK B |    | LINK C |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|----|--------|----|--------|----|
|                                                                                                                                                                                 | ROLE   | WT | ROLE   | WT | ROLE   | WT |
| photoreaction-diffusion<br>materials<br>thermal control<br>modeling, mathematical<br>testing techniques<br>solar radiation<br><br>3. materials .. Solar degradation<br><br>17-3 |        |    |        |    |        |    |