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A STUDY OF GAMMA-RAY PHOTOCONDUCTIVITY
IN ORGANIC DIELECTRIC MATERIALS

by

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ABSTRACT

The gamma-ray photoconductivities of polyethylene, polystyrene, polyvinylchloride, polypropylene, Teflon, nylon, Kel-F, and three thermosetting resins denoted as Epoxy 1478-1, 1478-3, and 1478-22 have been measured. The measurements were made at steady-state gamma-ray intensities ranging from $1.0 \text{ rad}(\text{H}_2\text{O})/\text{min}$ to $3.0 \times 10^5 \text{ rads}(\text{H}_2\text{O})/\text{min}$ and at controlled temperatures ranging from 90°F to 140°F . Conductivity changes resulting from the steady-state gamma-ray exposures were measured continuously throughout the exposure and after the exposure. The exposure period was of sufficient duration to allow all samples to achieve an equilibrium conductivity value. The conductivity was found to exhibit distinct features in three time intervals: interval 1 is where photoconductivity is responding to a step increase in radiation intensity; interval 2 is where the photoconductivity has reached an equilibrium value whose magnitude is defined by radiation intensity and temperature; and interval 3 is where the conductivity is recovering upon sample removal from the gamma-ray environment. The time required during interval 1 for the conductivity to reach the equilibrium value of interval 2 is defined as the rise time (τ_r) and was experimentally found to decrease with increased irradiation intensity according to the relationship

$$\tau_r = \tau_r' \dot{R}^{-\mu}$$

The equilibrium conductivity values of interval 2 give a dependence of photoconductivity on irradiation intensity at a given temperature which is characterized to good approximation in one or more regions, within which conductivity (σ) is expressed as

$$\sigma = \sigma_0' \dot{R}^{\delta}$$

Experimental values of δ range from 0.00 to 2.72. Conductivity decays with time (t) from an equilibrium value (σ_{eq}) after abruptly stopping radiation exposure. The photoconductivity decay is characterized to good approximation by

$$\sigma(t) = \sigma_{eq} \left[A e^{-t/\tau_1} + B e^{-t/\tau_2} \right]$$

where τ_1 and τ_2 are two distinct decay constants. Conductivity was observed to vary with temperature under both dark and radiation-induced conductivity conditions according to the relationship

$$\sigma = \sigma_o e^{-E/kT}$$

The thermal activation energy (E) is lowered by irradiation except for Epoxy 1478-1 which has one intensity interval, within which E is unchanged.

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CHAPTER I -- INTRODUCTION

The photoconductivity properties of some organic dielectric materials exposed to gamma radiation were measured at gamma-ray intensities in the range of $1.0 \text{ rad} \cdot (\text{H}_2\text{O})/\text{min}$ to $3.0 \times 10^5 \text{ rads}(\text{H}_2\text{O})/\text{min}$. The source of gamma radiation was the fission product inventory of reactor fuel elements. Measurements of the photoconductivities were made at controlled temperatures. Polystyrene, polyethylene, polyvinylchloride, polypropylene, Teflon, nylon, Kel-F, and three epoxy formulations denoted as 1478-1, 1478-3, and 1478-22 were studied. Polyethylene, polystyrene, and Epoxy 1478-1 were studied more extensively than the others. The temperature dependence of the magnitude of the photoconductivity was measured at 100, 120, and 140°F for polyethylene, polystyrene, and Epoxy 1478-1. Photoconductivities in the other materials were measured at 90°F.

The dependence of equilibrium photoconductivity on irradiation intensity ($\dot{R}$) at a given temperature in insulating materials can be characterized to good approximation in one or more regions of $\dot{R}$, within which conductivity (σ) is expressed as

$$\sigma = \sigma_0' \dot{R}^\delta \quad (1)$$

where σ_0' and δ are empirical constants. Photoconductivity of this form is based on the model of Rose¹ and has been found by Fowler² and by Coleman³ to exist at low intensities ($< 10^2 \text{ rads}(\text{H}_2\text{O})/\text{min}$) for the thermalplastic materials of this work.

* $\text{rad}(\text{H}_2\text{O}) = 100 \text{ ergs of energy absorbed per gram of } (\text{H}_2\text{O}) = 6.24 \times 10^{13} \text{ electron volts of energy absorbed per gram of } (\text{H}_2\text{O})$.

¹Rose, A., "An Outline of Some Photoconductive Processes," RCA Review, 12, 362 (1951).

²Fowler, J. F., "X-ray Induced Conductivity in Insulating Materials," Proceedings of the Royal Society of London, 464 (1956).

³Coleman, J. H., 23rd Annual Meeting, Conference on Electrical Insulation, Sponsored by National Academy of Science-National Research Council, 1955.

The photoconductivity properties of extremely low conductivity ($< 10^{15} \text{ ohm}^{-1} \text{ cm}^{-1}$) organic dielectric materials constitute a relatively unexplored, unresolved field. Basic investigations of the photoconductivity mechanisms have been restricted largely to single-crystal, high-purity inorganic materials. The photoconductivities of organic polymers reveal a quantitative behavior similar in form to that of the photoconductivities of inorganic crystalline structures and suggest the conclusion that the fundamental processes in both material types are in a general way related. The most distinctive structural difference between inorganic crystals and organic polymers is the amorphous and semicrystalline nature of the latter. Semicrystalline materials are those which have crystalline regions formed interspersed in the amorphous mass of the polymer chain. According to recent theoretical work by Lauritzen and Hoffman⁴ the organic crystalline unit cells are formed by chain folding, i. e., such crystalline regions consist of uniform lamellae with the organic molecules approximately normal to the plane of the lamellae in a sharply, regularly folded configuration.

Photoconductivity was first observed by Smith⁵ in 1873 when he found that a selenium resistor could not be depended upon to have the same resistance under light intensity variations (daylight or darkness). The observations of photoconductivity which followed this initial discovery were sporadic and not until early in the twentieth century did researchers find that many materials exhibited photoconductivity properties. The first comprehensive study of the photoconductivity process was conducted by Gudden and Pohl and their contemporaries between 1920 and 1930, principally with zinc sulfide, diamond, and alkali halides. They showed that light absorption, the excitation of luminescence by light, and the excitation of photoconductivity by light all had a similar dependence on the wavelength of the light for a given material. Of

⁴Lauritzen, J. I., and Hoffman, J. D., "Theory of Formation of Polymer Crystals with Folded Chains in Dilute Solution," J. Res. N.B.S., 64A, 73 (1960).

⁵Smith, W., "Effects of Light on Selenium During the Passage of an Electric Current," Nature, 7, 303 (1873).

prime importance to the interpretation of the phenomenon, they establish the quantum nature of "primary photocurrents" in the photoconductivity process by showing that one electric charge passes between electrodes for each light photon absorbed.⁶ In addition to primary photocurrents, Gudden and Pohl found many photoconductive effects of comparatively mysterious origin which they attributed to "secondary photocurrents". In 1937, Hilsch and Pohl⁷ proposed a theory for such currents. Even then it took several years for these secondary photocurrents to become accepted as a common and legitimate property of photoconductors. In 1952, Moss⁸ summarized the current state of thinking about photoconductivity. Numerous publications exist which are pertinent to photoconductivity and a concentrated discussion of the field as a whole exists in four references.⁸⁻¹¹

The term "photoconductivity" includes electrical conductivity changes associated with the absorption of gamma-ray, X-ray, ultraviolet, visible light, or infrared photons. Since photoconductivity is concerned chiefly with the rate of excitation and recombination of electrons, it is an artificial separation to exclude excitation by alpha, beta, or other nuclear particles even though they are normally described by the term "bombardment induced conductivity" rather than photoconductivity. Any material is considered to be a photoconductor if the absorption of energy from photons or particles changes the conductivity. Basically, the photoconductivity processes involve the

⁶ Gudden, B., and Pohl, R., "Photoelectric Conductivity", Phys. Zeits., 23, 417 (1922).

⁷ Hilsch, R., and Pohl, R., Phys. Zeits, 108, 55 (1953).

⁸ Moss, T. S., Photoconductivity in the Elements, Butterworth's Scientific Publications, London, 1952.

⁹ Proceedings of the IRE, 43, 1819 (1955).

¹⁰ Photoconductivity Conference, John Wiley and Sons, Inc., 1956.

¹¹ Bube, R. H., Photoconductivity of Solids, John Wiley and Sons, Inc., New York, 1960.

absorption of energy from radiation, the excitation of charge carriers from nonconducting states to conducting states, and the return of charge carriers from conducting states to nonconducting states.

There are three principal mechanisms by which gamma rays interact with matter to produce photoconductivity. These mechanisms are photoelectric effect, Compton effect, and pair production. These topics are discussed extensively in many texts, and Appendix A summarizes the salient features of each with appropriate references. The photon-electron interactions frequently produce ionization whereby the incident photon removes an electron from its parent atom or molecule leaving an electron deficiency, i. e., a hole associated with an atom or molecule. The ionized electron may have sufficient kinetic energy to cause secondary ionization and excitation in neighboring atoms where upon subsequent collisions they become sufficiently nonenergetic to become captured by the same or other atomic nuclei. The term "excitation" refers to a process by which an electron is raised to a high energy level but remains bound to its parent nucleus. Excitation can result from direct photon-electron interaction or as a secondary process as indicated above. Typical electron transitions in photoconductors are presented and discussed in Appendix B.

The subject of trapping has a distinct part in explaining the photoconductivity process. Trapping is the spatial confinement of an electron or hole such that the electron or hole is prohibited from moving freely through the material unless supplied with additional thermal or photon energy. In accord with photoconductivity terminology the term "trap" or "trapping" is reserved for centers whose occupancies are dictated by thermal equilibrium exchange with the nearest allowed band, i. e., thermal release of electrons and holes to the conduction and valence bands, respectively. The rate of release depends on temperature according to the relationship $\exp(-E/kT)$ where E is the depth of the trap. A material containing large numbers of deep "traps" may show reduced photoconductivity, and a slow "trap" decay as the carriers are released after removal of the photon source. Those traps which do not have a significant thermal exchange with the nearest allowed band are called "recombination centers." Because of this type of definition, there

is an inherent vagueness in defining what types of centers are "traps"; in fact, any center can be a "trap" under one condition of photon intensity and temperature, and a recombination center under another condition.

The above, brief discussion draws heavily on current single-crystal photoconductivity theory. This is the most logical starting point for photoconductivity work in insulating materials. Polymer-type organic structures are not so well defined and understood as are high-purity, single-crystal inorganics. Consequently, any basic study of the photoconductivity process in polymer materials is complicated by the completely homogeneous way that the polymer chains are intermingled. The electron energy levels are determined by the molecular and intermolecular forces, and the valence electrons that are dealt with are not necessarily associated with a single atom but are molecular valence electrons.¹²

This thesis is divided into three major chapters as follows: (1) a chapter which presents experimental procedures; (2) a chapter which presents and discusses data on conductivity versus time, conductivity rise time, conductivity versus gamma-ray intensity, conductivity versus temperature, conductivity versus accumulated gamma-ray exposure, and conductivity recovery; and (3) a summary chapter. Nine appendixes are included which contain more detail on certain select topics.

¹²Aftergut, S., and Brown, G. P., General Electric Co., Schenectady, N. Y., Paper given at Conference on Organic Semiconductors, Chicago, April, 1961.

CHAPTER II -- EXPERIMENTAL

The chemical structures of the materials used in this investigation are given in Appendix C. Each sample disc tested has been identified in Appendix D, and all figures and tables showing experimental data have the identification of the corresponding sample discs involved.

Each sample disc tested was thoroughly cleaned in alcohol, and aluminum electrodes were vacuum-metalized on the parallel surfaces to insure good electrical contact between the insulator material and the metal electrode. The discs were 10.16 cm in diameter and 0.119 cm to 0.368 cm thick as summarized in Appendix D. For convenience in calculating fringing effects for varying sample thickness, the electrode dimensions were as suggested by ASTM D 257-58.¹³ For the measurement of conductivity, each disc, along with electrodes and heaters, was encapsulated in a thermalsetting resin by a vacuum process. The test units, as shown in Fig. 1(a), include the disc of dielectric; the electrode system, consisting of a guarded electrode (dia. = 7.91 cm), an extended guard electrode (I. D. = 8.23 cm, O. D. = 10.16 cm), and a bottom electrode (dia. = 10.16 cm); two coaxial monitoring cables with the shields connected to the guard electrode; two parallel planes of heating elements located equidistantly above and below the electrodes; leads for heater power; and a thermocouple for control and recording of sample temperature. The encapsulated unit is shown in Fig. 1(b). The encapsulating material (Epoxy 1478-1) was for water proofing and reduction of ionization leakage currents.

The resistance of the sample discs was recorded continuously using a Brown strip-chart recorder driven by a Tera-Ohmmeter. The Tera-Ohmmeter is capable of measuring to 5×10^{15} ohms with an accuracy of ± 3 percent and with a comparative measurement capability of ± 1 percent. Repeated measurements with the Tera-Ohmmeter, Brown strip-chart recorder, and encapsulated test units revealed a system comparative measurement capability of ± 8 percent.

¹³ASTM Standards, Part 9, D 257-58, 1958, p. 612.

(a) TEST CONFIGURATION

(b) ENCAPSULATED UNIT (MATERIAL - EPOXY 1478-1)

FIG. 1. TEST CONFIGURATION AND ENCAPSULATED UNIT

The best estimate of the system accuracy is ± 30 percent. With voltage applied a stabilization time of 1.8×10^3 seconds was observed before data were taken on a given sample.

The built-in heater elements of Fig. 1 gave temperature control from 90°F to 160°F, $\pm 2^\circ\text{F}$.

Gamma-ray intensities, to 3.0×10^5 rads (H_2O)/min, were achieved with spent Engineering Test Reactor (ETR) fuel elements. As shown in Fig. 2, variations in gamma-ray intensity were obtained by positioning the encapsulated samples in a vertical water column at a variable distance, l , above the midplane at the array of fuel elements. The vertical column is an aluminum tube, 8 inches in diameter and 21 feet high, which is filled with water. Twelve ETR fuel elements were placed in a rectangular array around the base of the column.

Radiation intensities in the water column at the site of a sample were measured with ceric sulfate and ferrous sulfate chemical dosimeters, and additional comparative measurements were made with a graphite ionization chamber (pressure and temperature compensated) inserted into a cavity of a mock encapsulated sample. The chemical dosimeter measurements at the midplane revealed that radial intensity variations over the sample dimensions in the column did not exceed 5 percent; at other locations up the column, the radial variations in intensity were equal to or less than 5 percent.

Ionization leakage current between the measuring electrodes is eliminated by the guard electrode under nonirradiated conditions. However, in the presence of radiation the ionization of air provides a significant conduction path which is parallel to the conduction of the disc of material, thereby giving erroneous conductivity measurements. The successful elimination of leakage currents by encapsulation was assured by experimental measurements. The sufficient condition to assure that the leakage current of the encapsulating material did not contribute to the measurement of the photoconductivity of a material x is

$$\frac{I_{l,x}}{I_x} \leq \frac{I_{o,l,x}}{I_{o,x}} \quad (2)$$

FIG. 2. ABBREVIATED DRAWING OF FUEL ELEMENT ARRAY, ETR-CANAL, WATER FILLED TEST COLUMN, SAMPLE, AND SAMPLE POSITIONING WITH RESPECT TO MID-PLANE.

where

I_x = the measured photocurrent in the disc of material x ,

$I_{o,x}$ = the measured dark current in the disc of material x ,

$I_{\ell,x}$ = the measured photocurrent in the encapsulating material when tested as a disc x ,

and $I_{o,\ell,x}$ = the measured dark current in the encapsulating material when tested as a disc x .

For every encapsulated sample studied, the sufficient condition of Eq. (2) was satisfied for all levels of the radiation intensity used in this experiment.

Appendix E presents the development of Eq. (2).

CHAPTER III -- RESULTS AND DISCUSSION

Conductivity Versus Time

Typical data taken of conductivity versus time at a fixed temperature and gamma-ray intensity are shown in Fig. 3. The data are of one sample of polystyrene at 130°F and at a gamma-ray intensity of 1.9×10^5 rads (H_2O)/min. The beginning of an exposure is designated as "in" to note that the sample was lowered suddenly into the column to a predetermined intensity; the end of an exposure is designated as "out" to note that the sample was suddenly pulled out of the column to a point of no radiation exposure. The data taken on all materials have distinct features in three time intervals. Interval 1 is where photoconductivity is responding to a step increase in radiation intensity, but the conductivity has not yet achieved equilibrium. Interval 2 is where the conductivity has reached an equilibrium value determined for a specific material by the radiation intensity and temperature of the sample of material. Interval 3 represents the recovery of the conductivity upon removal of the sample from the gamma-ray field. In Fig. 3 it is noted in the third time interval that the magnitude of conductivity is affected by the previous history of exposure of the sample, and that conductivity is observed to increase with increased exposure.

Rise Time

The significant observation associated with Interval 1 of Fig. 3 is the conductivity rise time, τ_r . The rise time is the time required for the conductivity to reach an equilibrium value defined by the plateau of Interval 2. The plateau represents an equilibrium condition, a function of intensity and temperature, where the rate of generation of free carriers is equaled by the rate of carrier annihilation through recombination, and the rate of capture of free carriers in trapping (metastable) states is equal to the rate of release from trapping states. The rise time indicates that there is a finite interval associated with this equilibrium plateau before which the rate of generation of free carriers exceeds the rate of recombination of free carriers. The rise time decreases with increased intensity. The measured data for Epoxy 1478-1,

FIG. 3. CONDUCTIVITY VERSUS TIME FOR POLYSTYRENE AFTER THREE CONSECUTIVE EXPOSURES AT AN INTENSITY OF 1.9×10^5 RADS (H₂O)/MIN.

polyethylene, and polystyrene are presented in Fig. 4. A straight line on these $\ln \dot{R}$ versus $\ln \tau_r$ plots approximate the data points. The line is represented by the functional relationship

$$\tau_r = \tau_r' \dot{R}^{-\mu} \quad (3)$$

where τ_r' and μ are empirical constants, and are summarized in Table I. The rise times at 10^1 rads (H_2O)/min for polyethylene and polystyrene are, respectively, 460 seconds and 870 seconds. At 10^1 rads (H_2O)/min, Epoxy 1478-1 does not exhibit an observable increase in conductivity. The rise time at 2.2×10^5 rads (H_2O)/min for polyethylene, polystyrene, and Epoxy 1478-1 are, respectively, 10 seconds, 6.4 seconds, and 7.4 seconds.

TABLE I
Summary of μ and τ_r' as Defined by $\tau_r = \tau_r' \dot{R}^{-\mu}$

Material	μ	τ_r'
Epoxy 1478-1	0.41	$e^{7.0}$
Polyethylene	0.51	$e^{7.2}$
Polystyrene	0.50	$e^{7.9}$

Note: τ_r has units of seconds and $\dot{R}$ has units of rads (H_2O)/min.

Conductivity Versus Intensity

The plateaus (interval 2 of Fig. 3) of the continuously measured conductivity-time curves are used to obtain conductivity-intensity curves with temperature as a controlled variable. Typical conductivity-intensity data for Epoxy 1478-1 are shown in Fig. 5. The dependence of photoconductivity on irradiation intensity at a given temperature in all insulating materials studied can be characterized to good approximation in one or more regions of $\dot{R}$, within which conductivity, $\sigma(\text{ohm-cm})^{-1}$, is expressed as

$$\sigma = \sigma_o' \dot{R}^{\delta} \quad (4)$$

FIG. 4. Ln-Ln PLOT OF RISE TIME, SEC., VERSUS GAMMA-RAY INTENSITY, RADS (H_2O)/MIN., FOR EPOXY 1478-1, POLYETHYLENE, AND POLYSTYRENE.

FIG. 5. CONDUCTIVITY VERSUS INTENSITY FOR EPOXY 1478-1 AT 100, 120, AND 140° F.

where $\dot{R}$ is the gamma-ray intensity in rads(H₂O)/min, and σ'_0 and δ are empirical constants. σ'_0 and δ are summarized in Table II with temperature and intensity as variables. A dependence of photoconductivity of this form is expected from the model of Rose¹⁴ and has been previously found by Fowler¹⁵ and by Coleman¹⁶ at low intensities ($\dot{R} < 10^2$ rads(H₂O)/min). The magnitudes of σ'_0 and δ measured in this investigation agree, with a few distinct exceptions, with previous results. For example, the nonconstant slope of $\ln \sigma$ versus $\ln \dot{R}$ at higher intensities, as shown in Fig. 5 for Epoxy 1478-1, has not been observed in the intensity range and for the materials included in other reported work. The theoretical treatment of Rose predicts a range of values of $0.50 \leq \delta \leq 1.00$; whereas, values from 0.00 to 2.72 have been measured (Table II). Epoxy 1478-1, Epoxy 1478-3, polyvinylchloride, and nylon exhibit values of $\delta \approx 0.00$ within limited regions of $\dot{R}$. Epoxy 1478-1, polyvinylchloride, and Kel-F exhibit values of $\delta > 1.00$ also in limited regions of $\dot{R}$.

A mathematical treatment of the photoconductivity process, with appropriate references, is presented in Appendix F. Based on models by Rose, Fowler has shown how values of δ between 0.50 and 1.00 might be obtained for insulating materials considering an exponential distribution of trapping levels or a uniform distribution of trapping levels (see Appendix G). For an exponential distribution ($\delta \rightarrow 0.50$) the traps are considered to be distributed in exponentially decreasing numbers below the conduction band such that the energy distribution is given by

$$N_{E_x} dE_x = A e^{-E_x/kT_1} dE_x \quad (5)$$

where A and T_1 are constants for a given material and E_x is the photoconductivity activation energy. For a uniform distribution ($\delta \rightarrow 1.00$) the

¹⁴Rose, A., op. cit., (Ref. 1).

¹⁵Fowler, J. A., op. cit., (Ref. 2).

¹⁶Coleman, J. H., op. cit., (Ref. 3).

TABLE II

Measured Values of δ and σ'_0 for Ten Materials as Defined by $\sigma = \sigma'_0 \dot{R}^\delta$

Material	Sample No.	Temperature (°F)	δ	σ'_0	Range of $\dot{R}$, (rads (H ₂ O)/min)
Polystyrene ⁽¹⁾	K-20	100	0.97	7.51×10^{-19}	1.0 to 3.0×10^5
	K-18	120	0.97	7.51×10^{-19}	1.0 to 3.0×10^5
	K-19	140	0.97	7.51×10^{-19}	1.0 to 3.0×10^5
Polyethylene ⁽¹⁾	N-3	100	0.74	2.52×10^{-17}	5.0 to 1.0×10^5
	N-12	120	0.74	3.05×10^{-17}	5.0 to 1.0×10^5
	N-7	140	0.73	7.56×10^{-17}	5.0 to 1.0×10^5
Epoxy 1478-1 ⁽¹⁾	M-6	100	0.00	4.57×10^{-16}	1.0 to 1.0×10^2
			0.48	5.08×10^{-17}	1.0×10^2 to 3.5×10^3
			1.00	5.56×10^{-19}	3.5×10^3 to 2.5×10^5
	M-12	120	0.00	2.26×10^{-15}	1.0 to 5.4×10^2
			0.48	1.13×10^{-16}	5.4×10^2 to 1.5×10^4
			1.00	5.56×10^{-19}	1.5×10^4 to 2.5×10^5
	M-16	140	0.00	1.01×10^{-14}	1.0 to 4.5×10^3
			0.48	1.69×10^{-16}	4.5×10^3 to 3.3×10^4
			1.00	5.56×10^{-19}	3.3×10^4 to 2.5×10^5
Epoxy 1478-3 ⁽²⁾	C-2	90	0.00	1.66×10^{-15}	1.0×10^1 to 1.4×10^3
			0.94	2.04×10^{-18}	1.4×10^3 to 5.3×10^4
Epoxy 1478-22 ⁽²⁾	B-2	90	1.00	1.51×10^{-18}	1.0×10^1 to 5.3×10^4
Polyvinylchloride ⁽²⁾	1-1	90	0.00	1.37×10^{-17}	1.0×10^1 to 1.3×10^3
			2.72	5.62×10^{-26}	1.3×10^3 to 5.3×10^4

TABLE II (continued)

Material	Sample No.	Temperature (°F)	δ	σ'_o	Range of $\dot{R}$, (rads (H ₂ O)/min)
Polypropylene ⁽²⁾	A-3	90	0.82	1.51×10^{-18}	1.0×10^1 to 3.7×10^2
			-- (3)	-- (3)	3.7×10^2 to 9.0×10^2
			0.99	1.51×10^{-18}	9.0×10^2 to 5.3×10^4
Teflon ⁽²⁾	D-1	90	0.78	1.69×10^{-17}	1.0×10^1 to 5.3×10^4
Nylon ⁽²⁾	F-1	90	0.00	2.26×10^{-14}	1.0×10^1 to 1.9×10^4
			0.68	4.57×10^{-17}	1.9×10^4 to 5.3×10^4
Kel-F ⁽²⁾	G-2	90	0.44	1.85×10^{-18}	1.0×10^1 to 1.5×10^3
			2.00	2.05×10^{-23}	1.5×10^3 to 5.3×10^4

(1) Data taken under steady-state conditions at 500 v.

(2) Data taken at 500 v after 60 seconds of electrification.

(3) The relationship $\sigma = \sigma'_o \dot{R}^\delta$ will not hold in this region.

Note: σ has units of $\text{ohm}^{-1}\text{cm}^{-1}$ and $\dot{R}$ has units of $\text{rads (H}_2\text{O)/min}$.

traps are considered to be distributed uniformly in energy below the conduction band such that

$$N_E dE_x = \text{Constant } dE_x \quad (6)$$

For some of the materials in Table II the photoconductivity varies with a power of photon intensity greater than unity. This phenomenon is commonly called "superlinear photoconductivity." According to Rose,¹⁷ superlinearity will occur when the hole demarcation level,* the energy level of which is associated with the location of the electron Fermi level, moves down to include a class of defect centers as recombination centers that have small recombination cross sections. Superlinear photoconductivity is not uncommon and has been measured and reported by Bube¹⁸ in cadmium selenide (CdSe) and cadmium sulfide (CdS).

The conductivity values (σ) presented in this thesis include both the dark conductivity (σ_o) and photoconductivity (σ_p), i. e.,

$$\sigma = \sigma_o + \sigma_p = \sigma_o' \dot{R}^\delta \quad (7)$$

In most cases the photoconductivity completely masks the dark conductivity and

$$\sigma = \sigma_o' \dot{R}^\delta \approx \sigma_p \quad (8)$$

There are exceptions to Eq. 8 where the dark conductivity completely masks the photoconductivity and within the accuracy of the instrumentation no photoconductivity is measured, i. e.,

$$\sigma = \sigma_o' \dot{R}^\delta \approx \sigma_o \quad (9)$$

In such instances (see Table II) δ is considered to be zero and Eq. 7 reduces to

$$\sigma = \sigma_o' \approx \sigma_o \quad (10)$$

¹⁷Rose, A., "Recombination Processes in Insulators and Semiconductors," Phys. Rev., 97, 322 (1955).

*Hole demarcation level - defined as the energy level separating hole trapping and hole recombination levels in the band structure.

¹⁸Bube, R. H., "Photoconductivity of the Sulfide, Selenide, and Telluride of Zinc or Cadmium," IRE Trans., 43 (2), 1836, December (1953).

In all of this work "volume excited currents" are assumed, i.e., free positive and negative charges are equally distributed and space charge effects do not enter in. The rate of generation of these free positive and negative charges is a function of the gamma-ray intensity, and Appendix H presents and discusses a functional relationship for this generation rate, based on a best estimate of the average energy required for each hole-electron pair formed.

Conductivity Versus Temperature

Conductivity has been measured to vary with temperature under both dark and photoinduced conductivity conditions according to the general relationship

$$\sigma = \sigma_0 e^{-E/kT} \quad (11)$$

where $E = E_0$, the thermal activation energy for dark conductivity, or $E = E_x$, the thermal activation energy for photoconductivity. Values of E_0 and E_x for polyethylene, polystyrene, and Epoxy 1478-1 are presented in Table III. The thermal activation energy is lowered by irradiation except, as is noted, for the epoxy formulation in Region 1 where $E_0 = E_x$. E_x for the epoxy is zero in Region 3 which indicates that the photoconductivity is independent of temperature. Figures A-1, A-2, and A-3 of Appendix A represent conductivity versus (absolute temperature)⁻¹ data for Epoxy 1478-1, polyethylene, and polystyrene, respectively.

TABLE III

Thermal Activation Energies and Photoconductivity Activation Energies

Material	Thermal activation energy,	Photoconductivity
	E_0 , ev	activation energy, E_x , ev
Polyethylene	0.52	0.40
Polystyrene	0.50	0.13
Epoxy 1478-1	1.19	
Region 1		1.19
Region 2		0.48
Region 3		0.00

Conductivity Versus Accumulated Exposure

In addition to the gamma-ray photoconductivity effects in these insulating materials, a dark conductivity increase is sometimes measured after a given accumulated exposure, R . Figure 6 summarized such data for ten materials. These conductivities were measured 24 hours after exposure. Except for polyethylene and polystyrene, no extremely large changes are measured to 10^6 rads (H_2O). However, Teflon is beginning to show an upward trend, whereas polypropylene shows a distinct conductivity decrease.

Conductivity Recovery

Conductivity decays slowly after abruptly stopping radiation exposure. This slow rate of decay is assumed to be dictated by the effect of trapping. The effect of trapping is to make the measured decay time constant* of the photoconductivity longer than the carrier decay rate. In the absence of trapping centers, the measured photoconductivity decay will be equal to the recombination of the free carriers. If a discrete number of trapping centers is present, but the free carrier density is much greater than the trapped carrier density, then the observed initial decay of the photocurrent will again be the recombination rate of free carriers. When the density of free carriers is comparable to or less than the density of trapped carriers, the thermal freeing of trapped carriers during the decay process will prolong the decay so that the observed decay time constant is longer than the actual recombination rate. In the extreme case where the density of trapped carriers is much greater than the density of free carriers, the photoconductivity decay is effectively dominated by the rate of trap decay.

The measured photoconductivity decay for the organic materials of this work can be characterized as in Eq. 12

$$\sigma(t) = \sigma_{eq} \left[A e^{-t/\tau_1} + B e^{-t/\tau_2} \right] \quad (12)$$

by one or two time constants, τ_1 and τ_2 , where A and B are weighting factors. Decay data for polyethylene, polystyrene, and Epoxy 1478-1 after

*Decay time constant - time required for the conductivity to decay to $1/e$ its initial value.

FIG. 6. CONDUCTIVITY VERSUS ACCUMULATED EXPOSURE FOR TEN MATERIALS MEASURED 24 HOURS AFTER EACH EXPOSURE, AT 500 V., AFTER 60 SEC. OF ELECTRIFICATION, AND AT 90° F.

exposure to 2.0×10^5 rads (H_2O)/min at 130°F are presented in Fig.7. For polystyrene, $\tau_1 = 2$ seconds and $\tau_2 = 20$ seconds. For Epoxy 1478-1, $\tau_1 = 2.2$ seconds and τ_2 , if indeed it exists, is very long. In comparison, polyethylene has much longer time constants, and the shape of the decay curve does not permit the separation of these constants. Other measured data which support the existence of long decay time constants are presented in Fig. 8. This figure shows ascending and descending curves of photoconductivity for polyethylene, polystyrene, and Epoxy 1478-1 as a function of intensity with time allowed for conductivity stabilization at each plateau. Epoxy 1478-1 repeats a descent; polystyrene on descent departs from the ascending curve at a low intensity; and polyethylene on descent departs immediately from the ascending curve.

FIG. 7. RECOVERY CURVES AT 130°F AFTER EXPOSURE TO 2.0×10^5 RADS (H_2O)/MIN.

CHAPTER IV -- SUMMARY

This study of gamma-ray photoconductivity in organic dielectric materials has resulted in four distinct observations. The first measured phenomenon shows that the time required for the photoconductivity to achieve equilibrium upon exposure to a step increase in gamma-ray intensity ($\dot{R}$)--denoted as rise time, τ_r --to be inversely proportional to intensity, and the functional relationship characterizing this measured behavior is $\tau_r = \tau'_r \dot{R}^{-\mu}$. Secondly, a dependence of photoconductivity on irradiation intensity at a given temperature in all insulating materials studied was measured to be characterized to good approximation in one or more regions of $\dot{R}$, within which conductivity is expressed as $\sigma = \sigma'_0 \dot{R}^{\delta}$. The third observation concerns the conductivity decay upon removal of the sample from the gamma-ray environment. This decay was measured to be characterized by one or two decay constants, τ_1 and τ_2 , and is approximated by the relationship

$$\sigma(t) = \sigma_{eq} [Ae^{-t/\tau_1} + Be^{-t/\tau_2}] .$$

The fourth observation shows that the conductivity was measured to vary with temperature under both dark and induced conductivity conditions according to the relationship $\sigma = \sigma_0 e^{-E/kT}$

With the above qualitative information in hand, it is desirable to concentrate future experimental efforts toward the accumulation of knowledge as to the type and mobility of the carriers contributing to photoconductivity and toward a qualitative understanding of the distribution of states in the "band gap," all of which is needed for a better understanding of the mechanism of photoconductivity in organic dielectrics.

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APPENDIX A

MECHANISMS OF GAMMA-RAY INTERACTION WITH MATTER

There are three principal mechanisms by which gamma rays interact with matter to produce photoconductivity phenomena. These mechanisms are photoelectric effect, Compton effect, and pair production. These topics are discussed extensively in many texts. Five such texts are referenced here.¹⁹⁻²³

In the photoelectric effect, high-energy photons interact with the orbital electrons of the material. All of the photon energy is absorbed and the electron is ejected with an energy equal to that of the incident photon less the binding energy of the electron, i. e.,

$$E_k = h\nu - \omega \quad (A-1)$$

where E_k is the kinetic energy of the emitted electron, h is the Planck constant, ν is the frequency of the radiation, and ω is the energy necessary to eject the electron.

¹⁹Charlesby, A., Atomic Radiation and Polymers, Pergamon Press, New York, 1960.

²⁰Bovey, F. A., The Effects of Ionizing Radiation on Natural and Synthetic High Polymers, Interscience Publishers, Inc., New York, 1958, Vol. 1, Ch.1, p. 16.

²¹Sproull, R. L., Modern Physics, John Wiley and Sons, Inc., New York, 1956.

²²Birks, J. B., and Schulman, J. H., Progress in Dielectrics, Heywood and Company, Ltd., 1960, Vol. 2, p. 85.

²³Price, W. J., Nuclear Radiation Detection, McGraw-Hill Book Co., Inc., 1958.

The Compton effect is an elastic collision, to the first approximation, between a gamma-ray photon and an electron. Energy, which is sufficient to eject the latter with considerable velocity, is transferred. Compton electrons then lose their energy, as in the photoelectric effect, mainly by excitation and ionization of other atoms and may have initial energies ranging from 0 to a fraction,

$$\frac{2h\nu}{m_0c^2 + 2h\nu} \quad (A-2)$$

of that of the incident photon. The quantity $h\nu$ is the energy of the incident photon and m_0c^2 is the rest energy of the electron. For gamma-ray photoconductivity work in organic polymers, Compton effect is more pronounced than either photoelectric absorption or pair production. This is exemplified in Fig. A-1 where mass absorption coefficient* versus photon energy for carbon, the prime constituent of the polymer materials studied here, is presented. (These data taken from Bovey, Ref. 24.)

Electron-positron (pair) production results when the energy of an incident photon is greater than twice the rest energy of an electron ($2m_0c^2 = 1.02$ Mev). The photon ($h\nu$) interacts with the field of the nucleus to produce a positive and a negative electron. The excess energy (E_k)

$$E_k = h\nu - 2m_0c^2 \quad (A-3)$$

then appears as the sum of the kinetic energies of the electron and positron. The positron has a short life and eventually combines with an electron to give two photons.

* The mass absorption coefficient (μ) of an element is the fractional decrease in intensity per unit surface density.

²⁴Bovey, F. A., op cit., (Ref. 20, p. 20).

FIG. A-1. ABSORPTION COEFFICIENT VERSUS PHOTON ENERGY FOR CARBON.

APPENDIX B

TYPICAL ELECTRON TRANSITIONS IN PHOTOCONDUCTORS

The photoconductivity phenomenon is a consequence of the absorption of energy from electromagnetic radiation in a given material. This absorbed energy produces ionization and excitation by the three methods described in Appendix A. The more common electron transitions²⁵ which occur in the photoconductivity process are presented in Fig. B-1. Transition: (1) represents photon absorption by the atoms of the material producing a free electron and a free hole; (2) represents photon absorption at localized imperfections producing a free electron and a hole bound in the neighborhood of the imperfection; (3) represents photon absorption, raising an electron from the valence band to an unoccupied imperfection level, producing a free hole and an electron bound in the neighborhood of the imperfection; (4) represents trapping and thermal release of holes in hole traps (electron transition); (5) represents trapping and thermal release of electrons in electron traps; (6) represents recombination where a free electron combines directly with a free hole; (7) represents recombination through recombination centers where a hole is captured by an excited center containing an electron; and (8) represents recombination through recombination centers where an electron is captured by an excited center containing a hole.

²⁵ Bube, R. H., op. cit., (Ref. 11, Ch.2, p. 10).

FIG. B-1. COMMON ELECTRON TRANSITIONS IN PHOTOCONDUCTORS.

APPENDIX C

CHEMICAL STRUCTURE OF SELECTED ORGANIC MATERIALS²⁶⁻²⁸

This appendix is included to present a brief description of the molecular structure of those materials studied in this photoconductivity work. The thermalplastics discussed are polyethylene, polystyrene, polypropylene, nylon, Teflon, polyvinylchloride, and Kel-F. The three thermalsetting Epoxy formulations discussed are 1478-1, 1478-3, and 1478-22.

Polyethylene

The polyethylene (Marlex 50) polymer is reported to be as high as 60 percent crystalline. This is a linear polymer and is typically represented as

specific gravity 0.96

Polystyrene

Polystyrene has a long chain structure with a benzene ring attached as indicated below:

specific gravity 1.02

All presently available polystyrene is completely amorphous due to the random stereoisomerism of the structure.

²⁶Birks, J. B., and Schulman, J. H., op. cit., (Ref. 22, pp. 29-77).

²⁷Sheist, Irving, Epoxy Resins, Reinhold Publishing Corp., New York, 1959.

²⁸Lee, Henry, and Neville, Kris, Epoxy Resins, McGraw-Hill Book Co., Inc., 1957.

Polypropylene

The basic propylene structure is

Propylene does not polymerize readily. The polypropylene molecule can exist as an atactic (random) polymer, isotactic (all the substituents lie on one side of a theoretical plane containing the main C-C chain) polymer, or syndiotactic (the substituents alternate above and below a theoretical plane containing the main C-C chain) polymer. Here the polypropylene molecule is represented as a syndiotactic polymer.

specific gravity 0.91

Nylon

The nylon used here was Zitol 101 (66 nylon) and is formed from the six-carbon acid and six-carbon diamine, adipic acid, and hexamethylene diamine. The structure is as follows:

specific gravity 1.14

Polytetrafluoroethylene (Teflon)

Polytetrafluoroethylene, a crystalline polymer commonly known as Teflon, consists simply of a linear saturated fluorocarbon, i. e., linear polyethylene with all hydrogen atoms substituted by fluorine atoms.

specific gravity 2.15

Polyvinylchloride (PVC)

Polyvinylchloride, PVC, is generally considered to be a non-crystalline polymer. Random stereoisomerism at the carbon atoms attached to the chlorines is accepted as the reason for the inability of this polymer to crystallize. The polymer structure is:

specific gravity 1.36

Polychlorotrifluoroethylene (Kel-F)

Polychlorotrifluoroethylene, Kel-F, has properties which are in many respects similar to Teflon to which it is structurally closely related. Alternate carbon atoms have a fluorine atom replaced with a chlorine.

specific gravity 2.10

The substitution of a chlorine atom gives rise to possible stereoisomerism; however, apparently because of the close similarity in size of the chlorine and fluorine atoms it does not prevent crystallization, but does result in a much less, highly ordered organic crystalline structure.

Epoxy Formulations

The thermalsetting resins are basically Shell Epon 828 with variations in curing agents and fillers.

Epoxy 1478-1

This formulation has the following composition:

Base Resin: 60 PBW*, Shell Epon 828

Filler: 40 PBW, 4x mica

Curing agent: 7.2 PBW, diethanolamine (DEA)

*PBW - Parts by weight

Curing time: 15 hours at 165°F

Specific gravity: 1.52

The 4x mica filler used here is reinforcing.

Epoxy 1478-3

This formulation has the following composition:

Base resin: 100 PBW, Shell Epon 828

Filler: none

Curing agent: 7.2 PBW, diethanolamine (DEA)

Curing time: 15 hours at 165°F

Specific gravity: 1.20

Epoxy 1478-22

This formulation has the following composition:

Base resin: 100 PBW, Shell Epon 828

Filler: none

Curing agent: 20 PBW, "Z"; i.e., eutectic of H, 4' methylene
di-aniline and meta phenylene diamine

Curing time: 18 hours at room temperature + 15 hours at
120°F + 8 hours at 212°F

Specific gravity: 1.20

APPENDIX D
SAMPLE IDENTIFICATION AND THICKNESS

Material Type	Sample No.	Thickness, cm
Polyethylene	N-1	0.160
	N-2	0.160
	N-3	0.165
	N-5	0.151
	N-6	0.152
	N-7	0.152
	N-8	0.165
	N-10	0.162
	N-11	0.156
	N-12	0.146
Polystyrene	K-1	0.137
	K-2	0.143
	K-13	0.157
	K-14	0.160
	K-15	0.160
	K-16	0.159
	K-17	0.158
	K-18	0.163
	K-19	0.163
	K-20	0.157
Polyvinylchloride (PVC)	I-1	0.321
	I-2	0.314
Polypropylene	A-1	0.324
	A-3	0.325
Polytetrafluoroethylene (Teflon)	D-1	0.332
	D-2	0.335
Nylon	F-1	0.265
	F-2	0.268
Polychlorotrifluoro- ethylene (Kel-F)	G-2	0.165
	G-3	0.165

SAMPLE IDENTIFICATION AND THICKNESS (Continued)

<u>Material Type</u>	<u>Sample No.</u>	<u>Thickness, cm</u>
Epoxy 1478-1	M-1	0.152
	M-2	0.119
	M-5	0.313
	M-6	0.318
	M-7	0.310
	M-10	0.307
	M-11	0.310
	M-12	0.313
	M-13	0.306
	M-16	0.317
Epoxy 1478-3	C-2	0.294
	C-3	0.284
Epoxy 1478-22	B-2	0.368
	B-3	0.264

APPENDIX E

DISCUSSION OF LEAKAGE CURRENTS

The successful elimination of leakage current was assured by experimental measurements. The proof of this leakage current elimination is as follows:

- (1) The dark conductivity of each disc of all materials studied, including the encapsulating material, was measured before and after encapsulation. Symbolically, these measurements are

$$\sigma_{o,x,b} = \text{the dark conductivity } (\sigma_o) \text{ of} \\ \text{material (x) before encapsulation (b)}$$

and

$$\sigma_{o,x,a} = \text{the dark conductivity of the same} \\ \text{material after encapsulation (a)}$$

In all cases, within experimental error,

$$\sigma_{o,x,b} = \sigma_{o,x,a} \quad (E-1)$$

which demonstrated that no measurable leakage current passed through the encapsulating material under dark conditions.

- (2) Equation (E-1) is equal to

$$\sigma_{o,x,b} = \sigma_{o,x,a} = \sigma_{o,x} \quad (E-2)$$

or

$$\sigma_{o,x,b} = \sigma_{o,x,a} = \sigma_{o,\ell,x} = \sigma_{o,\ell} \quad (E-3)$$

where $\sigma_{o,x}$ = the dark conductivity of any disc of material x.

$\sigma_{o,\ell,x}$ = the dark conductivity of the encapsulating material when used as a disc of material x, and is equal to $\sigma_{o,\ell}$, the dark conductivity of the material comprising the leakage path.

- (3) The photoconductivities of each disc of all materials studied, including the encapsulating material, were measured in the encapsulated units during exposure.

Symbolically these measurements gave

σ_x = the photoconductivity (σ) of material (x) at any given
gamma-ray intensity ($\dot{R}$)

and

$\sigma_{\ell, x}$ = the photoconductivity of the encapsulation material when
used as material x at any given gamma-ray intensity, and
is also equal to σ_{ℓ} , the conductivity of the leakage path
under the same irradiation condition.

- (4) The sufficient condition to assure that the leakage current in the encapsulating material did not contribute to the measurement of the photoconductivity of a material x is shown in the Eq. (E-4).

$$\frac{I_{\ell, x}}{I_x} = \frac{A \sigma_{\ell} + B \sigma_{\ell, x}}{A \sigma_{\ell} + B \sigma_x} \leq \frac{A \sigma_{o, \ell} + B \sigma_{o, \ell, x}}{A \sigma_{o, \ell} + B \sigma_{o, x}} = \frac{I_{o, \ell, x}}{I_{o, x}} \quad (E-4)$$

where $I_{\ell, x}$ = the measured photocurrent in the encapsulating
material when tested as disc x. $I_{\ell, x}$ is related
to conductivity by

$$I_{\ell, x} = B \sigma_{\ell, x} V \quad (E-5)$$

where B is the effective area divided by the
thickness of the disc of encapsulation material
and V is the test voltage.

$I_{o, \ell, x}$ = the corresponding dark current in the encapsulating
material when tested as a disc x.

I_x = the measured photocurrent in the disc of
material x and is related to conductivity by

$$I_x = B \sigma_x V \quad (E-6)$$

where, as before, B is the effective area divided
by the thickness of the discs of any material x.

$I_{o,x}$ = the corresponding dark current in the discs
of material x ,

and A = the effective area of the leakage path divided by
the effective length of the leakage path.

(5) The sufficient condition of Eq. (E-4) reduces to

$$\frac{I_{l,x}}{I_x} = \frac{\sigma_{l,x}}{\sigma_x} \leq \frac{\sigma_{o,l,x}}{\sigma_{o,x}} = \frac{I_{o,l,x}}{I_{o,x}} \quad (E-7)$$

since conductivity measurements revealed that the following
conditions existed:

$$B \sigma_{l,x} \gg A \sigma_l$$

$$B \sigma_x \gg A \sigma_l$$

$$B \sigma_{o,l,x} \gg A \sigma_{o,l}$$

$$B \sigma_{o,x} \gg A \sigma_{o,l}$$

(6) The sufficient condition of Eq. (E-7) must be satisfied for all levels
of the radiation intensity to assure that leakage current is negligible
for each encapsulated sample studied.

APPENDIX F

MATHEMATICAL FORMULATION OF THE PHOTOCONDUCTIVITY
PROCESS IN SINGLE CRYSTAL PHOTOCONDUCTORS

The framework for a mathematical formulation of the photoconductivity process is substantially the same as that effectively used in semiconductor junction device physics.²⁹ Before presenting these mathematical functions it is necessary to make certain basic assumptions: (1) an ohmic contact exists at the photoconductor-electrode interface; (2) ionic currents are negligible; (3) photocarriers are produced by excitation from the valence to the conduction band (more simplified than the electronic transitions presented in Appendix B); and (4) the energy level scheme of Fig. F-1 is composed of a valence band, a conduction band, one type of donor and one type of acceptor level, and a single set of imperfection centers. The mathematical treatment based on these assumptions was first presented by Rittner (1954)³⁰ and later published in a more abbreviated and summarized form by Bube (1960).³¹ The equations governing the behavior of the free electrons, free holes, and trapped electrons associated with the abbreviated model of Fig. F-1 are as follows:

$$\frac{\partial p}{\partial t} = -\frac{p - p_o}{\tau_p} + g_{vt} - r_{tv} + f - e^{-1} \operatorname{div} \vec{J}_p \quad (\text{F-1})$$

$$\frac{\partial n}{\partial t} = -\frac{n - n_o}{\tau_n} + g_{tc} - r_{ct} + f - e^{-1} \operatorname{div} \vec{J}_n \quad (\text{F-2})$$

$$\frac{\partial n_t}{\partial t} = r_{ct} - g_{tc} + g_{vt} - r_{tv} \quad (\text{F-3})$$

²⁹Shockley, W., Electrons and Holes in Semiconductors, D. Van Nostrand Company, Inc., New York, (1959), Ch.12, p. 298.

³⁰Rittner, E. S., Electron Processes in Photoconductors, Photoconductivity Conference, Atlantic City, 1954.

³¹Bube, R. H., op. cit., (Ref. 11, Ch.11, p. 235).

- E_g - BANDGAP
- E_c - ENERGY LEVEL, BOTTOM OF CONDUCTION BAND
- E_v - ENERGY LEVEL, TOP OF VALENCE BAND
- E_t - ENERGY LEVEL, IMPERFECTION CENTERS
- E_d - ENERGY LEVEL, DONOR STATES
- E_a - ENERGY LEVEL, ACCEPTOR STATES
- N_c - DENSITY OF STATES IN CONDUCTION BAND
- N_v - DENSITY OF STATES IN VALENCE BAND
- N_t - DENSITY OF IMPERFECTION CENTERS
- N_d - DENSITY OF DONOR STATES
- N_a - DENSITY OF ACCEPTOR STATES

FIG. F-1. SIMPLIFIED ENERGY LEVEL DIAGRAM

$$\vec{J}_p = e\mu_p p \vec{E} - e D_p \text{grad } p \quad (\text{F-4})$$

$$\vec{J}_n = e\mu_n n \vec{E} + e D_n \text{grad } n \quad (\text{F-5})$$

$$\vec{J} = \vec{J}_n + \vec{J}_p \quad (\text{F-6})$$

$$\text{div } \vec{E} = \frac{4\pi q}{\epsilon} \quad (\text{F-7})$$

The seven equations just presented can be combined into four equations with four unknowns (n , p , n_t , and q).

Equations F-1 and F-2 are the continuity equations for free holes and free electrons, respectively. The first term on the right represents the disappearance of free carriers by recombination. τ_p and τ_n are hole and electron lifetimes, and p_0 and n_0 are the dark hole and dark electron densities. The lifetimes in general are considered concentration dependent. The second term represents the excitation of captured carriers with

$$g_{vt} = (N_t - n_t) N_v S_p e^{-(E_g - E_t)/kT} \quad (\text{F-8})$$

$$g_{tc} = n_t N_c S_n e^{-E_t/kT} \quad (\text{F-9})$$

where N_t is the density of imperfection centers, n_t of which are occupied by electrons with capture cross section S_p for a free hole when occupied by an electron, and with capture cross section S_n for a free electron when unoccupied; and v is the thermal velocity of a free electron. The third term represents the capture of free carriers with

$$r_{tv} = p n_t v S_p \quad (\text{F-10})$$

$$r_{ct} = n (N_t - n_t) v S_n \quad (\text{F-11})$$

The fourth term, f , represents the density of carriers generated per unit time by the incident photons. The fifth term represents the divergence of the current densities, i. e., the magnitude of charge flow across the photoconductor-conductor interface.

Equation F-3 is the continuity equation for electrons in the imperfection centers; excitation from or into these centers by photons has been neglected for this discussion. Equations F-4, F-5, and F-6 give, respectively, the definitions for the current density of holes, the current density of electrons, and the total current density. The current densities consist of two terms, the first a conduction term, and the second a diffusion term; where μ_p and μ_n are hole and electron mobility, E is the electric field, and D_p and D_n (hole and electron diffusion constants) are from the Einstein relationships, where

$$D_p = \frac{kT}{e} \mu_p \quad (F-12)$$

$$D_n = \frac{kT}{e} \mu_n \quad (F-13)$$

Equation F-7 is Poisson's relationship with q representing the space-charge density.

In order to reduce the mathematical complexity associated with the solution of Eqs. F-1 through F-7, certain assumptions can be made: (1) space-charge effects may be neglected, i. e., $q = 0$ and $\Delta n + \Delta n_t = \Delta p$; and (2) electron and hole lifetimes are equal, i. e., $\tau_n = \tau_p = \tau$. On substituting Eqs. F-4 and F-5 into Eqs. F-1 and F-2, F-14 is obtained.

$$\frac{\partial p}{\partial t} = -\frac{\Delta p}{\tau} + g_{vt} - r_{vt} + f + D_p \operatorname{div} \operatorname{grad} p - \mu_p p \operatorname{div} \vec{E} - \mu_p \vec{E} \cdot \operatorname{grad} p \quad (F-14)$$

$$\frac{\partial n}{\partial t} = -\frac{\Delta n}{\tau} + g_{tc} - r_{ct} + f + D_n \operatorname{div} \operatorname{grad} n + \mu_n n \operatorname{div} \vec{E} + \mu_n \vec{E} \cdot \operatorname{grad} n \quad (F-15)$$

Now multiplying Eq. F-14 by the quantity μ_n and Eq. F-15 by μ_p ; adding to eliminate $\operatorname{div} E$ terms; and with subsequent use of Eq. F-3, above assumption (1), and the following relationships

$$\begin{aligned} \Delta n + \Delta n_t &= \Delta p \\ \frac{\partial n}{\partial t} + \frac{\partial n_t}{\partial t} &= \frac{\partial p}{\partial t} = \frac{\partial \Delta p}{\partial t} \\ \operatorname{grad} n + \operatorname{grad} n_t &= \operatorname{grad} p = \operatorname{grad} \Delta p \end{aligned} \quad (F-16)$$

The following equation is obtained

$$\frac{\partial \Delta p}{\partial t} = -\frac{\Delta p}{\tau} + \frac{\gamma \Delta n_t}{\tau} + g_{vt} - r_{tv} + f + D \operatorname{div} \operatorname{grad} \Delta p \quad (\text{F-17})$$

$$- \gamma D_n \operatorname{div} \operatorname{grad} \Delta n_t + \mu^* \vec{E} \cdot \operatorname{grad} \Delta p - \gamma \mu_n \vec{E} \cdot \operatorname{grad} \Delta n_t$$

where

$$\gamma = \frac{1}{1 + \mu_n n / \mu_p p} \quad (\text{F-18})$$

$$D = \frac{n + p}{n/D_p + p/D_n} \quad (\text{F-19})$$

$$\mu^* = \frac{p - n}{n/\mu_p - p/\mu_n} \quad (\text{F-20})$$

In Eq. F-17 there are three unknowns: Δn , Δp , and Δn_t . There are also three equations relating these unknowns: Eqs. F-17, F-16, and F-3. In general, the task of finding a solution to Eq. F-17 satisfying appropriate boundary conditions is a quite formidable one because of the nonlinear nature of the differential equation. However, by imposing additional restrictions, useful solutions possessing a limited range of validity can be obtained.

One such restriction, neglecting impurity states, reduces Eq. F-17 by eliminating the g , r , and Δn_t terms and gives

$$\frac{\partial \Delta p}{\partial t} = -\frac{\Delta p}{\tau} + f + D \operatorname{div} \operatorname{grad} \Delta p + \mu^* \vec{E} \cdot \operatorname{grad} \Delta p \quad (\text{F-21})$$

Since this equation is still nonlinear because of the dependence of τ , D , and μ^* on n and p , additional simplification is desirable. If diffusion effects are neglected, i. e., neglect end effects in a uniformly excited, homogeneous photoconductor, so that $\operatorname{grad} \Delta p = 0$, then

$$\frac{d\Delta p}{dt} = -\frac{\Delta p}{\tau} + f \quad (\text{F-22})$$

This equation for hole generation under steady-state conditions reduces to

$$f \tau_p = \Delta p \quad (\text{F-23})$$

and conversely for electron generation using a similar method of solution

$$f \tau_n = \Delta n \quad (\text{F-24})$$

where τ_n is the free lifetime of an electron, τ_p is the free lifetime of a hole, and Δn and Δp are, respectively, the additional free-electron and free-hole densities present as a result of the absorption of photons. The incremental conductivity can now be written as

$$\Delta \sigma = e \mu_n \Delta n + e \mu_p \Delta p \quad (\text{F-25})$$

or

$$\Delta \sigma = f e (\mu_n \tau_n + \mu_p \tau_p) \quad (\text{F-26})$$

This relationship shows why the lifetime is a key parameter in photoconductivity and that, in this instance, incremental conductivity is directly proportional to the first power of f .

This simplified mathematical description of the photoconductivity process indicates the complexities of a complete solution, assuming photoconductivity material was available whose device physics was quantitatively understood and defined. In the case of organic insulating material whose photoconductivity properties are not explicitly defined and well understood, the situation is distinctly more complicated. An example is the inability, at the present time, to measure the Hall mobilities, μ_n , of low-conductivity organic dielectrics. Therefore, the effective combination of Hall effect and conductivity measurements to determine the concentration and mobility of the charge carriers is not possible. Consequently, no distinction can be drawn as to which of the two carriers is the majority or the minority carrier. The measurement of conductivity gives only $e(n\mu_n + p\mu_p)$.

The application of the basic continuity equations (F-1 through F-7) to the photoconductivity phenomena in organic dielectrics is valid and can be used to give a qualitative understanding of the processes involved.

APPENDIX G

MODELS WHICH FIT MEASURED PHOTOCONDUCTIVITY PHENOMENA

From a mathematical viewpoint, Appendix F discussed a simplified photoconductivity model with one type of donor and one type of acceptor level, and a single set of imperfection centers. This appendix will discuss models which better classify and describe observed photoconductivity behavior in organic dielectrics. The material for this discussion is based on a publication by Rose³² which discusses photoconductivity processes and on a publication by Fowler,³³ extending the publication by Rose, which explains measured photoconductivities in amorphous and semicrystalline insulating materials. The following models draw heavily on the depth and distribution of traps (imperfection centers) in the forbidden region, assume a conventional band structure, and assume conduction by electrons only.

Let the traps be distributed in exponential decreasing numbers below the conduction band such that the energy distribution is given by

$$n_{E_x} dE_x = A e^{-E_x/kT_1} dE_x \quad (G-1)$$

Such a distribution is presented in Fig. G-1. The temperature T_1 is used here to indicate a temperature higher than room temperature. Physically, T_1 is considered to be the temperature at which the traps were "frozen in" as the polymer structure was formed. Therefore, A and T_1 are constants for a given material, E_x is the photoconductivity activation energy, and n_{E_x} is the number of traps per unit volume per unit energy depth.

The number of electrons, n_t , trapped below E_x is equal to the number of traps, N_t , below E_x and is a good approximation of the number of holes.

³²Rose, A., op. cit. (Ref. 1).

³³Fowler, J. F., op. cit., (Ref. 2).

FIG. G-1.EXPONENTIAL TRAP DISTRIBUTION.

p, i.e., $n_t = N_t$ and $p = n + n_t \approx n_t$. Thus,

$$\begin{aligned} p \approx n_t &= \int_{E_x}^{\infty} A e^{-E_x/kT_1} dE_x \\ &= A k T_1 e^{-E_x/kT_1} = B T_1 e^{-E_x/kT_1} \end{aligned} \quad (G-2)$$

now combining p with the following expression for the number of conduction electrons, n, under steady-state conditions

$$n = f/vsp \quad (G-3)$$

Eq. G-4 is obtained

$$n = f/vsBT_1 e^{-E_x/kT_1} \quad (G-4)$$

where v is the thermal velocity of a free electron and s is the capture cross section of holes for free electrons. The value of the photoconductivity activation energy, E_x , is commonly given by

$$n = N e^{-E_x/kT} \quad (G-5)$$

or

$$E_x = kT \ln N/n \quad (G-6)$$

now combining Eqs. G-4 and G-6 gives

$$n = f/vsBT_1 \left(\frac{n}{N}\right)^{T/T_1} \quad (G-7)$$

or in a slightly more useful form solving for n

$$n = \left[f/vsBT_1 N^{-T/T_1} \right]^{T_1/(T+T_1)} \quad (G-8)$$

If $T_1 = T$, n (the photocurrent and the photoconductivity) increases as the square root of the light intensity. In brief, an exponential trap distribution in energy below the conduction band can yield a range of exponents between 0.50 and 1.00 for conductivity versus photo intensity depending on the temperature, T_1 , at which the traps were "frozen in." Being consistent with our notation for gamma-ray photoconductivity,

$$\sigma = \sigma_0' \dot{R}^\delta = \sigma_0' \dot{R}^{T_1/(T+T_1)} \quad (G-9)$$

where $\delta = T_1/(T + T_1)$. $\delta \rightarrow 0.50$ for an exponential trap distribution, T_1 low, and $T \approx T_1$.

$\delta \rightarrow 1.00$ for a uniformly distributed trap depth in energy below the conduction band. The energy diagram for such an assumed distribution is presented in Fig. G-2. The energy distribution function is

$$n_{E_x} dE_x = \text{constant } dE_x \quad (\text{G-10})$$

and as in the above case $p = n + n_t \approx n_t$. Thus

$$p \approx n_t = \text{constant} \quad (\text{G-11})$$

Combining p with the expression for conduction electrons, n ,

$$n \approx f/vsp \quad (\text{G-12})$$

it follows that n (the photocurrent and the photoconductivity) increases linearly with light intensity and for Eq. G-9 $\delta = 1.00$.

These two models have been used in the past to explain measured behavior when $0.50 \leq \delta \leq 1.00$. The band structure of Figs. G-1 and G-2 is used for convenience. Fowler has suggested that a discontinuous band structure, as shown in Fig. G-3, is more appropriate for the amorphous and semicrystalline organic insulators of this work. This structure predicts that the conduction levels of one spatially located group of atoms may be the trapping levels for a neighboring spatially located group and vice versa.

FIG. G-2.UNIFORM TRAP DISTRIBUTION.

FIG. G-3. DISCONTINUOUS BAND STRUCTURE OF AMORPHOUS AND SEMICRYSTALLINE ORGANIC INSULATORS AS SUGGESTED BY FOWLER.

APPENDIX H-RATE OF IONIZATION

The one distinct difference between gamma-ray photoconductivity in organic insulating material and visible light photoconductivity in single-crystal inorganic materials is the number of ionizations per absorbed photon. In the latter case, the ratio is generally assumed to be 1 to 1; i. e., for each photon absorbed by the material, one ion pair is formed.^{34,35} For gamma rays the ionized electrons have a "fast energy" associated with them. This excess kinetic energy is dissipated in secondary collisions and the resulting electron-electron interactions produce charge carriers. Thus, the common property of gamma-ray photons is that the amount of energy carried by each is approximately five orders of magnitude greater than that binding an orbital electron to its nucleus or an atom to its neighbor. These energies will usually be less than that required to affect the binding force within the atomic nucleus. In reality, gamma-ray photons lose most of their energy by interaction with orbital electrons to produce ions, free electrons, and excited atoms or molecules. Seitz and Koehler³⁶ have quoted a value of only 1 percent for the amount of energy lost in other ways.

Charlesby³⁷ quotes a figure for the average energy required per ion pair formed in air. This figure is 34 ev. In their passage through air, gamma rays produce ionization of the gas molecules and render the air conductive. The 34-ev energy is considerably greater than the minimum energy required to ionize either a neutral oxygen (O_2 - 12.2 ev) or nitrogen (N_2 - 15.6 ev) molecule.³⁸ The remaining energy absorbed is dissipated

³⁴Sproull, R. L., op. cit., (Ref. 21, Ch. 10, p. 304).

³⁵Kittel, C., Introduction to Solid State Physics, John Wiley and Sons, Inc., New York, 1957, Second Edition, Ch.18, p. 512.

³⁶Seitz, F., and Koehler, J. S., International Conference on Peaceful Uses of Atomic Energy, Geneva 7, 615, 1955.

³⁷Charlesby, A., op. cit., (Ref. 19, Ch. 2).

³⁸Charlesby, A., op. cit., (Ref. 19, p. 19).

in the form of electronic excitation, kinetic energy, or heat. The number of excited molecules produced cannot be measured, but Charlesby estimates that in many cases the total absorbed energy is shared between ionization and excitation in roughly equal amounts.

In liquids and solids, the measurement of ionization is greatly complicated by the close proximity of neighboring molecules or atoms. This allows reactions between ions, free electrons, and excited atoms or molecules to proceed very rapidly. The primary yield of ions cannot be measured directly, and in this work on organics it is assumed to be the same as air, 34 ev.

Based on the above discussion and the assumed quantity of 34 ev, the following relationship was developed for the rate of ionization in a given material.

$$F = \frac{K\dot{R}\rho V}{34} \quad (\text{H-1})$$

where F = ionization rate, no./sec

$\dot{R}$ = dose rate, rads/sec (rad = 100 ergs/gm = 6.24×10^{13} ev/gm)

ρ = density, gm/cm³

V = volume, cm³

K = constant, 6.24×10^{13} ev/gm-rad

34 = constant, ev/ionization

APPENDIX I

THERMAL ACTIVATION ENERGIES AND PHOTOCONDUCTIVITY ACTIVATION ENERGIES

Conductivity varies with temperature under both dark and photoinduced conductivity conditions according to the general relationship

$$\sigma = \sigma_o e^{-E/kT} \quad (I-1)$$

where $E = E_o$ the thermal activation energy for dark conductivity, or $E = E_x$ the thermal activation for photoconductivity. Measured values of E_o and E_x are presented in Fig. I-1 for Epoxy 1478-1, Fig. I-2 for polyethylene, and Fig. I-3 for polystyrene. E_x for the epoxy, as shown in Fig. 5, is a function of the region in question. E_x for polyethylene and polystyrene is constant for the gamma-ray intensity limits of this work.

E_o or E_x is calculated by knowing the sets of boundary conditions, (T_a, σ_a) and (T_b, σ_b) , which are taken from data plots of conductivity versus (absolute temperature)⁻¹ and by manipulation of Eq. I-1, i. e.,

$$\sigma = \sigma_o e^{-E/kT}$$

or

$$\ln \sigma = \ln \sigma_o - E/kT \quad (I-2)$$

then

$$E/kT = \ln \sigma_o - \ln \sigma$$

and

$$\ln \sigma_o = \ln \sigma + E/kT \quad (I-3)$$

In Eq. I-2 boundary condition (T_a, σ_a) gives

$$E/kT_a = \ln \sigma_o - \ln \sigma_a \quad (I-4)$$

and in Eq. I-3 boundary condition (T_b, σ_b) gives

$$\ln \sigma_o = \ln \sigma_b + E/kT_b \quad (I-5)$$

The combining of Eqs. I-4 and I-5 gives

$$E/kT_a = \ln \sigma_b + E/kT_b - \ln \sigma_a$$

or

(I-6)

$$\frac{E}{k} \left[\frac{1}{T_a} - \frac{1}{T_b} \right] = \ln \sigma_b - \ln \sigma_a$$

The solution for E, which is either E_o or E_x , gives

$$E = \frac{k \left[\ln \sigma_b - \ln \sigma_a \right]}{\left[1/T_a - 1/T_b \right]} \quad (I-7)$$

where $k = 8.62 \times 10^{-5}$ ev/°K