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16. Summary/Notes <p style="text-align: center;"><i>In this paper, we present the first characterization of a new composite material: Fe_2O_3 - impregnated polytetrafluoroethylene. The samples were prepared by impregnation of the polymer with $Fe(CO)_5$ followed by <u>in situ</u> oxidation of the iron carbonyl. Iron oxide particle size distributions, determined by electron microscopy, were found to be dependent on the oxide concentration in the polymer. The optical absorption spectra were obtained via Photoacoustic Spectroscopy and the spectral intensities correlated with the particle size distribution and concentration.</i></p>		
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"CHARACTERIZATION OF A NEW COMPOSITE MATERIAL: Fe_2O_3 - IMPREGNATED
POLYTETRAFLUOROETHYLENE-I. PHOTO-ACOUSTIC SPECTROSCOPY AND
PARTICLE-SIZE DETERMINATION"

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ABSTRACT

In this paper, we present the first characterization of a new composite material: Fe_2O_3 - impregnated polytetrafluoroethylene. The samples were prepared by impregnation of the polymer with $\text{Fe}(\text{CO})_5$ followed by in situ oxidation of the iron carbonyl. Iron oxide particle size distributions, determined by electron microscopy, were found to be dependent on the oxide concentration in the polymer. The optical absorption spectra were obtained via Photoacoustic Spectroscopy and the spectral intensities correlated with the particle size distribution and concentration.

I. Introduction

Polytetrafluorethylene (PTFE) is a highly inert and insoluble polymer of chemical composition $(-CF_2-)_n$ which has considerable technological importance ¹. Thus, PTFE resists attack by the most aggressive of chemical agents, with the exception of metallic sodium ² and alkalies ^{3,4} under extreme conditions. In addition it is highly immiscible with most solids or liquids.

This combination of properties is a serious obstacle to the development of useful composite materials in which PTFE is a component. We have found that a new approach can be successfully applied to this problem, leading to a host of new materials such as iron (III) oxide-impregnated PTFE, discussed in this paper. Our approach is based on the fact that some metalorganic substances with sufficiently low solubility parameters are predicted by Hildebrand's Theory of Regular Solutions ⁵ to be miscible with PTFE. Once the metalorganic substance is absorbed by the polymer, it can be made to react to yield other substances. In the present case, iron pentacarbonyl, $Fe(CO)_5$, was absorbed by PTFE and subsequently transformed into iron (III) oxide, thus generating the new composite material, Fe_2O_3 - PTFE. Since the individual components of this new material exhibit highly contrasting properties, one would expect that such features would be reflected in the properties of the composite. For instance, a dramatic change in the adsorbent properties of PTFE occurs upon surface modification with Fe_2O_3 .⁶

In this paper, we discuss the optical absorption spectra of Fe_2O_3 - impregnated PTFE. The spectral data are correlated with electron microscopy data which indicate the formation of essentially two different volume distributions

of Fe_2O_3 particles in the samples studied.

II. Sample Preparation and Analysis

PTFE samples were 0.2 mm-thick sheets, fabricated from Dupont Teflon by Incoflon (São Paulo). The identity and purity of the material was checked by melting-point measurements, infrared spectroscopy and electron spectroscopy (ESCA). The degree of crystallinity of the original material, determined by X-Ray diffraction, was found to be 65%. After thermal annealing (2 hours at 206°C), the degree of crystallinity was found to be 70%. Iron pentacarbonyl was obtained from Alpha Inorganics and distilled prior to use.

The PTFE samples were thoroughly washed with ethanol and dried under vacuum. After weighing, the samples were immersed in a 10% solution of iron pentacarbonyl in ethanol for varying periods of time. Following removal from the solution, the samples were subjected to a proprietary pretreatment⁷ and subsequently permitted to undergo complete oxidation under air. After three days, each sample was heated to 105°C to eliminate traces of iron carbonyl which might have remained unreacted. The samples were then washed with 1N sulphuric acid and ethanol and air-dried to constant weight. The composition of the samples was checked gravimetrically following thermal decomposition of the PTFE. The Fe_2O_3 - impregnated PTFE samples were obtained with concentrations of Fe_2O_3 varying from 0.34% to 1.50% (W/W). These samples are labelled by T_i (with $i = 0, 1, \dots, 8$).

In table I, we summarize the electron microscopy data for our samples, obtained using a Hitachi HU12 transmission

microscope.

The samples were subjected to electron bombardment under vacuum in the microscope to make them sufficiently thin for adequate transmission imaging. Photographs of the thinner regions were analysed assuming that the Fe_2O_3 particle size does not change during this treatment (i.e., that the only change caused by this treatment is the depolymerization of PTFE and evaporation of monomeric C_2F_4).

In Figs. 1 and 2 we show the resultant Fe_2O_3 particle size histograms for some of our samples obtained via electron microscopy. In Fig. 3, a typical electron microscope photograph is shown.

III. Optical Absorption

In this section, we present the results of optical absorption for our samples. Conventional optical absorption techniques failed to furnish reliable data due to the opacity of the samples. We have thus resorted to the photoacoustic spectroscopy technique. Photoacoustic spectroscopy (PAS) of solids has been found to be an extremely useful tool for studying the optical absorption spectra of crystalline, powdered, and amorphous solids. As has been shown by Rosencwaig⁸, the primary source of the acoustic signal is the periodic heat flow from the sample to the surrounding gas resulting from absorption of the chopped excitation light. The periodic flow of this heat into the gas cell produces pressure fluctuations which give origin to the acoustic signal.

Even though PAS may permit the determination of absolute optical absorption coefficients⁹, some caution

must be exercised when dealing with the PAS of fine-grain¹⁰ (powder) samples, as well as of amorphous systems consisting of an assembly of fine particles.

Our experimental apparatus consists of: a 200 watts tungsten filament lamp, a variable-speed light chopper, a monochromator, an air-filled aluminium cell with a condenser microphone, a low-noise preamplifier, and a lock-in amplifier. The sample compartment is a cylindrical chamber with a diameter of 1.0 cm; 1.0 cm diameter Fe₂O₃ - PTFE discs were weighed to correct for differences in masses between the samples¹¹.

Using powdered charcoal as a nearly perfect absorber, the fraction of the incident signal absorbed by the samples was calculated from:

$$\text{relative absorption} = \frac{\text{sample signal} - \text{undoped matrix signal}}{\text{charcoal signal} - \text{undoped matrix signal}}$$

The optical absorption spectra of typical samples are displayed in Fig. 4a and 4b; in Fig. 5, we show the dependence of the relative peak absorption signal on the concentration of Fe₂O₃ particles imbedded in the polymeric matrix.

IV. Interpretation

The spectra obtained (Fig. 4) exhibit strong absorption bands which are most readily attributable to charge transfer from oxygen to a central iron (III) in a octahedral configuration¹².

The dependence of the photoacoustic signal, taken at the maximum peak absorption (in the 3500 - 4000 Å region), on the concentration of Fe₂O₃ particles (Fig. 5) suggests the

existence of two different volume distributions for the samples examined. This conclusion is arrived at by taking into account the physical processes involved in the generation of the photoacoustic signal. Nonradiative de-excitation processes convert part or all of the light absorbed by the solid into heat. The periodic flow of this heat into the gas of a closed cell produces pressure fluctuations which are then detected by a sensitive microphone. The temperature in the sample, $\phi_s(x,t)$, can be evaluated from the thermal diffusion equation, assuming that the monochromatic light is sinusoidally modulated in intensity,

$$\frac{\partial^2 \phi_s}{\partial x^2} = \frac{1}{\alpha_s} \frac{\partial \phi_s}{\partial t} - Ae^{\beta x} (1 + e^{i\omega t}) \quad (1)$$

In eq. 1, α_s is the thermal diffusivity of the sample (equal to $k_s/\rho_s C_s$ where k_s , ρ_s and C_s are, respectively, the thermal conductivity, the density and the specific heat of the sample). In addition, $A = \beta I_0 \eta / 2 k_s$, where β is the optical absorption coefficient of the sample, I_0 the incident light intensity, and η the efficiency with which the absorbed light energy is converted into localized heat. The chopping frequency is $\omega/2\pi$.

Once equation (1) is solved for appropriate boundary conditions, the sample temperature $\phi_s(x,t)$ can be evaluated in terms of the optical, thermal, and geometrical parameters of the sample, the gas, and the backing material. The periodic temperature fluctuation produced in the gas by the varying temperature at the sample surface falls off exponentially with distance from this surface. For all practical purposes, the temperature oscillation is limited to a boundary layer of gas of thickness of the order of $2\pi/a_g$, where $1/a_g = (2\alpha_g/\omega)^{1/2}$

is the thermal diffusion length in the gas. For air at room temperature and pressure, this boundary layer is about 1 mm thick when $\omega = 1000$ rad/sec.

The pressure effect of the periodic temperature variation within this boundary layer can be approximated by considering the system to be an acoustic piston with a displacement given by

$$x(t) = \frac{2\pi}{a_g} \frac{\langle \phi_g(t) \rangle}{\phi_o(o)}$$

where $\langle \phi_g(t) \rangle$ represents the periodic temperature averaged over the boundary layer and $\phi_o(o)$ the steady-state temperature of the sample at $x = 0$. The time-dependent pressure in the cell is proportional to the displacement $x(t)$ given above.

Although the general expression for the acoustic signal generated is relatively complex¹³ for optically opaque and thermally thick samples, as in the present case, it reduces to¹³

$$Q = A\beta I \quad (2)$$

where Q is the photoacoustic signal, A a proportionality constant, β the absorption coefficient of the samples and I the intensity of light which is converted into heat.

We note, however, that this theory was developed for homogeneous solid samples. In our case, the sample contains absorbing particles distributed in the organic matrix; thus, the scattering by the Fe_2O_3 particles has to be considered. As we have pointed out, in the case of an assembly of fine particles, the scattered light plays an important role¹⁰. Taking into account, therefore, the influence of scattered light, we can express the intensity I in eq. (2) for opaque

samples as

$$I = I_0 e^{-\sigma/\beta} \quad (3)$$

where I_0 is the intensity of light reaching the sample. As the scattering coefficient σ is typically much smaller than the absorption coefficient β , equation (2) can be rewritten as

$$Q \cong AI_0(\beta - \sigma) \quad (4)$$

Since the wavelengths of light employed are much longer than the Fe_2O_3 particle dimensions, as evidenced by the electron microscopy data, the scattering extinction coefficient should conform to Rayleigh scattering. Consequently, taking $\sigma = bd^6$, where b is a proportionality coefficient, constant for all samples, and d is the mean diameter of the Fe_2O_3 particles, we can write the acoustic signal as

$$Q \cong AI_0 (\beta - bd^6) \quad (5)$$

Assuming β to be proportional to the concentration c of Fe_2O_3 , the existence of the two straight lines in Fig. 5 may therefore be associated with σ via the formation of two characteristic volume distributions of Fe_2O_3 particles as a function of the concentration. This can be seen by noting that the ratio of the two intercepts in Fig. 5 is 2.6, a value which should be comparable to the ratio of the corresponding mean diameters to the sixth power. From the electron microscopy data in Table I, we have $\bar{d}_1 \cong 36 \text{ \AA}$ and $\bar{d}_2 \cong 44 \text{ \AA}$ where 1(2) refer to the upper (lower) straight lines of Fig. 5. These values yield $(\bar{d}_2/\bar{d}_1)^6 \cong 3.3$, which agrees within experimental error with the value of 2.6 obtained above. On the other hand, the slopes of the two straight lines (1 and 2), determined by

a least squares fit, were found to be 1.29 and 1.26, respectively indicating that β is indeed insensitive to the particle size. The overall consistency evident in these results thus substantiates our initial assumptions.

Conclusions

In this paper, we present the results of an initial characterization of Fe_2O_3 - impregnated PTFE. The existence of two characteristic Fe_2O_3 volume distributions has been demonstrated via two different methods. Furthermore, the existence of these two distributions is confined to two different Fe_2O_3 concentration ranges.

We have also demonstrated the usefulness of PAS for estimating particle sizes in amorphous samples.

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Table Caption

Summary of the electron microscopy data for the samples examined.

TABLE 1

Sample	T ₀	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇	T ₈
Concentration (%)	0.34	0.58	0.62	0.70	0.94	1.10	1.16	1.39	1.50
Average Diameter (Å)	38.5	30.4	30.8	39.9	-	49.6	-	44.2	40.2
Peak Diameter (Å)	42.0	30.0	29.0	-	-	44.0	-	43.0	42.0
Spread, FWHM* (Å)	12	16	13	-	-	20	-	13	16

* Full width at half- maximum of distribution

Figure Captions

Fig. 1 : Fe_2O_3 particle size histogram for the lower concentration samples.

Fig. 2 : Fe_2O_3 particle size histogram for the higher concentration samples.

Fig. 3 : Typical microscopy photograph (150000 x):

Fig. 4 : a) Relative absorption spectrum for sample T_4
($c = .94\%$)

b) Relative absorption spectrum for sample T_7
($c = 1.39\%$).

Fig. 5 : Relative photoacoustic signal at the maximum absorption peak versus the concentration of the samples (c).

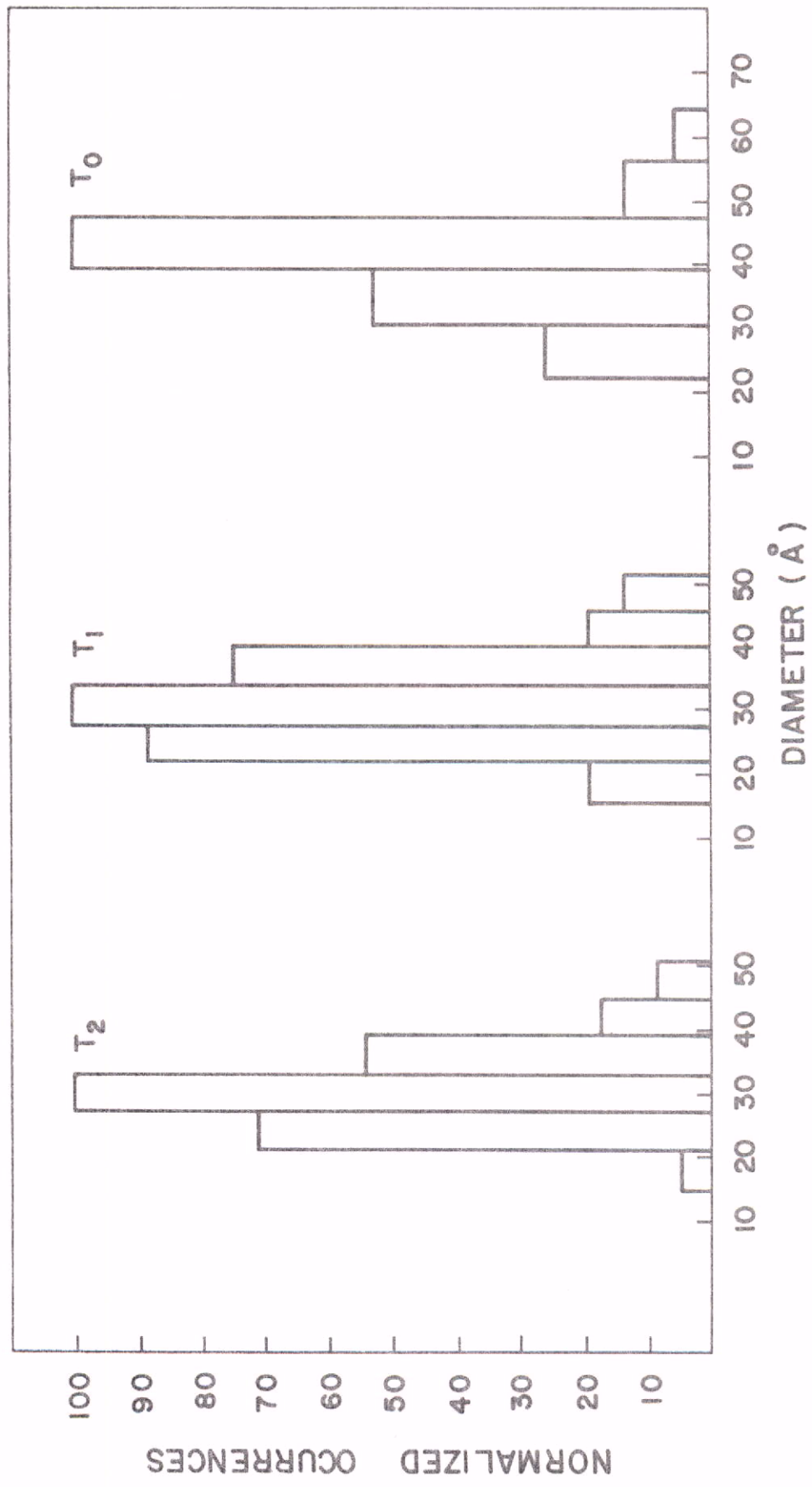


Fig. 1

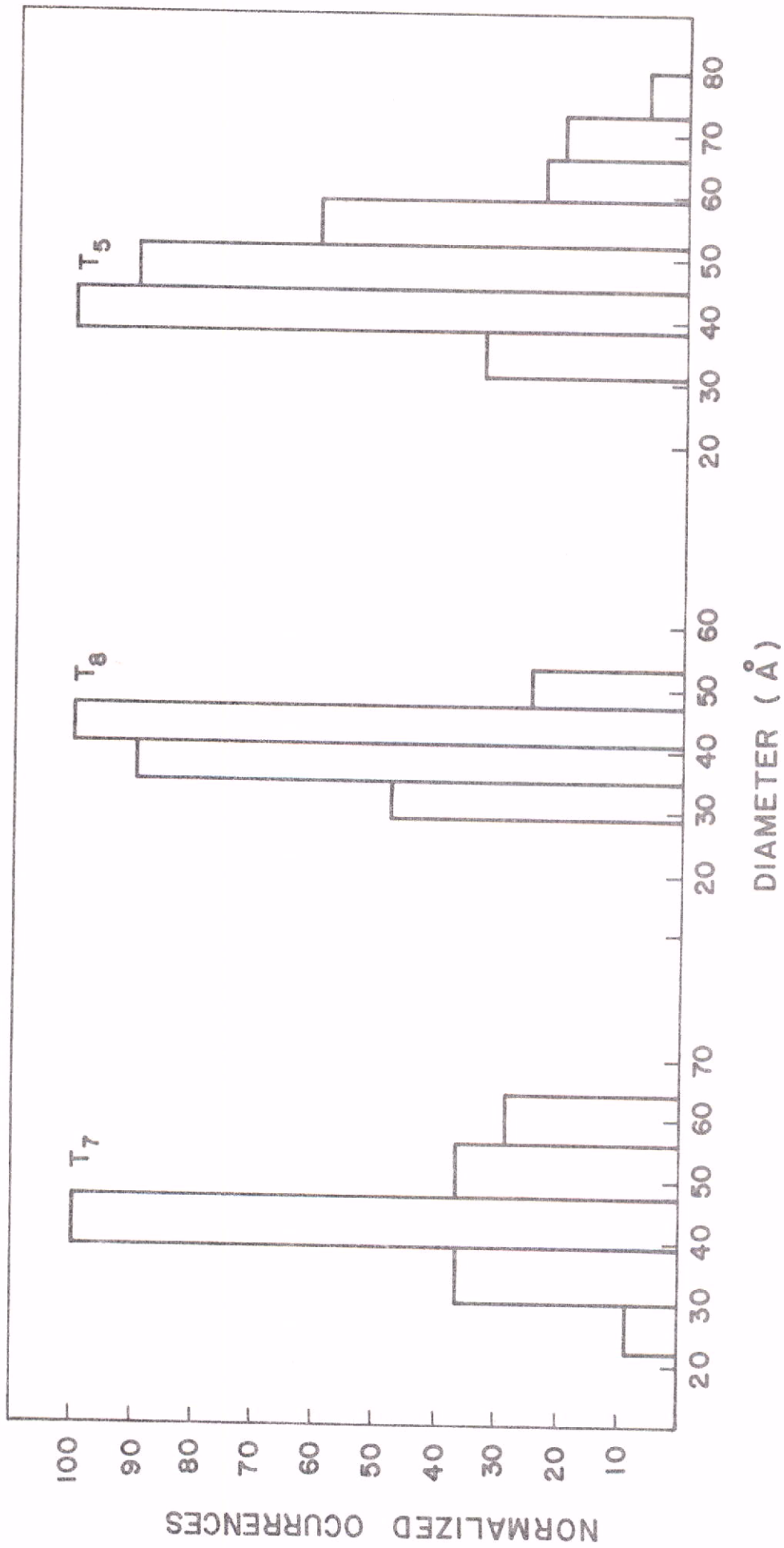
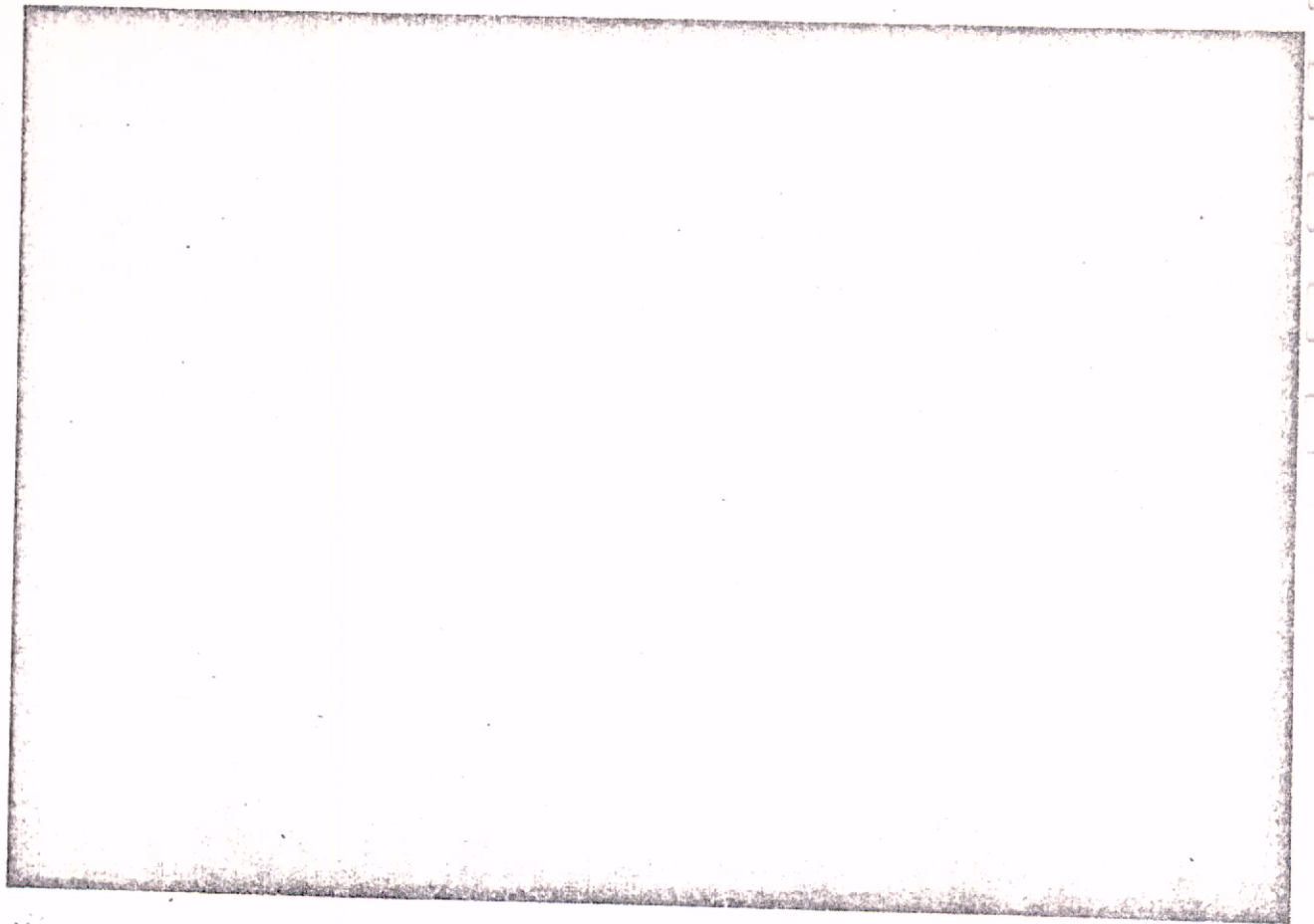
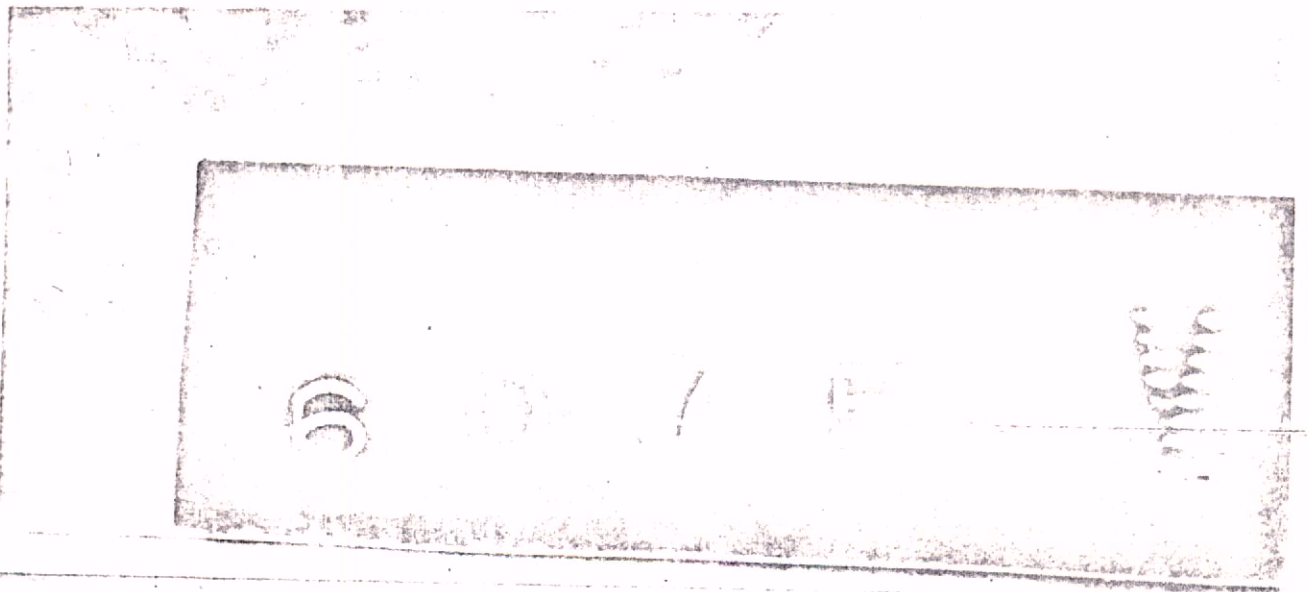


Fig. 2



200 Å
—|—



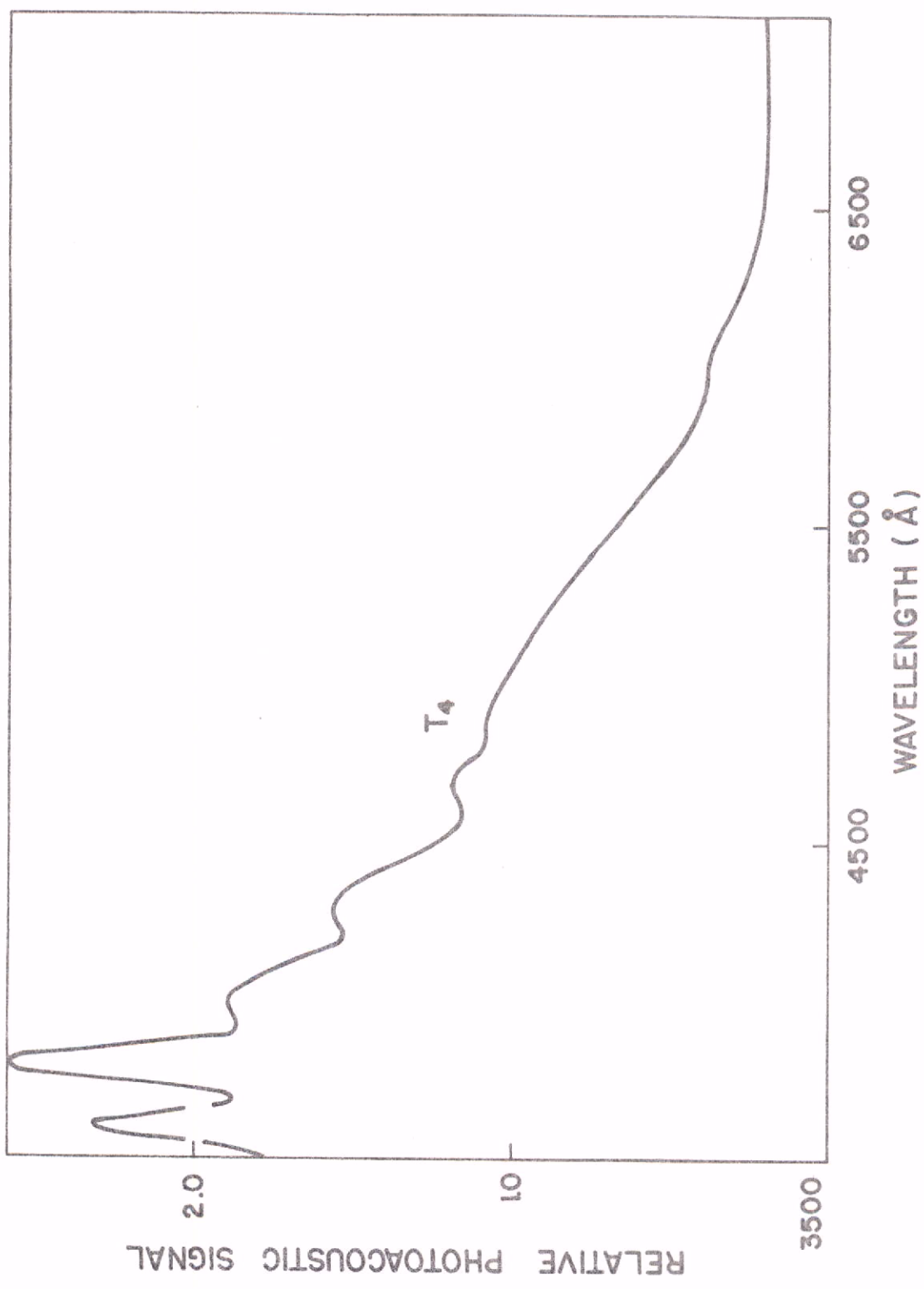


Fig. 4a

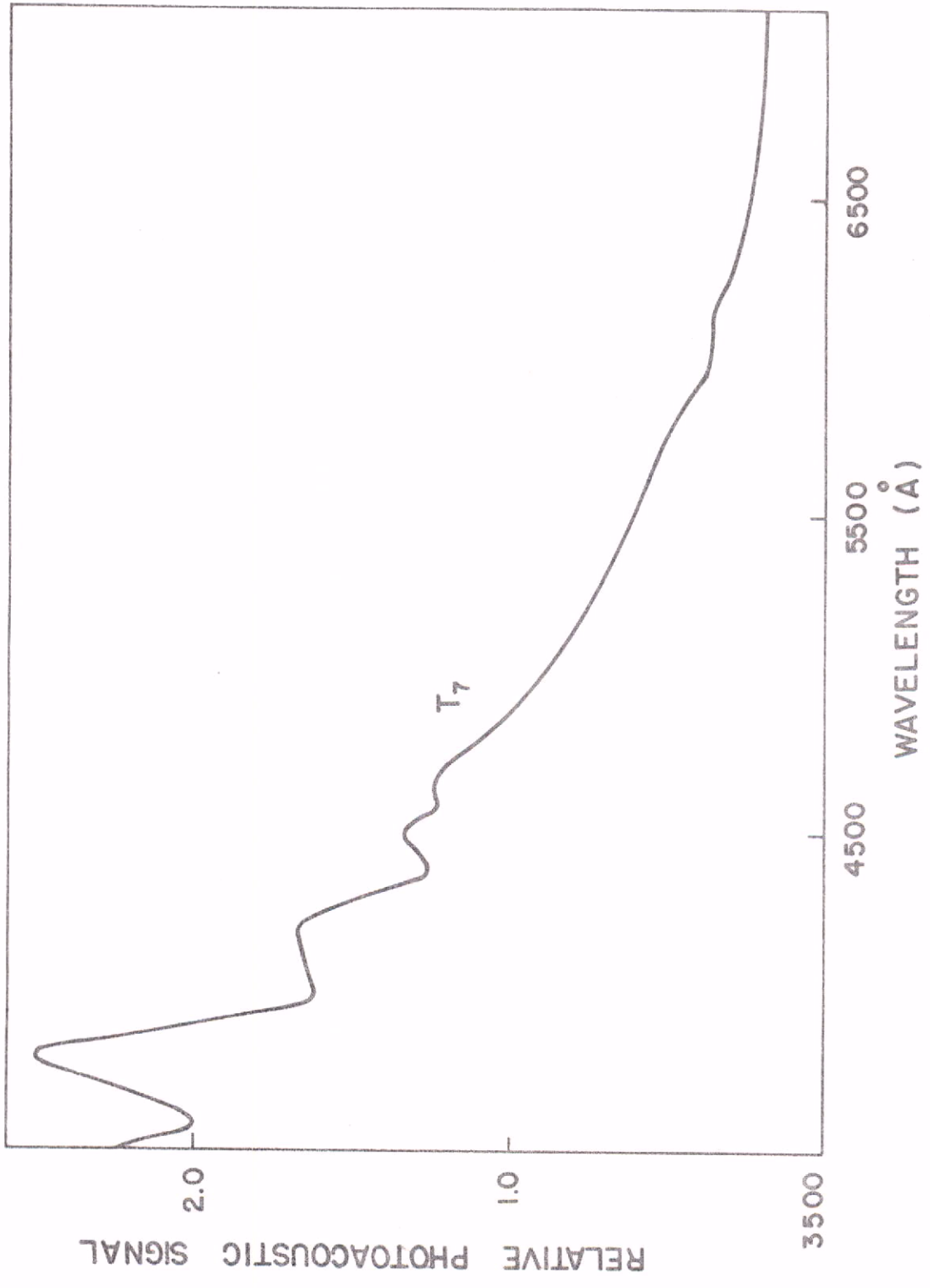


Fig. 4b

