ORNL-TM-2986

REACTOR CHEMISTRY DIVISION

THE DEVELOPMENT OF RADIATION-RESISTANT INSULATORS PROGRESS REPORT - JULY 1, 1967 to JULY 1, 1969

(OCD Project Order Number OCD-PS-66-115)

AEC Interagency Agreement 40-90-66

by

M. J. Kelly and W. W. Parkinson

for

Office of Civil Defense
Office of the Secretary of the Army
Washington, D. C. 20310

OCD REVIEW NOTICE

This report has been reviewed by the Office of Civil Defense and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Office of Civil Defense.

This document has been approved for public release and sale; its distribution is unlimited.

AUGUST 1970

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. Atomic Energy Commission

CONTENTS

PART A. THEORETICAL BACKGROUND

PART B. EXPERIMENTAL RESULTS AND DISCUSSION

THE DEVELOPMENT OF RADIATION-RESISTANT INSULATORS
PROGRESS REPORT - JULY 1, 1967 to JULY 1, 1969

M. J. Kelly and W. W. Parkinson

ABSTRACT

The apparent electrical conductivity of high-resistance plastics has been examined from the standpoint of dielectric relaxation processes as well as steady-state conductivity. The observed, time-dependent conductivity of high-purity polystyrenes, commercial plastics of lower purity and of the copolymer in use for dosimeters can be accounted for on the basis of dielectric charging and low values of conductivity, both varying with the polar nature of the base polymer and the impurities. During irradiation the conductivity increases greatly depending on the dose rate and decays after irradiation with a time dependence related to the composition of the specimen.

To be suitable for dosimeter use, the radiation-induced conductivity must decay rapidly, to values below 10^{-19} mhos/cm in 10^4 seconds. The currently used material, a copolymer of styrene and α-methyl styrene (Cerex 250B) was found to have unusually rapid decay of conductivity following irradiation. By polymer fractionation and by varying the synthesis ingredients, the chemical species active in reducing conductivity was identified as sulfate chain ends arising from persulfate initiator in the polymerization recipe.

Styrene homopolymers have been synthesized with sulfate end groups and shown to have as low conductivity as the copolymer. Polymers with sulfate end groups and (NH_4) cations have shown low but erratic conductivity and polystyrenes having end groups of moderate polarity have lower dielectric charging prior to irradiation and some reduction in postirradiation conductivity. Methods are proposed for development work to exploit these possibilities for improving plastic insulators.

Part A. Theoretical Background

I. INTRODUCTION

This report covers the period from July 1967 to July 1969 in a three-year project to develop improved insulating materials for use in electrostatic dosimeters. The scope of the project and the general method of approach to the problem were presented in the previous report[1] and will not be repeated here. Instead, broad discussion of the general

BLANK PAGE

problem is attempted using data and theory available from the open literature incorporated with observed data from our continuing experimental program.

It is not our intent to treat the problem rigorously or reach absolute conclusions. It is hoped, however, that generalized conclusions will be apparent in specific areas and that anomalies and areas of uncertainty will be brought into focus.

II. PRE-IRRADIATION PROPERTIES OF PLASTICS

A. Dielectric Charging Phenomena

Dielectric relaxation or "charging" corresponds to the increased capacitance due to the polarization of the dielectric in the sense that positive and negative charges within it are displaced slightly from their normal positions. If these positive and negative charges are considered to be dipoles caused by molecular grouping (e.g., the $>C=O$ or carbonyl group with the positive and negative charge centers near the carbon and oxygen respectively), the individual charges cannot move over large distances but can act as a vector under an applied field, altering length or direction to affect the apparent dielectric constant. In a real system, this effect does not result in charge transport (conductivity), but results in a change in charge density with time which may be confused with direct current conductivity.

The task of dielectric theory is difficult not so much because permanent dipoles cannot always be identified, but because they influence one another mutually, a dipole is not only subject to the influence of an external field but also has a field of its own. The mutuality of the influence of dipoles, permanent or otherwise, on one another makes the response of the assembly a cooperative phenomenon. The effective field acting on a dipole, in general, is not the externally applied field, E, but is augmented by a contribution from this cooperation.

In the case of symmetric polymers like polyethylene ($-CH_2-CH_2-CH_2-$) the dipole moment is frequently thought to be zero and any observed dielectric relaxation or loss tangent is attributed to impurities, polar end groups, and accidental oxidation products. This is not strictly true[2] since microwave spectroscopy studies have shown propane to have a dipole moment of 0.081 debye units and isobutane to have 0.132 debye units. Therefore, moments exist because of differences in polarity of carbon-hydrogen bonds. Methyl end groups and branching both will supply real moments however small.

B. Mathematical Treatment of Dielectric Relaxation or Charging

From the discussion above, we must always expect some dielectric relaxation when dc potential is impressed across a medium with a finite capacitance. Many authors have treated the simplified problem in detail. Fröhlich[3] considers a simple bi-stable model using a potential well concept. Debye[4] demonstrates the physical meaning of relaxation time in his classical treatment of dielectric relaxation in a dilute solution of dipolar molecules in a non-polar liquid. These and other treatments lead to the conclusion that each polarizable element obeys a linear differential equation of the form

$$\tau_\kappa \frac{dP_\kappa}{dt} + tP_\kappa = \alpha_\kappa E(t) \qquad (1)$$

where τ = relaxation time
α = dipolar polarizability
P = dipolar polarization
E = potential
t = time.

The number of different polarizable elements, κ, may be so large as to represent a continuous gradation and the definition of elements is not straightforward. This is primarily due to mutual dipole interactions. In normal dielectrics, this does not invalidate the formulation of a set of equations for a given material. It merely implies that the numerical values for α_κ and τ_κ cannot be simply ascribed to identifiable structural entities, such as a given dipolar molecule.

The experimental results on dielectric relaxation can, with few exceptions, be described by assuming a small set of first-order differential equations with constant coefficients (τ_κ and α_κ), Eq. (1). One of the most obvious properties of linear differential equations is the proportionality of stimulus and response. In terms of dielectrics this means that the dielectric properties are independent of applied voltage. This is found to be true for most dielectrics for fields up to 10^5-10^6 volts/cm, and constitutes a criterion for "normal" dielectrics.

If we consider a single element which obeys Eq. (1) and which has a single time constant, τ, and expression for polarization, P(t) can be written in the general form:

$$P(t) = \int_{-\infty}^{t} E(u)\, \dot{\psi}\, (t-u)\, du \quad . \tag{2}$$

The variable u is an expression of time and the function $\dot{\psi}(t-u)$ may be written $\dot{\psi}(t)$ where t now denotes a time interval. For our single element, $\dot{\psi}(t)$, the time-dependent polarizability, may be written as follows:

$$\dot{\psi}(t) = \frac{\alpha}{\tau}\, e^{-\frac{t}{\tau}} \quad . \tag{3}$$

If there are n_κ elements with characteristics κ, their contribution to P is given by $n_\kappa \dot{\psi}_\kappa$, and for the dielectric as a whole:

$$\dot{\psi}(t) = \sum_{\kappa} \frac{n_\kappa \alpha_\kappa}{\tau_\kappa}\, e^{-\frac{t}{\tau_\kappa}} \quad . \tag{4}$$

Perhaps more importantly a sum of elements sums leads to:

$$\dot{\psi}(t)_{net} = \dot{\psi}_1(t) + \dot{\psi}_2(t) + \ldots . \tag{5}$$

where 1, 2, ... refer to element types of varying α and τ values leading to a series of exponentially decaying functions of different time constants and magnitudes. This can readily yield the observed data since an analysis of Eq. (4) or (5) can give a function of the form:[5]

$$\dot{\psi}(t) = \frac{K}{t^m} \tag{6}$$

where K and m are fitting constants. Our own research data normally can be described by this simple function which is not in conflict with theory and is very useful for calculations. This behavior is demonstrated by our specimen of pure, commercial polystyrene (Dow OX-4500) in Fig. 1, where σ/c is plotted vs time on log-log coordinates since $c = \frac{A}{d}\epsilon$ and $\epsilon = \dot{\psi}(t) = \frac{K}{t^m}$. In these relations, σ is conductivity, c is capacitance, A is area, and d is thickness. The best value for m in unirradiated samples appears to be -1. It is tempting to picture some kind of kinetic process as accounting for this value, but at this stage selection of a process is not justified. After irradiation individual processes of the exponential form $e^{-\frac{t}{\tau}}$ dominate to the extent that humps of this kind are seen in the log-log plot (Fig. 1). The behavior of the current upon reversal of potential during the occurrence of these humps suggests that there is actual conductance by mobile charge carriers which disappear through exponential decay.

C. Steady-State Conductivity

In insulating materials the concept of "Ohmic" conductivity, in which charge is transported by mobile electrons, tends toward failure. A special case of Ohm's law may be useful:

$$i_c \frac{L}{VS} = un; \frac{i_c}{V} = un \frac{S}{L} = \sigma \quad , \tag{7}$$

where n is the number of ions of either sign per cubic centimeter, $u = u_+ + u_-$ is the sum of the mobilities of the positive and negative ions, i_c the current flux in the material expressed in ions/sec (i_c = Amperes x 6.24 x 10^{18}), V the applied voltage, L the distance between parallel electrodes, and S their area.

The source of the charge carriers becomes the problem. For conjugated π-electron organic substances the dark conduction is usually expressed as

$$\sigma = \sigma_o \; e^{-\frac{\Delta E}{2kT}} \text{ ohm}^{-1} \text{ cm}^{-1} \quad . \tag{8}$$

Assuming electrons (n) and holes (p) are generated by thermal excitation within the bulk:[6]

$$\sigma_o = q(u_n + u_p)(N_c N_v)^{\frac{1}{2}} = q(u_n + u_p)(2)\left(\frac{2\pi kT}{h^2}\right)^{\frac{3}{2}}(m_n m_p)^{\frac{3}{4}} \tag{9}$$

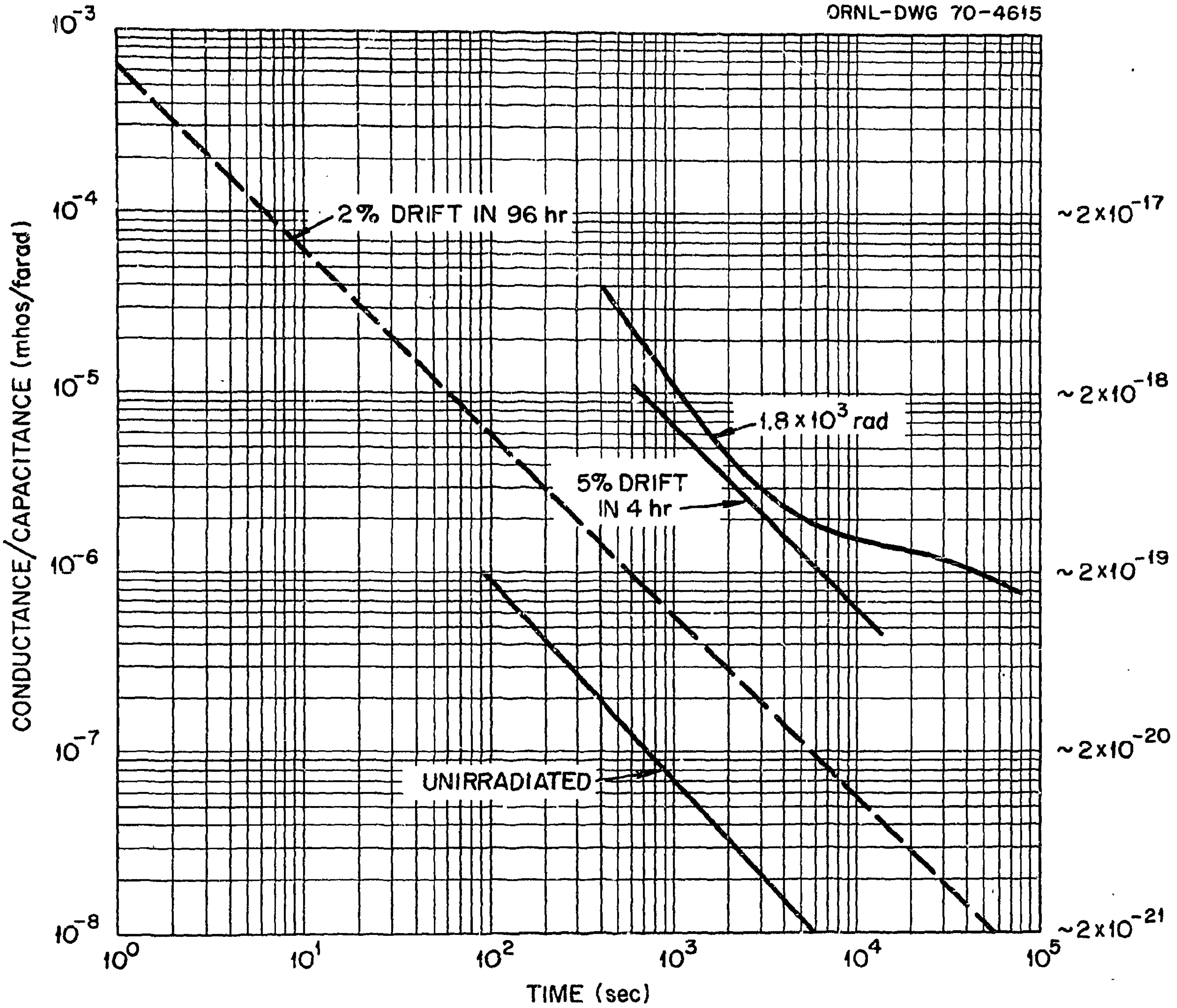

Fig. 1. Dielectric Charging and Conductivity of Polystyrene. (Dow OX-4500).

where u_p, u_n = mobility of positive and negative charge carriers,

N_c, N_v = density of energy states in the conduction and valence bands respectively,

m_n, m_p = effective mass of negative and positive charge carriers,

q = charge.

This formulation moves us from the electro-chemical concept to solid state physics theory, essentially applicable to semiconductor crystals. Applying these theories to amorphous or partially crystalline polymers and glasses is in no sense rigorous but does allow use of mathematical models to describe observed phenomena within a consistent framework.

One advantage to this treatment is the defined separation between intrinsic conductivity which is a property of the "pure" material and extrinsic conductivity which is a property of the impurities present in the bulk system. To calculate the intrinsic conductivity[7] we must find the equilibrium concentration N_e of electrons in the conduction band, which is equal to the equilibrium concentration N_n of holes in the valence band. We must know the relative mobilities. We may expect a temperature dependence of the form $e^{-E_i/kT}$ and after considerable formal treatment we arrive at the equation shown above.

Eley[6] presents data showing σ_o varying over the range 10^{-9} to 0.1 $\text{ohm}^{-1}\ \text{cm}^{-1}$ for $\Delta E = 1.0$ ev and from 10^{12} to 10^{16} for $\Delta E = 4.0$ ev for various organic materials. This corresponds to a maximum room temperature conductivity, σ, of 10^{-18} $\text{ohm}^{-1}\ \text{cm}^{-1}$, from Eq. (8), with the bulk of the data yielding much lower values.

Most semiconductor calculations yield mobility values inconsistent with these data; however, calculations for organic molecular crystals ("monomers") based on tight-banding methods give a maximum u of 30 $\text{cm}^2/(\text{volt-sec})$. (Ref. 8) The corresponding upper value for σ_o would be 120 $\text{ohm}^{-1}\ \text{cm}^{-1}$ if the effective mass is equal to that of a free electron. For $\Delta E = 1.0$ ev the specific conductivity at 300° Kelvin would be 6×10^{-15} $\text{ohm}^{-1}\ \text{cm}^{-1}$. In general observed ΔE values are appreciably higher and it seems unlikely that thermal dissociation of the pure bulk solid will provide a supply of charge carriers sufficient to provide a measurable conductivity under normal experimental conditions. Our specimens (unirradiated) had such low steady-state conductivities that we were unable to determine ΔE for conduction. We did observe $E_{(act)} = 0.4$ to 0.8 ev for dielectric charging, and after irradiation $E_{(act)} = 1.0$ to 1.5 ev for combined charging and transient conductivity.

Extrinsic conductivity or impurity caused conduction we shall not limit to the narrow definition used in semiconductor theory where the impurities act within the lattice structure. Instead we shall include matrix or network contributions from those substances added to polymeric materials during polymerization, from plasticizers added to improve fabrication methods, and from antioxidants to improve chemical stability. We shall also include the effects of moisture both on polymeric materials, glasses, and oxides.

In the case of ionic crystals or those materials with a lattice structure of semiconductor type, it is well substantiated that impurity atoms may be ionized to give up an electron (donors). Impurity atoms can also take up electrons from the valence band (acceptors) leaving holes in the band that can act as charge carriers. In each case the ionization energies involved are low (ca. 0.1 ev). It is not at all clear that such events are of any consequence in the observed preirradiation conductivity of amorphous or partially crystalline insulators and therefore no discussion of the effect will be attempted here.

A more likely source of dc conductivity in polymers is the interconnecting network structure formed in these amorphous or partially crystalline materials by plasticizers or antioxidants deliberately added during processing to improve the characteristics of the final product. Most of these "additives" are polar in nature and tend to ionize. Even in "pure" polymers, polar end groups may occur from the catalysts used. In addition, ions from the surfactants used to lower surface tension in emulsion polymerizations may not be removed in processing. These probably do not provide "conductivity" from their own ionization but they do serve to adsorb water vapor from the air and this moisture is the prime supplier of ionized carriers.

The tremendous effect of humidity on resistivity is shown in a paper by Killam,[9] who tested eighteen polymers in equilibrium with air, over the range of 50 to 90 percent relative humidity. Significant observations and conclusions by Killam were:

1. Exposure to 90 percent relative humidity compared to 50 percent relative humidity reduced resistivities by up to 2.5 decades.

2. Surface resistivity measurements of clean surfaces of many polymers are probably measurements of the resistivity of the volume adjacent to the surface.

3. Increased humidity resulted in increased capacitance roughly according to the polarization contributed by the sorbed water.

4. Generally, sorbtion of water was higher for higher permittivity materials.

Most of these conclusions have been observed by others, and Ramsey[10] has shown that under anhydrous conditions "good insulators" have resistivities about four orders of magnitude higher than the values under moist conditions.

Our own observations are in basic agreement with these generalizations. For surface and volume resistivity at 90% relative humidity, polyethylene and polystyrene were best. At 50% relative humidity polypropylene, polyethylene terephthalate, and polymethyl methacrylate were close competitors. Our experiments at much lower humidities also find these materials very good.

III. CONDUCTIVITY DURING IRRADIATION

The fact that solid dielectrics change their resistance when subjected to ionizing radiation has been known for about sixty years and has been the object of much experimental and theoretical investigation. Probably the most useful work appeared after World War II. In 1957 the conductivity of amber, polystyrene of various purities, polymethyl methacrylate, polyethylene, and polychlorotrifluoroethylene was studied by Rozman and Tsimmer.[11] These relatively unsophisticated experiments using ionization chambers kept and irradiated in dry air led to significant conclusions:

1. The activation energy for conductivity for these dielectrics is between 0.3 to 0.5 ev before irradiation and between 1.0 to 1.5 ev

after irradiation, with the increase in activation energy remaining even after the conductivity returns to its original value.

2. Under irradiation these substances have an electrical conductivity several orders of magnitude less than a similar volume of air.

3. A surface contribution to the conductivity after irradiation was observed.

During the same period Fowler[12] published a coordinated explanation of the conductivity induced by ionizing radiation in solid insulating materials. His model based on conduction by free electrons and including the presence of electron traps is still used and may be considered the most generally accepted explanation of the observed effects to date.

On a more practical basis it was clearly demonstrated that during irradiation the current varied with dose rate according to the relationship, $i_x = KR^{\Delta}$, where Δ lies between 0.5 and 1.0 and is characteristic of the material although "additives" to the bulk polymer (see Table 1) do have a pronounced effect on the result. These experiments, at relatively low dose rates, confirm quantitatively the more qualitative results of Rozman and Tsimmer.[11]

Somewhat similar work by Harrison and Proulx[13] with no theoretical treatment, demonstrated similar effects at much higher dose rates. Direct comparison of the data is difficult since "in-field" activation energies were not determined by Harrison. Data on some classes have been reported by Culler et al.[14] and qualitatively the results are very similar to those observed for polymeric materials. Table 1 summarizes these data in order of relative merit at 8 R/min with no temperature correction. The two glasses where no Δ value was reported were calculated using $\Delta = 1$. In the case of 1723 glass, this may yield a very optimistic value since Culler[14] reports 4.7×10^{-17} ohm^{-1} cm^{-1} at 58 R/sec and Bradley[15] reports 2×10^{-17} ohm^{-1} cm^{-1} at 5.5 R/sec. Bradley's measurements, however, were made at 65°C using beta radiation from a krypton-85 source and did not seem directly comparable. All of these values are nominally at steady state with the radiation field present. Under these conditions and given no other information the best prospective candidates are apparent. Several important aspects, however, are not presented in this table.

Table 1. Comparison of Induced Conductivity of Various Insulators at 8 R/Min.

Material	Δ	E_X	σ	Ref	T_e
Alkali-free aluminosilicate glass, Corning 1723	-	-	$\sim 10^{-20}$	14,15	25
Polyethylene Terephthalate	0.83	0.18	$6\text{x}10^{-20}$	12	20
Alkali lead silicate glass, Corning 8871	-	-	$5\text{x}10^{-19}$	14	25
Natural Amber	1.0	0.22	$1\text{x}10^{-18}$	12	20
Polystyrene (USA)	0.75	0.18	$1\text{x}10^{-18}$	12	20
Polymethyl Methacrylate (unplasticized)	0.55	0.5	$2\text{x}10^{-18}$	12	20
Polystyrene	0.65	0.44	$2\text{x}10^{-18}$	12	20
96% silica glass, Corning 7900	-	-	$2.25\text{x}10^{-18}$	14	29
Polymethyl Methacrylate (Plasticized)	1.0	0.10	$3\text{x}10^{-18}$	12	20
Polystyrene	0.97	-	$5.6\text{x}10^{-18}$	13	38
Polystyrene	0.88	-	$6.4\text{x}10^{-18}$	13	38
Teflon	1.0	-	$1.6\text{x}10^{-17}$	13	38
Polymethyl Methacrylate Red "400"	0.93	0.07	$2\text{x}10^{-17}$	12	20
Fused Silica, Corning 7940	-	-	$2.3\text{x}10^{-17}$	14	29
Polyethylene	0.81	0.35	$9\text{x}10^{-17}$	12	20
Polyethylene	0.74	-	$1.2\text{x}10^{-16}$	13	38

Δ = exponent for dose rate

E_X = apparent activation energy, ev

σ = observed conductivity, ohm^{-1} cm^{-1}

T_e = experimental temperature, °C

Ref = reference, see reference list

It is noted by Harrison[13] and others that a finite time is required after commencement of irradiation to reach equilibrium conductivity, and this time is a function of dose rate. This is of little consequence to the low-range OCD and military dosimeters, which may be expected to receive low enough dose rates that equilibrium will always be achieved. Furthermore, since the conduction of a polymer is several orders of magnitude lower than that of an equivalent volume of air,[11] and since the dielectric volume is much less than the active air volume, we will suffer virtually no error due to the dielectric contribution.

In the case of the military SEMIRAD dosimeter (IM-185) where secondary electrons collected under high vacuum conditions are the measured species, it is not clear that this is true. The fact that an equilibrium value in the insulator will not be reached during the collection time does serve to mitigate the problem. This is also helped by the geometry factor since the plastic component is truly an insulator and not a capacitor dielectric used for ranging. This is brought out by Kronenberg[16] who discusses the overall operational requirements in some detail.

The other important factor is the decay of the excess conductivity after the radiation exposure ceases. This is discussed in the following section.

IV. POSTIRRADIATION CONDUCTIVITY

A. The Nature of Postirradiation Decay of Conductivity

It is evident that for an air chamber dosimeter the contribution to the collected charge from the insulator and/or ranging capacitor is negligible during the irradiation period. The primary problem is what happens after the period of irradiation. One would expect prompt disappearance of excess charge carriers but this is not observed. Early investigations[11,12] noted the existence of long-term decay decreasing in rate at longer times. Fowler[12] was able to establish the decay as a hyperbolic function using fairly low dose rates and explained these results by trap theory. In 1963 Harrison[17] presented experimental data for six polymers showing the decay could be described to a good approximation by

$$\frac{\sigma(t)}{\sigma_o'} = \sum_{i=1}^{n} K_i \, e^{-\frac{t}{\tau_i}}$$

where $\sigma(t)$ is the conductivity as a function of time during the decay, σ_o' is the conductivity at the cessation of radiation, n the number of decay time constants in the decay, τ_i the magnitude of the i^{th} decay time constant, and K_i the weighting factor associated with the i^{th} decay time constant. This equation was interpreted in terms of a trap-controlled process.

In 1965 Compton _et al._[18] in an extremely well reported study on polyethylene terephthalate at dose rates up to 10^{10} rad/sec reported the decay as a hyperbolic function over a few hundred microseconds. This work also seems to demonstrate that the conducting state observed in a radiation field is achieved instantaneously for practical purposes at high dose rates. The postirradiation effects are reported to saturate at 10^{10} rad/sec but this does not appear to be substantiated by the data. At constant dose rate with increasing dose, it is shown that the post-irradiation current, after a given decay period does tend toward a saturation value. This is shown from our own work on capacitor insulator film in Fig. 2. This work together with the compilation of Wicklein _et al._[19] appears to prove that the relationship, $\sigma \propto R^{\Delta}$, holds for all insulating materials to dose rates as high as 10^{10} rad/sec, the decay from these values being the important problem.

B. The Probable Mechanism of Conduction

Present evidence substantiates that the materials undergo ion pair formation during irradiation largely from electron release in Compton events. These electrons are then responsible for the observed prompt current associated with irradiation under an accelerating potential gradient. Only the "free" fraction of electrons is available. After irradiation ceases these free electrons are rapidly scavenged and new electrons are only available from "traps." The ions formed during the irradiation possibly serve as traps. Several workers[18,20] cite evidence that after irradiation conduction is by the holes remaining after Compton

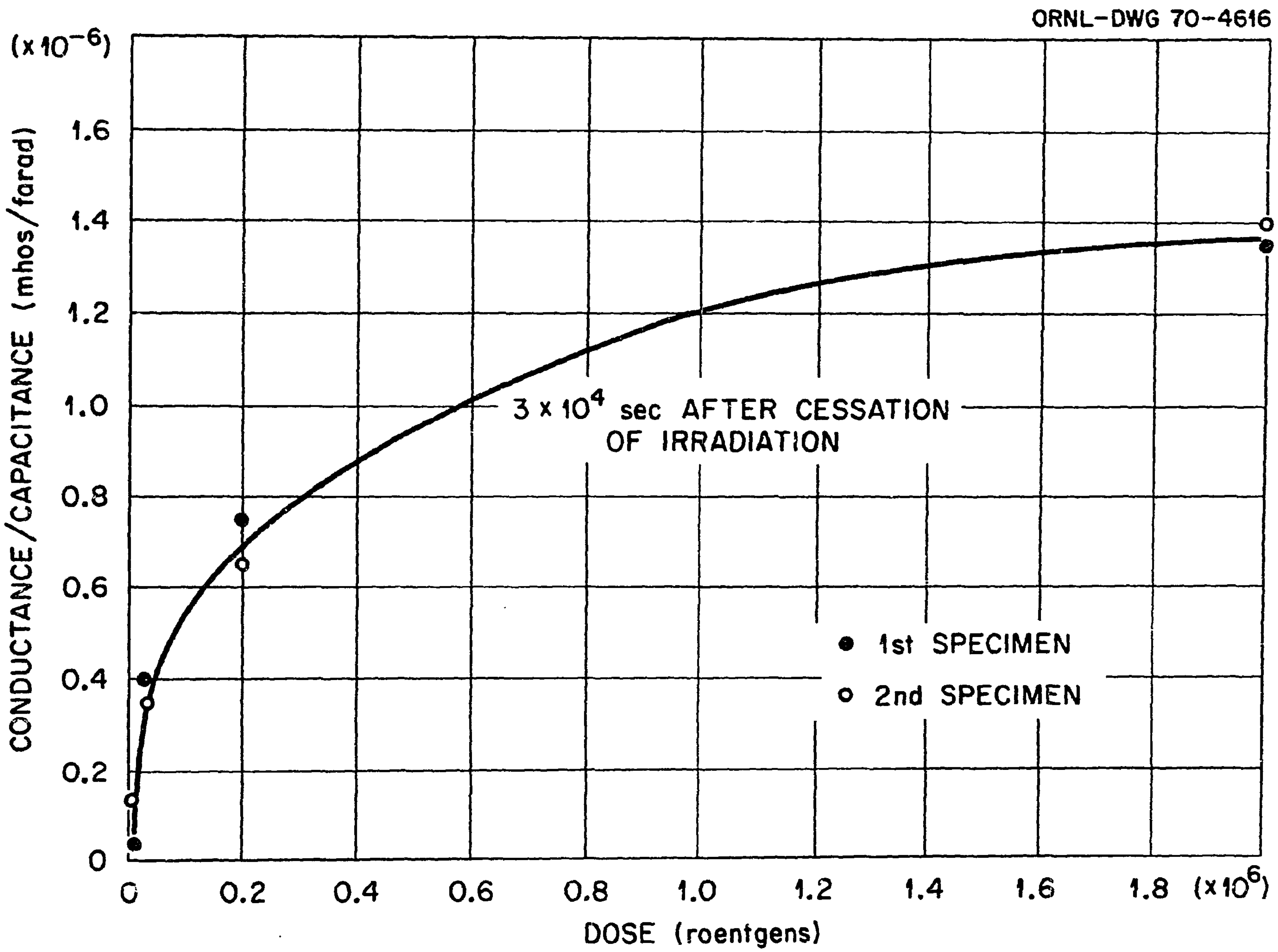

Fig. 2. Conductivity vs Radiation Dose, Cerex 250B.

and secondary electrons are trapped on sites which are limited in number in any given specimen.

More importantly, the ion-pair concentration continues to increase with irradiation, saturating at values consistent with a matrix of pairs in the solid dielectric where each charge is just at the limit of coulombic attraction for its opposite polarity neighbor. This is the point where their mutual coulomb energy equals the energy of thermal agitation, kT.[21] Then $r_c = e^2/\epsilon kT$, where r_c is the distance to the neighbor charge, e is the electronic charge, and ϵ the dielectric constant. For a typical insulating material $r_c \sim 200\text{Å}$, which is so large that the character of the ions should have little effect on the interaction. The <u>full</u> matrix represents some 10^{17} pairs/cm^3. For a "good" material where one pair results per 1000 ev, saturation would occur at 10^{20} ev or saturation would take about 2×10^6 R. For very poor material (like air) saturation occurs with doses as low as 10^5 R.

This naive explanation is consistent with observed data. The nature of the charge pairs is unknown but the definitions advanced by Pohl[22] may be useful: "Exciton: A negative-positive charge pair residing on different nearby molecules." If they remain close so that they cannot be split by an external electric field then they cannot act as carriers for static fields. They can, however, contribute to dielectric polarization.

When the charge pair is separated by a great distance then either charged entity (M^+ and M^-) can act as a carrier and move relatively independently. Since "exciton" is conventionally applied to the bipolar entity, these should be called deep transitory cation-anion pairs. In the carrier view, the deep transitory anion is the lowest lying negative carrier entity and is a molecular ion. It can diffuse (rare) or transfer its charge to neighboring molecules by a "tunneling" or "hopping" mechanism. If excited further by an energy equal to the molecular electron affinity, Ag, it can give rise to a relatively free electron traveling in the upper conduction bands (Ag = 1-3 ev).[23] Species and processes of this sort can provide a basis for explanation of all observed effects.

Using this concept and realizing that only low doses are of interest (200 R or less) we can see that materials with low G values are necessary since this minimizes the number of "ions" and "excitons" formed per unit of dose. Those ions within coulombic attraction range of each other appear to external observation as a changing dielectric polarization as they disappear by slow recombination. Isolated charge carriers migrate under the applied field until immobilized or until they reach an electrode where they would appear as space charge if the energy required for discharge is unavailable. More likely, a carrier would pass close enough to an oppositely charged species to form a new coulombically bound pair. This pair would then destroy itself as a normal exciton. We have not specifically discussed electrons, holes, and trapping processes but the definition of these processes is so broad that our general discussion above provides the framework which would certainly include the detailed mechanisms of conduction active in both pure and emulsion polymers.

With the generation and migration of charged species in a solid matrix the development of polarization is certainly possible. Temporary polarization in the form of dielectric charging or relaxation has been treated thoroughly in Sect. II. Similar dipole orientation can have long-term duration if polarization takes place above the softening temperature of the insulator. Such polarized dielectrics, "electrets," have been studied for many years. Another form of persistent polarization results when mobile charge carriers generated by radiation are trapped in a non-uniform distribution under an external electric field. This type of polarization has been termed "persistent internal polarization."

The electrets for the most part comprise waxes and polymers having strongly polar groups. Carnauba wax has been most extensively studied[24] since it can be highly polarized by cooling from the melt in fields of about 5 kv/cm. By measurement of the polarization through the "lifted plate" and complete thermal discharge methods it has been found that the charge distribution consists of "homocharge" imparted by the electrodes to the adjacent layer and "heterocharge" which is a true volume effect over microscopic dimensions. Polymers of low polarity, namely polystyrene and polymethyl methacrylate, have been polarized as electrets by proper treatment. The part played by polar groups was demonstrated by greatly increased polarization when sulfonated styrene or acrylic acid was incorporated in the polymer.[25] Electrets were formed not only by solidification under a potential field but also in the absence of a field by application of sufficient pressure to produce orientation through flow.

More closely related to our observations herein that radiation-induced conductivity decays more rapidly in polymers having polar groups are experiments on radiation discharge of electrets. Gross and deMoraes[26] showed that doses which were appreciable for organic materials, i.e., 2 x 10^6 rads, eliminated the polarization of carnauba wax electrets. So-called electrets have also been formed by the irradiation of carnauba wax and polytetrafluoroethylene in a potential field[27] although in current terminology, "persistent internal polarization" might be a more appropriate term.

Persistent internal polarization, P.I.P., as implied above, can be developed by the irradiation of dielectrics, organic or inorganic, in an electric field under conditions giving a non-uniform distribution of trapped charge. Most investigations have been on photoconducting materials utilizing visible or ultraviolet radiation to generate charge carriers.[28] In contrast to electrets, these photoconductors can also be discharged by radiation of photon energies below the ionizing level.

Polarization may be of two types, barrier and bulk. Barrier polarization occurs when the resistance of the electrode interface exceeds the volume resistance for the charge carriers. A concentration of charge in a thin layer develops adjacent to the electrodes. Bulk polarization results when the radiation is absorbed in a thin layer at the electrode toward which the less mobile charge carriers move. Under these conditions the mobile carriers are distributed through the bulk of the specimen and it is possible to develop a net charge in the specimen as a whole. Net inbalance of charge is also possible in barrier polarization if there is sufficient disparity in the resistances of the two electrode interfaces. P.I.P. is studied by measurement of the discharge of the image charge induced on grounded electrodes on the specimen. By comparing the charge released under uniform illumination with that released by radiation absorbed strongly at one face, the relative mobilities of positive and negative carriers may be determined.

Moore and Silver[29] observed that the organic photoconductor, anthracene, gave conduction by holes, with a low electron mobility because of a high trapping rate. Electron injection by the electrode was found and it was concluded that carriers were generated and electrons trapped at defects or impurities in the extrinsic mode of photoconduction. Källmann et al.[30] reported that the similar compound, α-methyl naphthalene, had a hole mobility of 10^{-4} cm^2/v-sec, about twice as large as the mobility of electrons.

In this program of developing radiation-resistant insulators, the emphasis has been on postirradiation conductivity, a determining factor in the performance of electrostatic dosimeters. The experimental conditions for this study precluded the observation of persistent internal polarization. On the other hand, if polystyrene is sufficiently photoconducting, the techniques of P.I.P. offer the possibility of delineating the nature of the charge carriers in polystyrene and the function of the polar groups in reducing postirradiation conductivity. With such information, the probability of developing a more radiation-resistant insulator would be greatly enhanced over our current procedure of trying first one polar group after another in styrene-based polymers.

Part B. Experimental Results and Discussion

I. DEVELOPMENT OF TECHNIQUES FOR PREPARATION OF MOISTURE-RESISTANT FILMS

To indicate the suitability of insulators for dosimeter use, sensitive measurements of very high values of resistance are required. These measurements quickly revealed that plastic films prepared by simple and convenient solvent casting from dilute solutions are too variable and susceptible to moisture for use as test specimens.

Solutions of 4 to 5% polymer in benzene, toluene, carbon tetrachloride or tetrahydrofuran are convenient for spreading but were found to give films having conductivities and dielectric charging much higher than that allowed for dosimeter use. These properties could be improved by exhaustive drying or outgassing near the softening temperature of the film, but subsequent exposure to the atmosphere regenerated the excessive values. Free evaporation of solvent from a spread solution frequently produced a rippled surface and occasionally cloudy areas. Air drying at room temperature for several days permitted retention of about 4 wt % solvent (as measured in the case of toluene solutions). Such films usually exhibited troublesome sensitivity to moisture. Furthermore, casting films from reagent-grade benzene solutions gave more reproducible results than casting from toluene and tetrahydrofuran and films from carbon tetrachloride consistently showed excessive conductivity. It was also observed that monomer, moisture, and other volatiles were much more thoroughly removed by vacuum outgassing the polymer at elevated temperature in the form of finely divided powder than in the form of cast film. High volatile content appeared to lead to excessive dielectric charging and conductivity, at least in the early stages of electrification.

A procedure was evolved for preparing film specimens obviating the observed difficulties as follows:

(a) Finely divided bulk polymer is vacuum outgassed at 90-95°C for 24 hours if there is any indication that there is an appreciable content of volatiles.

(b) A solution of 20-25 wt % polymer is made up in freshly opened, dry reagent-grade benzene. Such a concentrated solution requires mechanical spreading but gives less contraction upon drying and apparently a more dense surface which is relatively insensitive to moisture.

(c) This viscous solution is spread over a leveled glass plate with a straight-edge blade. A spacing of 0.006 inch between blade and glass surface gives films about 0.001 inch thick after drying.

(d) Evaporation of solvent is controlled to require a period of 16-20 hours at room temperature by arranging the casting plate in a covered petri dish containing a small pool of solvent. Such retarded evaporation prevents the development of ripples and cloudy areas.

(e) The film is removed from the glass plate by immersion in distilled water and peeling from the glass surface.

(f) The film is "conditioned" (dried, outgassed, and perhaps densified) by evacuating at 90-95°C for 24 hours.

(g) Aluminum electrodes are applied to each side by vacuum deposition with appropriate masking to give the desired shape.

II. SURVEY TESTING OF COMMERCIAL PLASTICS

Survey measurements of the electrical resistance of a variety of commercially available plastics proceeded concurrently with the development of the techniques of film casting. Whenever commercial films of about 0.001-inch thickness were available, these were tested, but in most cases the films were prepared by solvent-casting or, for polyethylene, hot-pressing. Since it was observed that such low values of conductivity were somewhat dependent on specimen preparation techniques, it was not possible to catalogue precise values for these materials. Furthermore, in the materials of higher resistivity, dielectric charging (Sect. II. A) was continuing after 24 hours to give an apparent current completely masking the very low steady-state conductivity. Consequently, the apparent conductance to capacitance ratio after two time intervals is listed in Table 2. This can be converted to conductivity as indicated in the table with only "order of magnitude" accuracy.

After initial measurement, the specimen films were rolled into cylindrical form and irradiated at 29 or 300 r/sec to the doses listed. The conductivity after irradiation was found to decay in a complex manner, with one or more long-lived components in most materials. The behavior

Table 2. Measured Conductivity of Plastics Before and After Irradiation

Specimen	Before Irradiation[b] Time After Electrification		After Irradiation[c] Time After Irradiation		Radiation Dose
	10^2 Sec mho/farad[a]	10^4 Sec mho/farad	10^3 Sec mho/farad	10^5 Sec mho/farad	10^3 rad
Polyethylene	2×10^{-6}	$\ll 10^{-8}$	2×10^{-4}	$\sim 6 \times 10^{-6}$	1.8
Polystyrene	9×10^{-7}	$< 10^{-8}$	1×10^{-5} 4×10^{-5}	$\sim 9 \times 10^{-7}$ $\sim 8 \times 10^{-7}$	1.8 18.
Poly-α-methyl styrene	6×10^{-7}	$< 10^{-8}$	5×10^{-5}	$\sim 1 \times 10^{-7}$	20.
Styrene-methyl styrene (Cerex 250B)	4×10^{-6}	4×10^{-8}	3×10^{-6} 1.5×10^{-5}	1.5×10^{-8} 1.5×10^{-7}	2. 20.
Poly-p-xylylene (Parylene "N")	6×10^{-6}	6×10^{-8}	8×10^{-7}	2×10^{-8}	1.8
Polycarbonate (Lexan)	10^{-5}	10^{-7}	4×10^{-6}	3×10^{-7}	2.
Polyethylene terephthalate	1×10^{-5}	1×10^{-7}	$<10^{-5}$	$<10^{-7}$	~1.8
Polymethyl methacrylate	1×10^{-4}	1×10^{-6}	7×10^{-5}	$\sim 3 \times 10^{-6}$	20.
Polyvinylidene fluoride	7×10^{-4}	4×10^{-5}	- - - - too high for irradiation - -		
Polyphenylene oxide	$<5 \times 10^{-6}$	$<10^{-7}$	2×10^{-6}	8×10^{-7}	1.8
Polypropylene	- - - - - - - - - - similar to polyethylene - - - - - - - - - - - -				
Polymethyl pentene-1	- - - - - - - - - - similar to polyethylene - - - - - - - - - - - -				

[a] To convert to $(\text{ohm-cm})^{-1}$ multiply by $\sim 2.1 \times 10^{-13}$.

[b] Specification: <2% drift in 96 hr requires $< 7 \times 10^{-8}$ mho/f at 10^4 sec.

[c] Electrification began 300 to 800 sec after irradiation ceased. Specification: <5% drift in 4 hr requires $< 10^{-5}$ mho/f at 10^3 sec and $< 7 \times 10^{-8}$ at 10^5 sec.

before and after irradiation of three very low conductivity materials is shown in Figs. 3 and 4.

The requirements for service as a capacitor dielectric in a dosimeter are indicated as footnotes in Table 2 and as limiting curves in Figs. 3 and 4. From Table 2 it is seen that of the materials tested, only polyethylene, styrene polymers, poly-p-xylylene, and polyphenylene oxide have low enough conductivity prior to irradiation for consideration. After irradiation, only Cerex 250B and poly-p-xylylene show sufficiently rapid decay of conductivity to meet dosimeter specifications, although polystyrene and polyphenylene oxide are prospects for use with additives which might reduce the decay time.

III. IDENTIFICATION OF THE GROUP GIVING DECAY OF CONDUCTIVITY

It was evident from the survey of various polymers (Table 2) that only materials with a high content of phenyl groups showed very low changes in properties after irradiation. This has been observed in chemical changes as well as electrical properties and has been attributed to the absorption of radiation energy by low-lying triplet states of the phenyl ring. Such states can dissipate their excitation energy in the form of thermal energy or light without undergoing decomposition, thereby imparting radiation resistance. On the other hand, neither polystyrene nor poly-α-methyl styrene homopolymers showed the rapid decay of conductivity measured in the copolymer (Cerex 250B) and in poly-p-xylylene.

The latter polymer is prepared by polymerization on a solid surface from reactive radicals in a low-pressure, vapor phase. It is insoluble, may have impurity atoms incorporated during the polymerization process, hence is not amenable to an investigation of the constituents which might affect the electrical properties.

The copolymer, however, is soluble and suitable for fractionation and separation of minor constituents. To determine whether a unique arrangement of the monomer units or impurities produce the decay of conductivity, a fractionation was carried out. To a 1 wt % solution of Cerex 250B in butanone (a "poor" solvent) sufficient propanol-2 was added to produce the onset of turbidity. An additional volume of

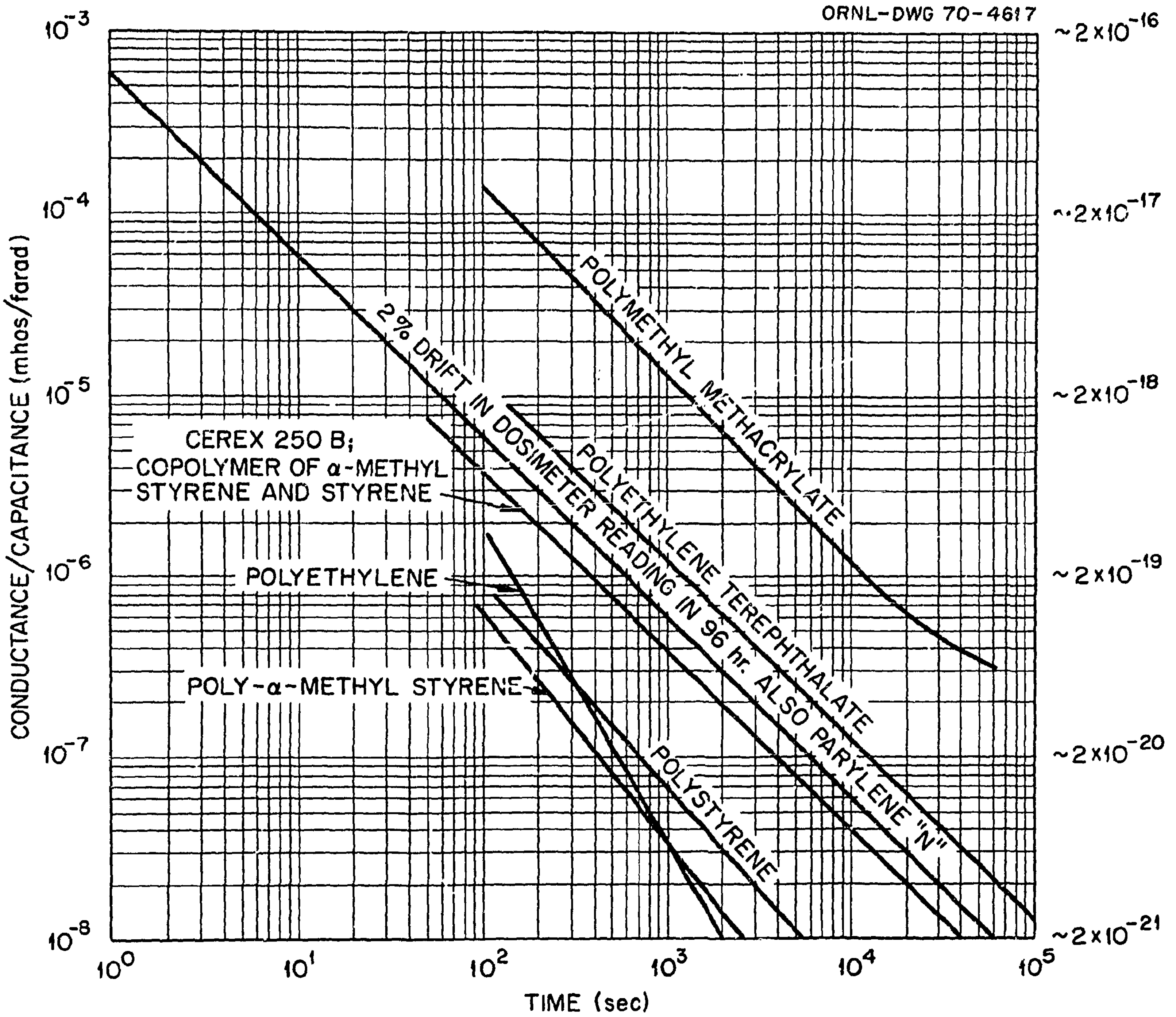

Fig. 3. Dielectric Charging Curves of Polymeric Materials - Unirradiated.

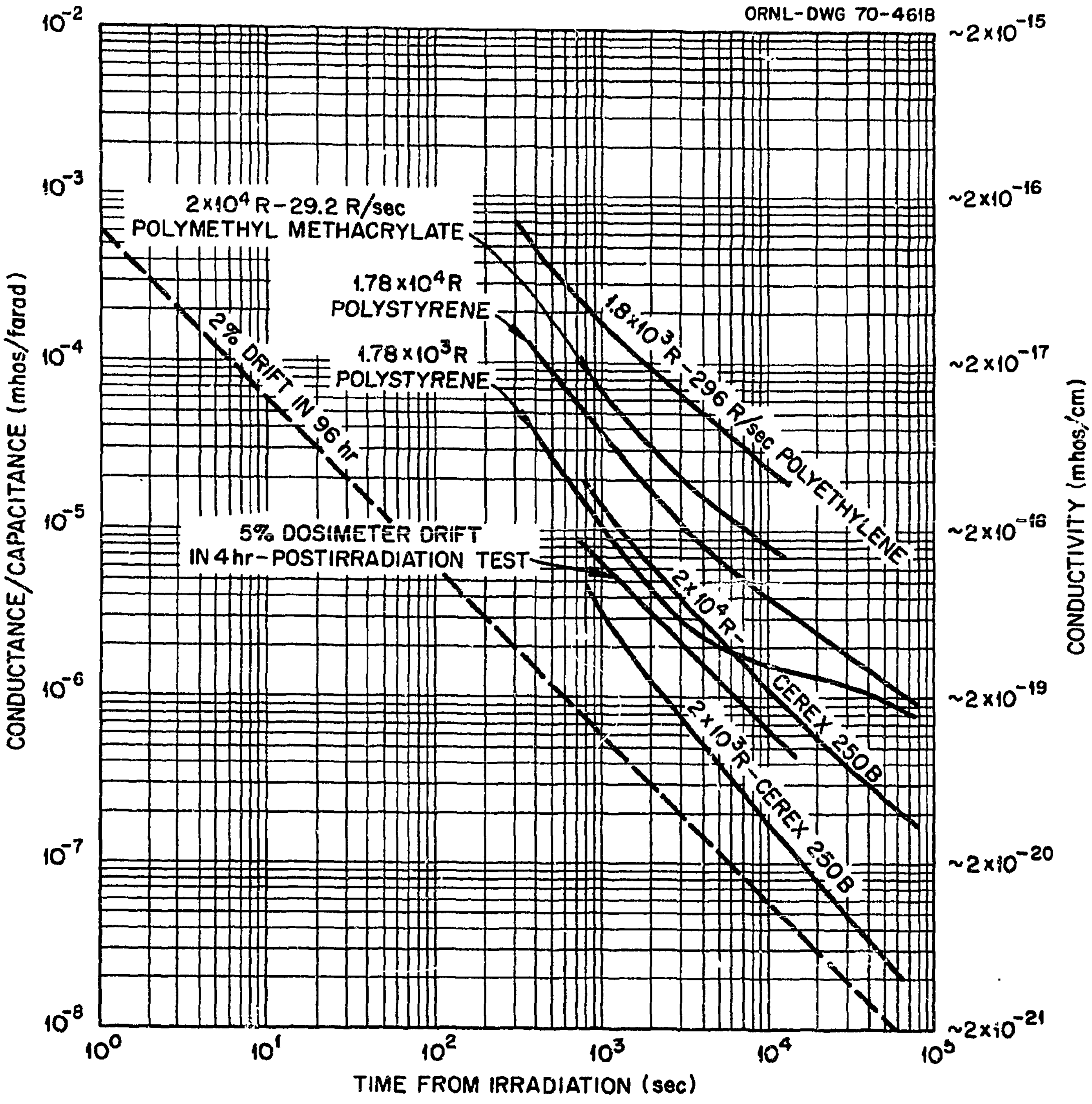

Fig. 4. Dielectric Charging Curves of Polymeric Materials - Irradiated. Note: See doses on curves.

propanol-2 which from previous trials was adequate to precipitate 25% of the copolymer, was then added with vigorous stirring. The cloudy mixture was warmed until clear and finally was chilled with stirring and aged at 0°C for about five hours to obtain the precipitate in filterable form. The precipitated fraction was separated by filtration, washed with additional propanol, and dried under vacuum at 85-95°C for 24 hours or longer.

By similar precipitation and filtration steps, two additional fractions were separated and the fourth was collected by evaporating the final filtrate to dryness. These four fractions were cast into film by the usual technique. Infrared spectra of the fractions showed that the first, the high molecular weight fraction, contained an increased concentration of the group having the band at 1130 cm^{-1}, the C—O—C or S = O group.[1]

The electrical conductivity of the four fractions was measured before and after irradiation. Prior to irradiation, the fourth fraction showed excessive conductivity resulting from the accumulation of polar impurities. After irradiation, the first two, higher molecular weight fractions, showed long-lived conductivity similar to ordinary polystyrene. But the lower molecular weight fractions showed decay of conductivity rapidly enough to meet the specifications for dosimeter use ($\sim 10^{-6}$ mho/f at 10^{3} sec and $\sim 7 \times 10^{-8}$ at 10^{5} sec).

The long-lived conductivity of the first two fractions indicates that the rapid decay in the original copolymer does not result from contributions of the comonomers, since the infrared spectra showed no great differences in methyl content of the fraction. But the accelerated decay in the last two fractions suggests that polar groups or impurities shorten the duration of conductivity.

Further indications of the effect of polar groups were furnished by additions of antioxidants and ultraviolet stabilizers to a pure polystyrene. While most of these materials merely increased the conductivity of the specimen film, some to an excessive degree, tris-chloroethyl phosphite reduced postirradiation conductivity considerably.

A systematic study of the effect of impurities from the polymerization recipe of α-methyl styrene copolymer was performed through a contract between the Monsanto Research Corporation and the Office of Civil Defense. Although α-methyl styrene is an unreactive monomer it can be copolymerized to the extent of 30-40% with styrene in a simple emulsion polymerization recipe. A copolymer similar to Cerex 250B was prepared in the laboratory (Monsanto) using a recipe and procedure analogous to production methods.[31] This product (93369) was tested and found to have electrical properties comparable to Cerex 250B, as listed in Table 3.

To confirm the absence of an effect of copolymer structure, a styrene homopolymer was synthesized by the same recipe and procedure. This specimen (93371) had the short-lived decay characteristics of Cerex 250B. The possibility of active impurities or groups from the emulsifier, a complex, sulfonated aromatic by-product of oil refining (Acto 450, Esso Corp.) was investigated by substituting an alkyl phenyl sulfonate in one recipe (93421) and sodium stearate in another (107124). These copolymers showed postirradiation electrical behavior very similar to that of Cerex 250B, and products having an ash content similar to Cerex 250B would meet the dosimeter criteria.

Since it appeared that groups or residues introduced by the polymerization catalyst or initiator were influencing the electrical properties, this ingredient was varied, replacing $K_2S_2O_8$ by $(NH_4)_2S_2O_8$ in 93433 and by H_2O_2 in 107130. The product from the (NH_4) initiator showed very low postirradiation conductivity and rapid decay, but generally erratic electric currents. The H_2O_2 polymer had long-lived conductivity after irradiation, nearly as large as that of a pure polystyrene.

It is known that the persulfate initiators, $S_2O_8^{=}$, produce sulfate end groups in emulsion polymerizations.[32] Three thermally initiated polymerizations were carried out in "bulk", two in vacuum, one in air, to give only styrene-type end groups, although the polymer prepared in air may contain –OH end groups. Furthermore, these bulk polymerized products (OR-1 to 3) would contain no initiator nor emulsifier residues. These polystyrenes had postirradiation conductivities far higher than Cerex 250B, comparable to commercial, pure polystyrene, although the air-polymerized product showed the lower postirradiation conductivity (Table 3).

Table 3. Styrene Polymers and Copolymers:** Electrical Properties Before and After Irradiation

Specimen Number	Comp.	Emuls.	Init'or	Prep. Method	Sep'tn Method and Ash[d] Wt. %	Inherent Visc.	Yield %	Film Preparation Method			Electrical Conductivity				Radiation Dose
								Solvent	Conc.	Outgassing Remarks	Before Irradiation[b] Time After Electrification		Irradiated[c] Time After Irradiation		
											10^2 sec mho/farad[a]	10^4 sec mho/farad	10^3 sec mho/farad	10^5 mho/farad	10^3 rads
Cerex 250B*	S + α MS 64/36	- - - - Plant Production - - - -			Evp. 0.3-0.4	0.8-0.9		Toluene	5-25%	16h - 90°	4×10^{-6}	4×10^{-8}	3×10^{-6}	2×10^{-8}	*2.0
OX-4500	Styrene	- - - - - - Dow Plant Production - - - - - - - - - -						Toluene	25%	16h - 90°	10^{-6}	7×10^{-9}	7×10^{-5}	9×10^{-7}	2.0
93369*	S + α MS 64/36 (93419D)	Acto 450	$K_2S_2O_8$	Lab Cerex (3hr add, refl. ½hr)	Frz. 0.08	0.897	91	CCl_4	--	---	$>10^{-4}$	$>10^{-6}$	---	---	---
								Toluene	25%	16h - 90°[e]	$>2 \times 10^{-5}$	$>2 \times 10^{-7}$	---	---	---
								Benzene	~30%	16h - 85°	2×10^{-5}	7×10^{-8}	3×10^{-6}	1.5×10^{-8}	*2.0
93371*	Styrene	Acto 450	Same as above	Same as above	Frz.0.10	1.58	98	Toluene	25%	16h - 90°	---	---	1.5×10^{-6}	7×10^{-9}	*2.0
93421*	S + α MS 64/36	Sulfonate	Same as above	Same as above	Evp. 0.53	1.13	96	Benzene	20%	16h - 90°	(55°) 5×10^{-5}	(55°) 2×10^{-7}	(55°) 5×10^{-6}	(55°) 2×10^{-8}	2.0
					Frz.0.27	0.944		Benzene	20%	16h - 90°	(55°) 4×10^{-6}	(55°) 2×10^{-8}	(55°) 1.5×10^{-6}	(55°) 1.5×10^{-8}	*2.0
93433	S + α MS 64/36	Acto 450	$(NH_4)_2S_2O_8$	(3hr add, refl. 4hr)	Evp.0.10	1.36	79	Benzene	20%	16h - 90°	9×10^{-6}	1.5×10^{-7}	(55°) 4×10^{-7}	(55°) $<3 \times 10^{-8}$	2.0
					Frz.0.06	1.41		CCl_4	--	16h - 90°	---	$\sim 4 \times 10^{-7}$	$\sim 4 \times 10^{-6}$	$\sim 4 \times 10^{-8}$	2.0
					Frz.0.06	1.41		Benzene	20%	16h - 90°	9×10^{-6}	6×10^{-8}	3×10^{-6}	8×10^{-9}	2nd 2.0
107130	Styrene	Stearate	H_2O_2	(3hr add at 90°)	Frz.	2.48	91	Benzene	6%	16h - 90°	$>2 \times 10^{-5}$	$>3 \times 10^{-7}$	---	---	
								Benzene	>10%	---	5×10^{-6}	7×10^{-8}	8×10^{-6}	4×10^{-7}	2.0
107124*	S + α MS 64/36	Stearate	$K_2S_2O_8$	(3hr add, refl. ½hr)	Frz.	1.13	87	Benzene	20%	16h - 90°	4×10^{-6}	7×10^{-8}	1.5×10^{-6}	3×10^{-8}	*2.0
														(55°) 5×10^{-7}	2.0
OR-2	Styrene	None	None	16h at 125°	Bulk	--		Benzene	20%	16h - 90°	1.5×10^{-6}	$\sim 5 \times 10^{-8}$	$\sim 5 \times 10^{-4}$	1.5×10^{-6}	2.0
OR-3	Styrene	None	Air	16h at 125°	Bulk	--		Benzene	20%	16h - 90°	2×10^{-6}	9×10^{-9}	4×10^{-6}	2×10^{-7}	2.0
											(55°) 3×10^{-6}	(55°) 1×10^{-7}		(55°) 5×10^{-6}	2.0

---

[a] To convert to $(ohm\text{-}cm)^{-1}$ mupltiply by ~2.1 x 10^{-13}.

[b] Specification: < 2% drift in 96 hr requires < 10^{-5} mho/f at 10^2 sec and < 7 x 10^{-8} at 10^4 sec.

[c] Electrification began 200 to 500 sec after irradiation ceased. Specification: <5% drift in 4 hr requires <10^{-5} mho/f at 10^3 sec and <7x10^{-8} at 10^5 sec.

[d] Evp. = Evaporation. Frz. = Freezing. Ash is residue after careful burning and heating in air to ~ 1000°C.

[e] Fibrous polymer outgassed 24 hrs at 90°C.

* Film passing specifications.

** Specimens with 5 and 6 digit numbers prepared by Monsanto Research Corporation.

These results of varying recipe ingredients demonstrate that sulfate end groups from persulfate initiators produce rapid decay in conductivity following irradiation. Inconclusive measurements on fractionated copolymers and on various laboratory polymers indicate that there may be a dependence of decay rate on concentration or distribution of these initiator products and residues.

IV. PREPARATION OF IMPROVED POLYMERS

A. The Influence of Additives

The demonstration of the influence of polar impurities and end groups on the postirradiation decay of conductivity opens the possibility of using additives to obtain superior insulating plastics. The pure hydrocarbon polymers show very low conductivity in the absence of radiation but the characteristic long-lived conductivity after irradiation must be shortened to permit use in dosimeters. The efforts to improve the available materials have proceeded along two lines: the testing of additives for effect on decay rates and finally, changing the concentration or nature of the end groups of the polymer chain.

It is common commercial practice to use organic compounds of several types and varying complexity to protect against light, against oxidation, and against chemical or other forms of deterioration. The action of light is similar to that of radiation with the exception of the production of ionization. Antioxidants function in part by scavenging free radicals which are reactive intermediates in the case of radiation as well as in oxidation. Consequently, several types of ultraviolet stabilizers and antioxidants, already known to be compatible in polystyrene, were tested for their influence on electrical properties.

The results of this search for commercial additives which would have beneficial effects are presented in Table 4. The substituted phenols and carbonyl compounds which serve as antioxidants or uv stabilizers are listed under Group 1 additives. Although two of these polar compounds gave films having low conductivities prior to irradiation, neither reduced the postirradiation conductivity adequately.

Table 4. The Effect of Ultraviolet Stabilizers and Antioxidants on the Electrical Properties of Polystyrene and Polyphenylene Oxide

Additive	Conc. Wt. %	Electrical Conductivity[a]			
		Before Irradiation		After 2000 rads	
		Time (sec)	Conduct. mho/farad	Time (sec)	Conduct. mho/farad
polystyrene[b] *None	0.0	10^4	7×10^{-9}	10^5	9×10^{-7}
Group 1					
di-t-butyl-p-cresol*	0.3	10^4	$<6 \times 10^{-8}$	10^5	$>5 \times 10^{-7}$
styrene-butyl-cresol	0.6	$\sim 10^4$	$>10^{-7}$	pre-irradiation high	
dihydrobenzophenone*	1.0	$\sim 10^4$	$<6 \times 10^{-8}$	$\sim 10^5$	$>5 \times 10^{-7}$
methyl-t-butyl pheynl-crotonaldehyde[d]	0.5	-	$>>10^{-6}$	pre-irradiation high	
methyl thiophenol[d]	1.0	∞	4×10^{-5}	" "	"
dichlorobenzophenol[d]	1.0	10^4	2×10^{-7}	" "	"
Group 2					
tristearyl thiophosphite[d]	1.0	-	$>>10^{-6}$	" "	"
nonyl phenyl phosphite[d]	8.0	6×10^4	5×10^{-5}	" "	"
bis(tridecyl) hydrogen-phosphite[d]	1.0	10^4	10^{-6}	" "	"
triphenyl phosphine[d]	1.0	6×10^4	2×10^{-6}	" "	"
polymeric phosphite (hydrolysable) Wytox 540**	4.0	10^4	$<6 \times 10^{-8}$	10^5	2×10^{-8}
{di-t-butyl-p-cresol** tris(2-chloroethyl)phosphite	0.3 7.5	10^4	$<6 \times 10^{-8}$	10^5	$<5 \times 10^{-7}$
polymeric phosphite[d]* Argus M260	1.0	10^4	$<6 \times 10^{-8}$	10^5	$>5 \times 10^{-7}$
polymeric phosphite[d]* Argus M329	1.0	10^4	$\sim 10^{-7}$	10^5	$\sim 5 \times 10^{-7}$
polymeric phosphite[d]** (non-hydrolysing) Wytox 355	1.1	10^4	$<6 \times 10^{-8}$	10^5	$<5 \times 10^{-7}$
Group 3					
phenyl-2-naphthylamine	0.6	$\sim 10^4$	$>10^{-6}$	pre-irradiation high	
dihydro trimethyl quinoline[d]	1.0	∞	10^{-6}	" "	"
antioxidant "Nevastain B"[d]	2.0	10^4	10^{-6}	" "	"
chlorethyl toluene sulfonate[d]*	1.0	10^4	$<6 \times 10^{-8}$	10^5	$>5 \times 10^{-7}$
chlorethyl toluene sulfonate[d]	2.0	10^4	$\sim 10^{-7}$	pre-irradiation high	
bis(methyl-hydroxy-t-butyl phenyl) sulfide[d]*	1.0	10^4	$<6 \times 10^{-8}$	10^5	$>5 \times 10^{-7}$
dilauryl thio dipropionate[d]*	1.0	10^4	$<6 \times 10^{-8}$	10^5	$>5 \times 10^{-7}$
Group 4					
polyphenylene oxide[c]*(none)	0.0	10^4	$<10^{-7}$	10^5	8×10^{-7}
tris(chloroethyl)phosphite[c]**	1.0	10^4	$<10^{-7}$	10^5	5×10^{-8}

---

[a] To convert mho/farad to $(\text{ohm-cm})^{-1}$ multiply by $\sim 2 \times 10^{-13}$.

[b] All additives except those of Note(c) were in a pure, low-monomer commercial polystyrene, Dow OX-4500.

[c] These additives were in polyphenylene oxide.

[d] Measured at 57°C.

* These materials meet 2% drift in 96 hr prior to irradiation.

** These specimens meet 5% drift in 4 hr after 2000 rads.

The phosphites, and other phosphorous-containing antioxidants, are tabulated as Group 2 compounds. These compounds are not only polar but in at least one case (the hydrogen phosphite) have ionic character in the bonding. Nevertheless, several of these additives showed conductivities before irradiation low enough for dosimeter use. Since a few of these compounds accelerated postirradiation decay of conductivity a large assortment was tested. Unfortunately, the only effective additive of known composition, tris(chloroethyl)phosphite, was not reproducible in its effect, probably because of its volatility. This property also gave difficulty on prolonged testing or conditioning under vacuum so polymeric phosphites of unknown composition and proprietary types were tested. Two of these, Wytox 540 and 355 (National Polychemicals Co.), reduced postirradiation conductivity sufficiently for the films to meet dosimeter specifications at room temperature, but reproducibility from one film to another was very poor.

It was found that the tris(chloroethyl)phosphite also accelerated decay of conductivity in polyphenylene oxide listed in Group 4. These polar phosphites, of relative low molecular weight, have much higher mobilities than the base polymer and their electrical properties are strongly temperature-dependent. Consequently, testing was extended to cover the upper temperature of the dosimeter specifications, 55°C. These elevated temperature tests are described below.

In Group 3 are listed amine, sulfur-containing, and miscellaneous antioxidants. None of these additives reduced the decay time of the postirradiation conductivity. It is noteworthy that the sulfonate, having some ionic character like the phosphites, showed low conductivity at 1% concentration but exceeded the specification limit at 2%. Evidently the phosphite group offers the best prospect of reducing conductivity by the use of additives.

B. The Effect of Elevated Temperatures

Testing in the range of the upper temperature of the dosimeter specifications has been carried out since the polar end groups and impurities necessary for limiting postirradiation currents have enhanced mobility and ionization at higher temperatures. In pure polystyrene, prior to irradiation, little increase was noted in simple dielectric charging on increasing the temperature from 22 to 56°C. On the other hand, it was noted that polar impurities greatly increase the dielectric charging. This is shown in the preirradiation measurements on a Monsanto Cerex-type laboratory copolymer (93421) polymerized with dodecylphenyl sodium sulfonate instead of Acto 450 as emulsifier. The batch recovered by freezing and having low ash (0.27%) showed a dielectric charging curve at 57°C similar to production-type Cerex 250B copolymers, i.e., $\sim 4 \times 10^{-8}$ mho/farad at 10^4 sec. The batch recovered by evaporation, 0.53% ash, however, would not pass the 2% drift in 96 hours specification, conductivity was $\sim 2 \times 10^{-7}$ at 10^4 sec, prior to irradiation. Because of this temperature effect in polymers having polar impurities, many of the antioxidant and uv stabilizer additives were screened by testing initially at 57°C (Table 4).

Another feature of raising the temperature of measurement was current reversal. After prolonged dielectric charging at room temperature, increasing the temperature of a film to 57°C has been observed to give a reverse current. Presumably this current results from accumulated charge on the electrodes, polarized dielectric ("persistent internal polarization") and a decreased dielectric constant upon heating, with the resultant decrease in capacitance of the film-electrode combination. The discharge of this internal polarization in a short-circuited specimen after prolonged testing is also much more rapid at 57° than at 22°C.

The greatest effect of temperature, however, appears in the long-lived conductivity following irradiation of polymers not having the rapid, postirradiation decay characteristic of Cerex 250B. With pure polystyrene (OX-4500) the postirradiation conductivity at 57°C is 15 to 20 times that at 22°, giving apparent activation energies of 1.3-1.4 ev. Probably, the higher temperature moves the major first-order decay hump in the log-log plot to shorter times. Consequently, any ratio of conductivities at different temperatures is dependent on the time after electrification (Fig. 5). Cerex 250B and similar styrene polymers that have rapid postirradiation decay of conductivity show relatively low activation energies of conductivity, 0.9 to 1.1 ev, with currents at 57° less that 15 times currents at room temperature. Such low activation

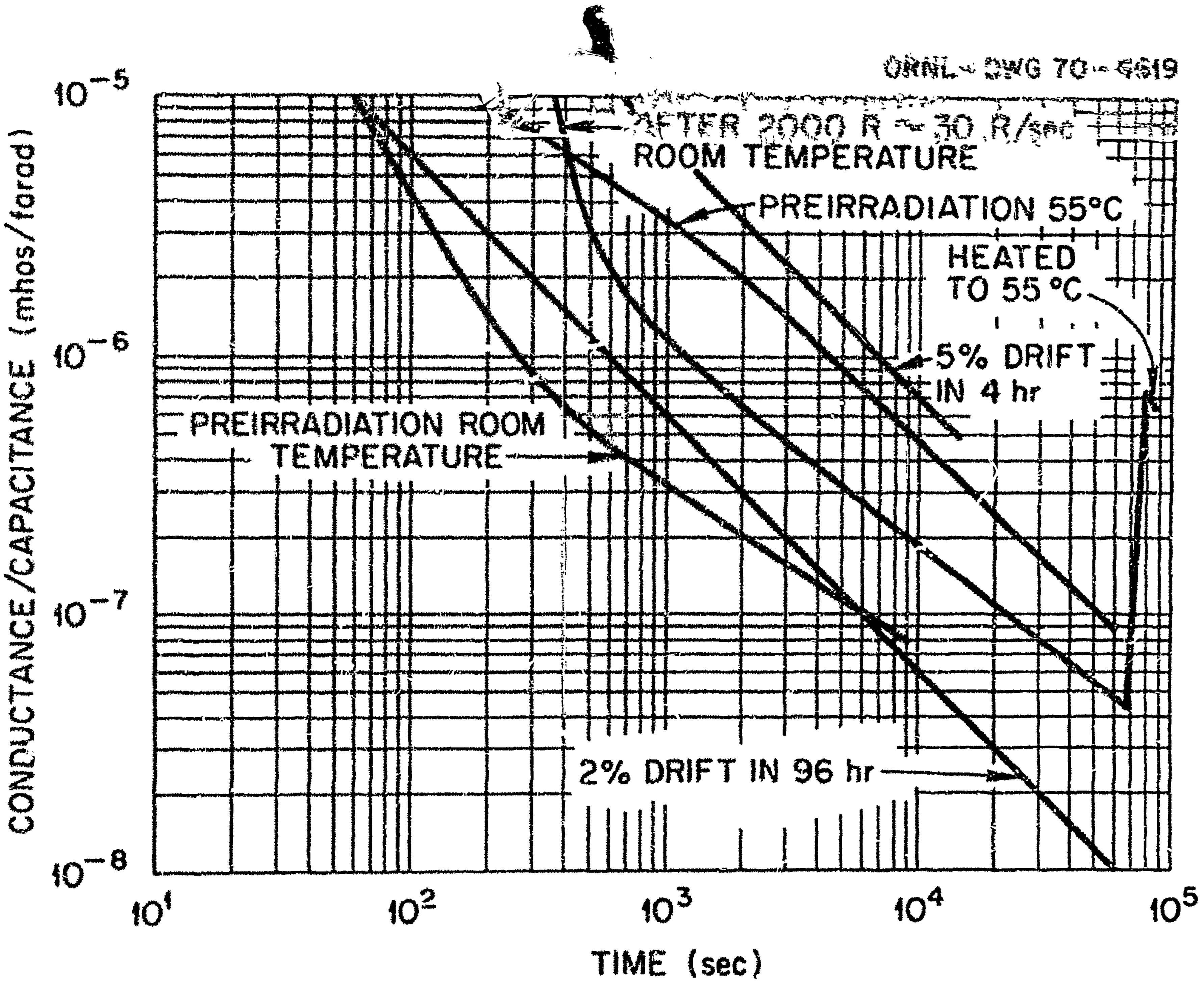

Fig. 5. Effect of Temperature on the Conductivity of a Styrene - α-Methyl Styrene Copolymer, Before and After Irradiation.

energies (or current ratios) enable these materials to meet the dosimeter requirements at the upper specification temperature (5% drift in 4 days at 57°C). Unfortunately, the phosphite additives giving postirradiation reduction of conductivity were very inconsistent from one film to another in this effect of temperature, for reasons which are not yet clear. Other materials showing anomalous temperature effects are the polymers prepared using (NH_4) cations described below.

Strongly polar polymers such as polyesters and polycarbonates would be expected to show much higher dielectric charging currents at elevated temperatures. This behavior was observed in polyethylene terephthalate (Mylar) and polycarbonate (Lexan, Fig. 6) and prevents these materials from meeting the high temperature drift specifications.

The changes observed in conductivity decay curves at various temperatures should assist in identifying fundamental mechanisms leading to charge transfer. The long-lived postirradiation currents appear to be carried by mobile charged species since potential reversal gives equal but opposite currents. The increased currents upon heating could result from increased carriers released from traps or increased mobilities. The indication that decay times were shortened could clarify recombination or re-trapping processes. If time allows, these temperature studies will be pursued to provide more definitive information about the conduction and decay processes.

C. Alteration and Increase in Concentration of End Groups

As mentioned earlier, the duration of conductivity following irradiation appears to be reduced by polar end groups and perhaps by polar or ionic impurities in aromatic polymers. The first experimental polystyrene initiated by H_2O_2 and presumably having $-OH$ end groups (107130) had a very high molecular weight as indicated by an inherent viscosity of 2.48. Polymers of such high molecular weight give films that are very sensitive to atmospheric moisture and erratic in electrical properties. In addition, this polymer had a relatively low concentration of end groups. It showed postirradiation conductivity intermediate between pure styrene homopolymer (OX-4500) and the low values required for dosimeter service, as listed in Table 5. A second homopolymer was prepared

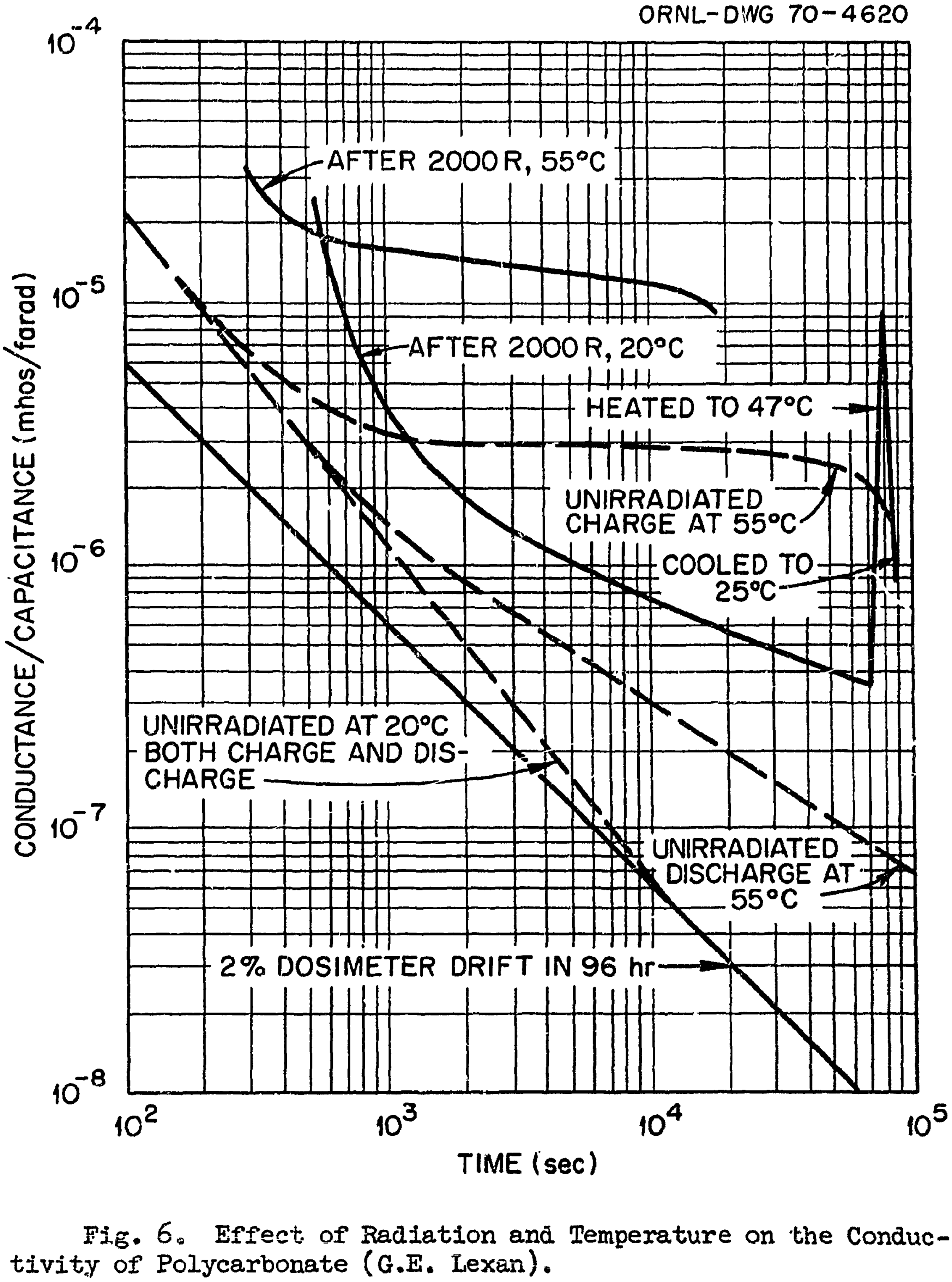

Fig. 6. Effect of Radiation and Temperature on the Conductivity of Polycarbonate (G.E. Lexan).

Table 5. Styrene Polymers and Copolymers with Various End Groups and Ionic Residues: Electrical Properties Before and After Irradiation**

Specimen Number**	Comp.	Emuls.	Init'or	Prep. Method	End Group	Sep'tn Method and Ash[d]	Inherent Visc.	Film Preparation Method	Electrical Conductivity[a]				Remarks
									Before Irradiation[b]		Irradiated to 2000 rads[c]		
									Time After Electrification		Time After Irradiation		
									10^2 sec mho/farad	10^4 sec mho/farad	10^3 sec mho/farad	10^5 sec mho/farad	
Cerex 250B*	S + α MS 64/36	Plant Production		--	--	0.3-0.4%	0.8-0.9	See Table 3	4×10^{-6}	4×10^{-8}	3×10^{-6}	2×10^{-8}	*
QX-4500	Styrene	- - Dow Plant Production - -			--	---	---	See Table 3	10^{-6}	7×10^{-9}	7×10^{-5}	9×10^{-7}	
OR-1	Styrene	None	None	16h -100°	Styrene	Bulk	---	C_6H_6-20% 16h-90°	2×10^{-6}	1×10^{-7}	4×10^{-5}	1×10^{-6}	
OR-2	Styrene	None	None	16h-125°	Styrene	Bulk	---	C_6H_6-20% 16h-90°	1.5×10^{-6}	$\sim 5 \times 10^{-8}$	$\sim 3 \times 10^{-4}$	1.5×10^{-6}	
OR-3	Styrene	None	Air	16h-125°	?(-OH)	Bulk	---	C_6H_6-20% 16h-90°	2×10^{-6}	9×10^{-9} (55°)1×10^{-7}	4×10^{-6}	2×10^{-7} (55°)5×10^{-6}	High conductivity at 55°C.
107130	Styrene	Stearate	H_2O_2	Table 3	-OH	Frz.	2.48	C_6H_6>10% ?	5×10^{-6}	7×10^{-8}	8×10^{-6}	4×10^{-7}	
111332*	Styrene	Sulfonate	H_2O_2	90°-100°	-OH	Frz.	1.10	C_6H_6-20% 16h-90°	1×10^{-5}	3×10^{-7}	9×10^{-6}	$\sim 7 \times 10^{-8}$	*After dose of 2×10^4R. Marginal pre-irrad.
93433	S + α MS 64/36	Acto 450	$(NH_4)_2S_2O_8$	Table 3	$-SO_4^{-}$	Frz. .06	1.41	Same as above	9×10^{-6}	6×10^{-8}	3×10^{-6}	8×10^{-9}	Erratic. 2nd irradiation.
111365*	Styrene	(NH_4) Sulfonate	$(NH_4)_2S_2O_8$	90°-2h	$-SO_4^{-}$	Frz.	1.07	Same as above	6×10^{-6}	7×10^{-8}	1×10^{-5}	3×10^{-8}	*Erratic. Marginal pre-irrad.
OR-4*	Styrene	Acto 450	$K_2S_2O_8$	100°-1h	$-SO_4^{-}$	Wash	---	Same as above	3×10^{-6}	3×10^{-8}	3×10^{-6}	5×10^{-8} (55°)3×10^{-7}	* Discolored.
111337*	Styrene	Sulfonate	$K_2S_2O_8$	90°-2h	$-SO_4^{-}$	Frz.	1.24	Same as above	8×10^{-6}	1×10^{-7}	2×10^{-6}	$<8 \times 10^{-8}$	*Marginal pre-irradiation.
111345*	Styrene	Sulfonate	$K_2S_2O_8$	Blend	$-SO_4^{-}$	Frz.	1.17	Same as above	$\sim 3 \times 10^{-5}$	5×10^{-8}	2×10^{-6}	1×10^{-8} (55°)4×10^{-8}	*Marginal pre-irradiation.

---

[a] To convert mho/farad to $(\text{ohm-cm})^{-1}$ multiply by $\sim 2.1 \times 10^{-13}$.

[b] Specification: < 2% drift in 96 hr. requires $< 10^{-5}$ mho/f at 10^2 sec and $< 7 \times 10^{-8}$ at 10^4 sec.

[c] Electrification began 200 to 500 sec after irradiation ceased. Specification: < 5% drift in 4 hr. requires $< 10^{-5}$ mho/f at 10^3 sec and $<7 \times 10^{-8}$ at 10^5 sec.

[d] Evp. = evaporation. Frz. = freezing. Ash is residue after heating in air to about 1000°C.

* Film passing specifications. **Specimens with 5 and 6 digit numbers prepared by Monsanto Research Corporation.

with H_2O_2 using reaction conditions yielding a lower molecular weight (111,332) as shown in Table 5. Although films of this polymer were marginal in conductivity prior to irradiation, the postirradiation decay was quite rapid. Films met the dosimeter specification after the usual dose of 2000 rads and after 2 x 10^4 rads showed less than 10^{-7} mho/f at 10^5 sec, the approximate conductivity of Cerex 250B under these conditions (Fig. 4, Table 5). Further work on polymers initiated by peroxide appears desirable.

An additional variation in the type of end groups appears in the bulk-polymerized polystyrenes, OR-1, -2, and -3. No initiator was used in these polymers and the end groups are presumed to be styrene, except for small amounts of oxidized species in OR-3. This polymer was polymerized in air and may have a small fraction of the end groups in the form of hydroxy (-OH), carbonyl (C=O), or carboxy (COOH) groups. Although this polymer showed lower postirradiation conductivity than OR-1 or -2, the results from a single batch are inadequate for positive conclusions.

The measurements on OR-1, bulk polymerized at 100°C, revealed that conductivities were approaching steady-state values both before and after irradiation, at the longer times of measurement. A similar effect was noted at 55°C in the films of OR-3, bulk-polymerized in air. This apparent conductivity probably arises from the movement of low molecular weight polymers and monomer in these products formed under relatively mild conditions. The behavior is similar to that observed in the polystyrene to which low molecular weight antioxidants and stabilizers had been added (Table 4). The elimination of low molecular weight material evidently is mandatory for good electrical properties.

Another constituent of the styrene-based polymers which can be varied in the search for improved properties is the ionic residue remaining from the polymerization recipe. These ionic constituents are indicated as the ash content of the finished polymer as long as the cations of the recipe are metals. A convenient variation is the substitution of ammonium compounds for the potassium and sodium compounds of the recipe. This change will alter the ionic residue, but probably not reduce it, although the ash content will be reduced since ammonium compounds are not stable at the conditions under which ashing is carried out. A methyl styrene copolymer (93433) was synthesized substituting $(NH_4)_2S_2O_8$ for the $K_2S_2O_8$ of the usual Cerex 250 recipe. The polymer showed good postirradiation decay of conductivity but was quite erratic prior to irradiation.

A second polymer, a styrene homopolymer, substituting ammonium compounds for all the ingredients of the polymerization process, was prepared (111365). This product, although erratic and moisture sensitive enough to be marginal prior to irradiation, met the dosimeter specifications after irradiation.

Since mounting evidence indicates that sulfate end groups play an essential part in postirradiation decay of conductivity, an obvious variation is to increase their concentration in the polymerization of the very reactive monomer, sytrene. Two samples, prepared under this procedure by the Monsanto Research Corporation, were tested. The first polymer (111337) had a higher molecular weight than optimum and was marginal preirradiation. The postirradiation conductivity was acceptable although it had a long-lived component. The second sample (111345) was a blend of low and high molecular weight polymers, both of high sulfate content, to optimize both the molecular weight range and the end group concentration. It had lower conductivity after irradiation than the reference film of Cerex 250B but was marginal prior to irradiation in the early stages of dielectric charging.

These experiments demonstrate that the electrical properties of polymer films are a sensitive function of molecular weight, impurity content, and type of end group. After irradiation, low conductivity is not achieved simply by high purity and an idealized, regular monomer arrangement. Instead, it appears that improvements are possible through optimum combinations of end groups, molecular weight, and possibly impurities, although the fundamental mechanisms of charge transport, trapping, and recombination through which the controlling factors operate are not yet clear. A recipe for preparing a polymer embodying the best features revealed by our experimental work to date appears as Appendix II.

V. BEHAVIOR OF GLASS AND QUARTZ

Glass and quartz are more resistant to radiation than most plastics in their mechanical properties, and they can be obtained in types having very high electrical resistivity. In a preliminary screening, a commercial capacitor (Corning type CY-20C) was tested before and after irradiation. The shape of the conductivity vs time curve was very similar to those of plastic films both before and after irradiation. The dielectric charging curve before irradiation was excessive, $\sim 2 \times 10^{-5}$ mho/f at 10^2 sec and 4×10^{-7} at 10^4 sec. A quartz plate 0.06 inch thick showed pre-irradiation dielectric charging considered marginal ($\sim 10^{-7}$ mho/f at 10^4 sec) but after 2000 rads conductivity was quite excessive.

An alkali-free alumino-silicate glass (Corning type 1723) was tested because of its known electrical resistance. The conductivity before irradiation was acceptable, although higher than Cerex 250B. After irradiation, the conductivity decayed sufficiently to make the material marginal for dosimeter use, but was certainly low enough to warrant further studies of glasses and ceramics.

The major utility of glasses would come in an evacuated dosimeter where the outgassing characteristics of the insulator bead are important, as well as resistivity before and after irradiation. For such applications the surface resistivity is a critical property and survey testing has been performed on this property of a number of glasses and ceramics.

For these tests, electrodes were not bonded to the specimens and were stainless steel plates. Edge-to-thickness ratios ranged from 100 to 150 and area-to-thickness ratios were 50 to 70. The criterion for acceptability was 10^{19} ohm/unit square within 10^4 sec of electrification since insulator shape should permit a geometrical factor of 10 giving an actual resistance of 10^{20} Ω. The results of this preliminary testing are presented in Table 6. Only $MgAl_2O_4$ and MgO show properties both before and after irradiation that warrant further testing.

An additional type of alumino-silicate glass (Corning type 9753) similar to type 1723, also low in alkali and reportedly of higher resistivity, has been received recently. Specimens of this glass were prepared in the same manner as plastic films, that is aluminum electrodes

Table 6. Survey Testing of Quartz, Glasses, and Ceramics

Material	Surface Resistivity			
	Before Irradiation		After 2000 Rads	
	Time of Electrification 10^3 sec	ohm/unit square	Time of Electrification 10^3 sec	ohm/unit square
Quartz (fused)	7	30×10^{18}	4.5	0.3×10^{18}
			100	2×10^{18}
Corning 1723	10.1	8×10^{18}	---	Marginal
Al_2O_3 (single crystal)	9	5×10^{18}	7.2	1×10^{18}
$ZrSiO_4$	58	$\sim 10^{18}$	---	---
TiO_2	2	$<10^{16}$	---	---
ZrO_2	3	$<10^{17}$	---	---
$MgAl_2O_4$ (Spinel)	8	15×10^{18}	7.2	7.5×10^{18}
			70	75×10^{18}
MgO	5	$\sim 10^{19}$	5	7×10^{18}
			50	15×10^{18}
BeO		$\ll 10^{16}$	---	---
Porcelain		$\ll 10^{16}$	---	---
Lead Glass	11	1×10^{18}	---	---
HfO_2		$\ll 10^{16}$	---	---
ThO_2		$\ll 10^{16}$	---	---

were vacuum-deposited on thin plates. Volume conductivity was then measured before and after irradiation since the screening tests on the ceramics above indicated that the measured surface resistance was actually volume resistivity in suitably dry samples. The conductivity prior to irradiation was lower than that of type 1723 and was acceptable although not as low as the conductivity of Cerex 250B. After irradiation (Fig. 7) the conductivity was about one-third that of type 1723 and was considerably better than that of Cerex 250B.

Proposals for needed development work are being prepared along two lines. The first approach is through additional synthesis work trying various combinations of polymer end groups, molecular weight and detergent residue. The second is the utilization of Persistent Internal Polarization to clarify the nature of the charge carriers, the conduction process and the manner in which the polymer constituents influence the production, trapping, and recombination of charge carriers. Several proposals at different levels of funding are in preparation and tentative versions are being circulated.

VI. SUMMARY OF RESULTS. PROPOSALS FOR FUTURE RESEARCH AND DEVELOPMENT

A. Results and Conclusions

The properties of insulating materials, as discussed in Part A, Sect. II, are adequate for dosimeter use in the absence of radiation. The measured electrical properties of typical high-resistance plastics can be accounted for by dielectric charging and negligible steady-state conductivity. During exposure to radiation, the conductivity of plastic insulators may increase several orders of magnitude but this change can be accommodated by the calibration procedures for the dosimeter. After irradiation, however, the conductivity must decay rapidly and all commercially available polymers showed a long-lived conductivity which rendered them unsuitable for dosimeter use.

A former commercial plastic, a persulfate-initiated copolymer of styrene and α-methyl styrene (Cerex 250B) and a developmental polymer, poly-p-xylylene, had rapid decay of postirradiation conductivity permitting them to meet dosimeter requirements. Poly-p-xylylene must be synthesized and deposited in thin layers by means of a proprietary vapor

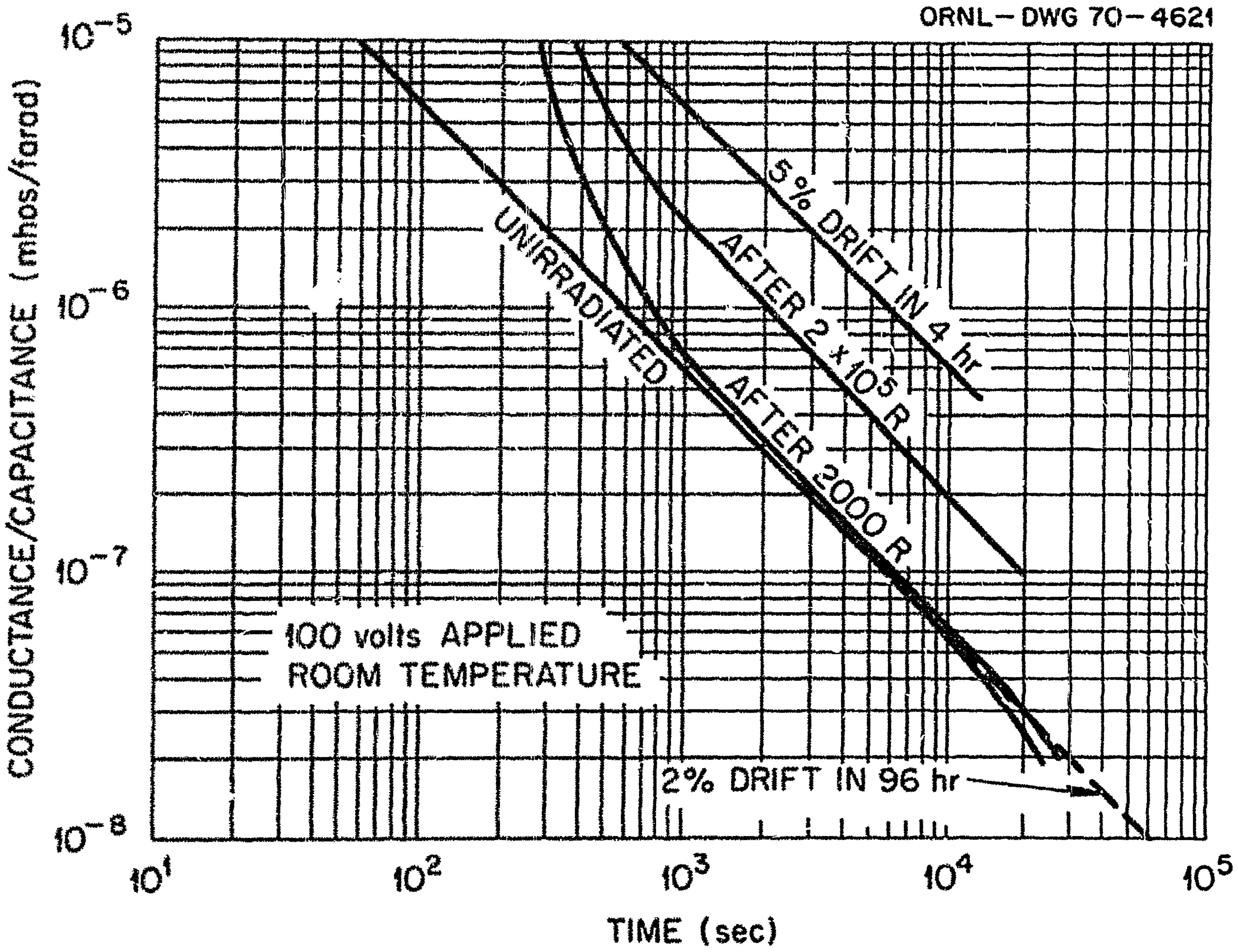

Fig. 7. Effect of Radiation on the Conductivity of an Alumino-Silicate Glass (Corning 9753).

deposition process so no further investigation of the features of this material was performed.

The behavior of the electrical conductivity of various plastics following irradiation suggested that Cerex 250B had an active ingredient or chemical group which was accelerating the decay of conductivity. Fractionation and washing of the copolymer revealed that the active agent was a group incorporated in the polymer chain itself. Coordinated testing by ORNL and synthesis by Monsanto Research Corporation proved that sulfate end groups accelerated the decay of conductivity and that the methyl styrene constituent of the copolymer structure was not controlling the electrical behavior.

Based on these findings, efforts to synthesize polymers with lower conductivity both before and after irradiation were undertaken. Styrene polymers were prepared in which the sodium and potassium cations in the original recipe were replaced with (NH_4) ions. The electrical properties of these polymers were erratic but postirradiation conductivity was low and decayed sufficiently rapidly. Synthesis methods which gave increased concentration of sulfate end groups in the product yielded polymers having suitable postirradiation decay of conductivity but high dielectric charging prior to irradiation.

It is evident that the electrical properties of polymers both before and after irradiation are dependent on ingredients in the emulsion polymerization process. Proper selection of ingredients can be employed to optimize the electrical properties before and after irradiation. However, the electrical characteristics and the mechanical and fabrication requirements are sufficiently restrictive that extensive efforts compromising improvements in one property against changes in others will be necessary for overall gains.

B. Proposals for Future Research and Development

The experimental approaches and operations outlined below are listed approximately in order of priority and chronological sequence. The results from some measurements should guide the work undertaken in subsequent investigations. In some instances, certain results could eliminate the need to perform one or more of the later experiments.

1. Explore the effect of ionic end groups of various types on the decay of postirradiation conductivity. Sulfate end groups should not be unique in the elimination of charge carriers and it is possible that end groups giving greater reduction in conductivity can be incorporated in the polymer. Peroxy carbonate and peracetate initiators would be candidates for preparing such polymers. If sulfur and non-sulfur emulsifiers were used, the influence of residues from the emulsifier would be clarified.

2. Ascertain whether sulfur-containing emulsifier residues are capable of reducing conductivity following irradiation. If, in the previous experiment, polymers with sulfonate emulsifiers do <u>not</u> show acceleration of decay of conductivity, then the information from this experiment will not be needed. Otherwise, polymers with inactive end groups should be made with sulfonate emulsifier and tested.

3. Determine the effect on postirradiation conductivity of substituting sulfonate side groups in low concentration in the polystyrene chain. The terminal positions in the chain probably are not unique in processes involving charge carriers.

4. Investigate "Persistent Internal Polarization" resulting from exposure of insulators to radiation while subjected to a potential field. Techniques of thermal discharge and illumination with locally absorbed radiation (uv) can indicate the quantity and distribution of trapped charge carriers. This information would be useful in guiding the experiments above and is a priority item, but the necessity of constructing apparatus and developing the methodology puts this work in a later chronological position. As nearly as possible, this work should be carried out concurrently with the studies above, and these measurements should be performed on all the polymer products having significant properties.

5. Clarify the effect of replacing alkali cations with (NH_4) ions. Determine the electrical properties of polymers having (NH_4) residues after washing and adjusting the pH of the washed polymer solution. As indicated above, the electrical properties of emulsion polystyrene having only (NH_4) cations showed promise if erratic variations with time could be eliminated.

6. Measure the effect of end groups of intermediate polarity on conductivity before and after irradiation. Studies on polystyrenes with $-OH$ end groups (peroxide-initiated) suggest that postirradiation conductivity may be reduced by these groups and that a highly polar, salt-type group is not necessary. Groups of intermediate polarity reduce dielectric charging and give improved performance prior to irradiation. Furthermore, since this type group is produced by many chain-transfer agents, suitable electrical properties would permit the use of these agents to control molecular weight during polymerization. Molecular weight distribution may present a problem through its influence on mechanical and fabrication properties.

7. Pursue earlier indications that polystyrenes having a high concentration of sulfate end groups have superior postirradiation decay of conductivity. The use of non-sulfur emulsifier during polymerization will permit correlation of sulfur analysis with end group concentration.

8. In consultation with the U.S. Army Electronics Laboratory, measure the conductivity of selected glasses as compositions become available which might have low conductivity after irradiation. Measurements of "P.I.P." should indicate whether the charge carriers in glasses are of the same polarity as those in organic polymers. In most non-polar organics the charge carriers are reported to be positive holes, but in ionic materials the electrons have much greater mobility and are the current carriers.

9. Develop methods of fabrication of thin film suitable for dosimeter capacitors. Presently used solution-casting methods yield films of varying susceptibility to atmospheric moisture. The more uniform surface and probably higher density of films produced by blow extrusion and biaxial stretching seem to offer improved resistance to humidity.

10. Provide the Office of Civil Defense and the U.S. Army Electronics Laboratory with consulting services and limited laboratory testing on a continuing, level-of-effort basis.

(a) Consultation will assure that the O.C.D. and U.S.A.E.L. make their selection of materials for dosimeters cognizant of the state-of-the art in materials development.

(b) Laboratory testing will serve to evaluate new materials and assist in trouble-shooting should production difficulties arise.

(c) Laboratory synthesis and testing as time permits, especially measurement of "Persistent Internal Polarization," will contribute information on the production and trapping of charge carriers by the various ingredients in insulating materials. Direction for continued improvement thus will be provided.

REFERENCES

1. M. J. Kelly, B. J. Sturm, and W. W. Parkinson, Annual Summary Report on the Development of Radiation-Resistant Insulators, ORNL-TM-2077 (February 1968).
2. A. J. Curtis, Dielectric Loss of Non-Polar Polymers, *J. Chem. Phys.*, 36, p. 3500, 1962.
3. H. Fröhlich, *Theory of Dielectrics*, Oxford University Press, London (1958).
4. P. Debye, *Polar Molecules*, Dover Publications, London (1945).
5. J. Hopkinson, *Original Papers*, Vol. 2, p. 119, Cambridge University Press, London (1901).
6. D. D. Eley, Energy Gap and Pre-Exponential Factor in Dark Conduction by Organic Semiconductors, *Polymer Symposia*, **17**, 73, 1967, Interscience.
7. Charles Kittel, *Introduction to Solid State Physics*, John Wiley and Sons, Inc., p. 348 (1956).
8. S. H. Clarum, *J. Phys. Chem. Solids*, **24**, 1577 (1963).
9. D. L. Killam, Effect of Humidity on the Dielectric Properties of Some Polymers, Conference on Electrical Insulation, p. 125-128, 1964.
10. N. W. Ramsey, *Proc. Phys. Soc.* (London), **B63**, 590-594 (1950).
11. I. M. Rozman and K. G. Tsimmer, Investigation of the Electrical Conductivity of Insulating Materials Before, During, and After Irradiation, *J. Tech. Phys.*, **1**(8), p. 1634-41 (1957).
12. J. F. Fowler, X-Ray Induced Conductivity in Insulating Materials, *Proc. Roy. Soc.* (London), **A-236**, 464 (1956).
13. S. E. Harrison and P. F. Proulx, Measured Behavior of Gamma-Ray Photoconductivity in Organic Dielectrics, Sandia Corporation Report SCR-526, June 1962.
14. V. E. Culler and H. E. Rexford, Gamma-Radiation-Induced Conductivity in Glasses, *Proc. IEE*, Vol. **112**, No. 7, p. 1462, July 1965.
15. A. Bradley, Insulation for a Radiation Environment: Inorganics, *Insulation*, October, 1961, p. 23.
16. Stanley Kronenberg, Tactical Radiation Dosimetry in the U.S. Army, *Health Physics*, Vol. **14**, pp. 41-44, Pergamon Press (1968).

BLANK PAGE

REFERENCES (Cont'd)

17. S. E. Harrison, Gamma-Ray Photoconductivity Decay in Organic Dielectric Materials, Sandia Corporation Paper No. CP 63-1143, June 1963.

18. D. M. J. Compton, G. T. Cheney, and R. A. Poll, Radiation-Induced Conductivity in Plastic Films at High Dose Rates, J. Appl. Phys., 36, 2434 (1965).

19. H. W. Wicklein, H. Nutley, and J. M. Ferry, IEEE Trans. Nucl. Sci., NS-10:5, 131 (1963).

20. J. E. Barnes, F. E. Hoecker, and L. Kevan, Radiation Research (in press).

21. P. Debye, Trans. Electrochem. Soc., 82, 265 (1942).

22. H. A. Pohl, Electronic Behavior in Macromolecular Solids, Polymer Symposia, 17, 13 (1967), Interscience.

23. F. A. Matsen, J. Chem. Phys., 24, 602 (1956).

24. B. Gross and R. J. deMoraes, Polarization of the Electret, J. Chem. Phys., 37, 710 (1962).

25. M. L. Miller, J. Polymer Sci., A2, 4, 685 (1966).

26. B. Gross and R. J. deMoraes, Gamma Irradiation Effects on Electrets, Phys. Rev., 126, 930 (1962).

27. P. V. Murphy, S. Costa Ribiero, F. Milanez, and R. J. deMoraes, J. Chem. Phys., 38, 2400 (1963).

28. J. R. Freeman, H. P. Kallmann, and M. Silver, "Persistent Internal Polarization," Rev. Mod. Phys., 33, 553 (1961).

29. W. Moore and M. Silver, J. Chem. Phys., 33, 1671 (1960).

30. H. P. Kallmann, V. J. Krasnausky, and A. Orenstein, J. Chem. Phys., 40, 3740 (1964).

31. I. O. Salyer, E. V. Kirkland, and R. L. Seelig, "Cerex 250 Film for Dosimeters," First Quart. Rept., Cont. No. DAHC 20-68-C-0127 Monsanto Research Corp. to Office of Civil Defense, Washington, D. C. (1968).

32. F. A. Bovey et al., Emulsion Polymerization, Interscience Publishers, Inc., New York, p. 67 (1955).

APPENDIX I

APPLICATION OF DOSIMETER SPECIFICATIONS TO TESTING OF PLASTICS

Although the test requirements for electrostatic dosimeters are completely arbitrary, they do provide a convenient framework to analyze the problems involved in testing an insulating dielectric film sample.

The capacitance associated with the quartz fiber section of the dosimeter is extremely small and a storage capacitor is used to extend the range to desired values of radiation indication.

This capacitor provides a much larger electrical leakage path than other possible leakage circuits within the dosimeter and therefore is the only part of the assembly contributing significantly to observed leakage problems.

A preirradiation requirement for these dosimeters is that not over 2% drift in 96 hours shall be observed after charging to the zero of the dose scale. Since potential controls the position of the indicator fiber, to determine our steady-state requirements, we may use from elementary theory:

$$\frac{dv}{v} = \frac{dt}{RC}$$

where v = potential in volts

t = time in seconds

R = resistance in ohms

C = capacitance in farads.

For a typical dosimeter, the voltage of scale zero is 160 volts and at full scale is 100 volts. For 2% scale change 1.2 volts loss is required assuming linearity.

The required value of $\frac{1}{RC}$ becomes

$$\frac{1}{RC} = \frac{1.2}{160 \times 3.46 \times 10^5} = \frac{\text{volts}}{\text{volts-sec}} = 2.17 \times 10^{-5} \frac{\text{Mhos}}{\text{Farad}} = \frac{1}{\text{sec}} .$$

This is the highest steady-state value that can be tolerated for the capacitor dielectric. This situation is further complicated by dielectric charging effects. These dipole polarization effects result in $\frac{1}{RC}$ being a time-dependent function. Typically, an insulating dielectric shows a time dependence plotting as a straight line with a fixed negative slope on a ln $\frac{1}{RC}$ vs ln time plot. Integration under this curve results in a leakage value which may be compared to the required steady-state value of not more than 0.75% loss of applied voltage on the quartz fiber in four days. The termination time for this integral is 3.46×10^5 seconds but no simple method of fixing the starting time is available. It takes a finite time to charge and zero the dosimeter. Insofar as observed charge change is concerned this time is lost to the integral. An arbitrary assignment of one second for integral initiation and a slope of minus one will be used for calculation purposes. This is a much more rigorous test than would be required in practice. In fact one would assume that the dosimeter would be charged to see that it would operate successfully sometime before the 96-hour drift test. Then when it is set to zero for the 96-hour drift test the dielectric charging observed would be only that fraction associated with the new voltage charge; presumably less than full scale or less than 1/3 of total voltage.

Assuming the dosimeter meets the requirements of this preirradiation test it is then irradiated to 2000 R at a dose rate not exceeding 2.78 R/sec.

Within ten minutes after the radiation source is withdrawn the dosimeter is recharged to zero reading. It then must not drift over 5% of range in four hours. Since the dosimeter was completely discharged by the radiation field, maximum dielectric charging effects will be observed. Because of the short collection time the steady-state $\frac{1}{RC}$ value allowable is larger than the preirradiation case by sixty-fold ($1.3 \times 10^{-6} \frac{\text{Mhos}}{\text{Farad}}$) and most of the leakage observed is caused by excess charge carriers provided by the radiation dose.

Forty-eight hours later, if this test is passed, the dosimeter is again charged to zero reading and the 2% in 96-hour test is again applicable. Radiation effects have had two days to disappear at this point and another four days during the test period. It should be noted that again only a small potential change is applied to the dosimeter and for practical purposes the only requirement is that $\frac{1}{RC}$ has reached 2×10^{-8} $\frac{\text{Mhos}}{\text{Farad}}$ after 48 hours of postirradiation decay. During postirradiation decay, observed values must be below 4×10^{-7} $\frac{\text{Mhos}}{\text{Farad}}$ at 10^4 seconds with a log-log slope of minus one to meet this requirement. It is preferable to measure the decay until it actually reaches 2 x 10^{-8} $\frac{\text{Mhos}}{\text{Farad}}$.

The final dosimeter requirement is that raising the temperature to 135°F (57°C) for 96 hours shall not result in over 5% shift in reading. Some mechanical bias can be observed here but the primary problem still is apparent film conductivity.

These acceptance tests for the dosimeter can be altered to provide test requirements for insulating dielectric film samples quite easily by calculating the charge change on a sample held at constant potential compared to the total charge on the sample which would result in the same shift of the quartz fiber under the dosimeter test criteria. This is 0.75% of total charge for the 2% tests and 1.88% of total charge for the 5% tests. Since it has been shown that the observed current through most films decreases with time, with a plot of $\frac{\text{Mhos}}{\text{Farad}}$ versus time on log-log paper having a slope of minue one, these criteria can most easily be illustrated graphically. Figure A1 summarizes the test requirements for insulating dielectric films.

It is important to remember that these calculated lines represent pessimistic values and that equally important are the necessary state values of 2.17 x 10^{-8} $\frac{\text{Mhos}}{\text{Farad}}$ at room temperature and 5.43 x 10^{-8} $\frac{\text{Mhos}}{\text{Farad}}$ at 135°F.

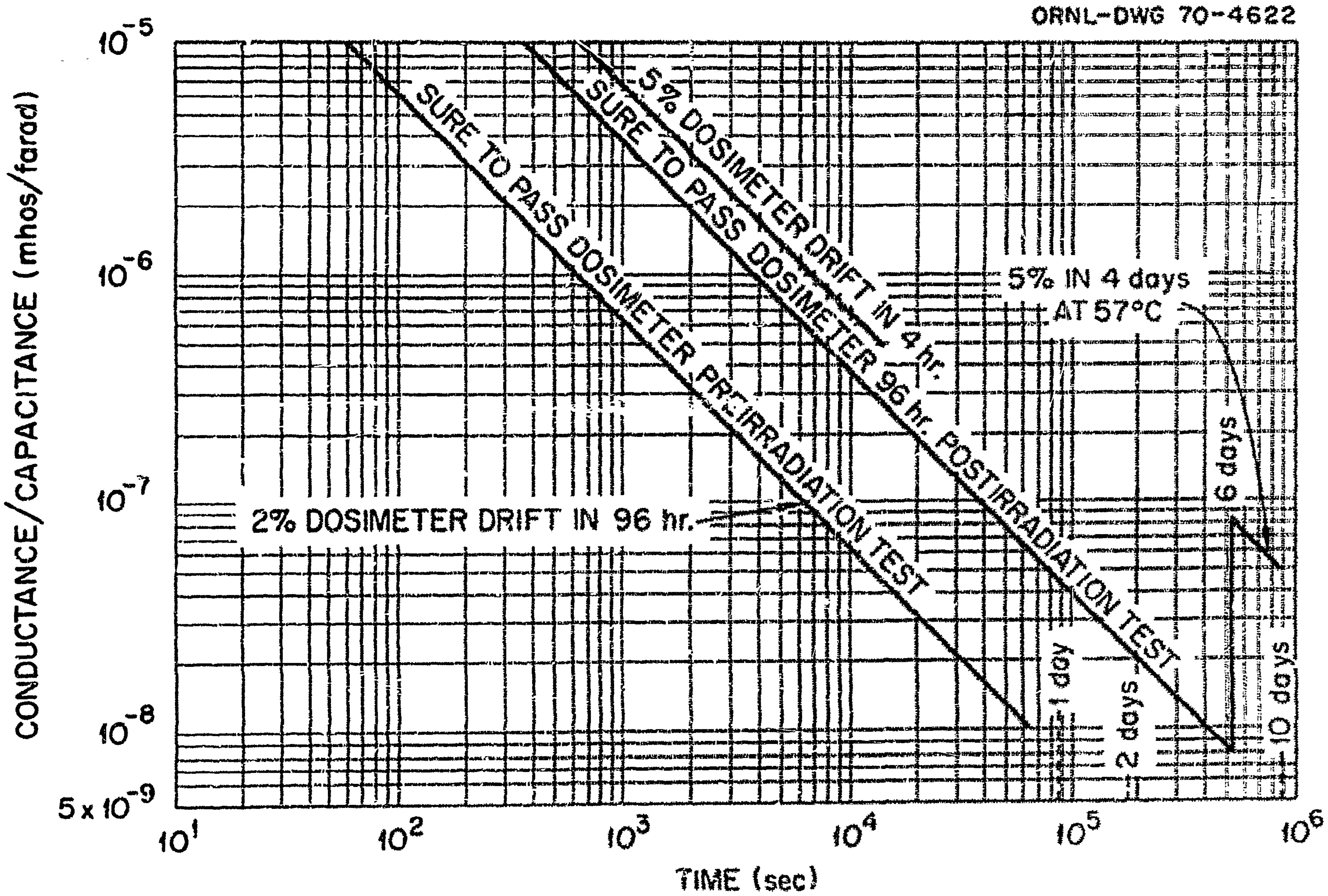

Fig. A1. Test Requirements for Insulating Films for Electrostatic Dosimeters.

APPENDIX II

PREFERRED RECIPE AND PROCEDURE FOR POLYMER

Ingredient		Weight (per 100 g water)
Monomer	- styrene	40 g
Emulsifier	- Acto 450*	0.5 g
pH Control	- sodium hydroxide	0.02 g
Initiator	- potassium persulfate	0.04 to 0.2 g, see below

Procedure: The initiator should be dissolved in approximately one-tenth of the total water and should be added to the monomer emulsion at the proper rate, temperature, and agitation to give a polymer having a inherent viscosity** of 0.8 to 0.9. Unreacted monomer should be stripped from the reaction mixture by steam distillation carried out to distill twice the volume required to carry over the last visible trace of monomer. Separation of the polymer from the aqueous phase should be by freezing, with dilution and washing as necessary to give an ash content of less that 0.15 wt % (ASTM-D-817). The polymer product should have a softening temperature (Deflection Temperature at 264 psi, ASTM-D-648) of greater than 90°C. The monomer content should be less than 2%.

---

*Acto 450 - Humble Oil product based on alkyl aryl sulfonate ~45%, petroleum (mineral) oils ~25%, isopropyl alcohol 10-15%, and water.

**Inherent viscosity - natural logarithm of the ratio of solution to solvent viscosity divided by concentration at 0.1 wt % polymer in benzene.

The initiator concentration should be adjusted to give 85 to 100% conversion of monomer in a reasonable reaction time with a molecular weight range having the viscosity specified above.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) OAK RIDGE NATIONAL LABORATORY Operated by Union Carbide for the USAEC	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE
The Development of Radiation-Resistant Insulators Progress Report - July 1, 1967 to July 1, 1969

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Progress Report - July 1, 1967 to July 1, 1969

5. AUTHOR(S) (First name, middle initial, last name)
M. J. Kelly and W. W. Parkinson

6. REPORT DATE July 1970	7a. TOTAL NO. OF PAGES 64	7b. NO. OF REFS 32
8a. CONTRACT OR GRANT NO. b. PROJECT NO. OCD-PS-66-115 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) ORNL-TM-2986 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT
This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Civil Defense Washington, D. C.

13. ABSTRACT

The apparent electrical conductivity of high-resistance plastics has been examined from the standpoint of dielectric relaxation processes as well as steady-state conductivity. The observed, time-dependent conductivity of high-purity polystyrenes, commercial plastics of lower purity and of the copolymer in use for dosimeters can be accounted for on the basis of dielectric charging and low values of conductivity, both varying with the polar nature of the base polymer and the impurities. During irradiation the conductivity increases greatly depending on the dose rate and decays after irradiation with a time dependence related to the composition of the specimen.

To be suitable for dosimeter use, the radiation-induced conductivity must decay rapidly, to values below 10^{-19} mhos/cm in 10^4 seconds. The currently used material, a copolymer of styrene and α-methyl styrene (Cerex 250B), was found to have unusually rapid decay of conductivity following irradiation. By polymer fractionation and by varying the synthesis ingredients, the chemical species active in reducing conductivity was identified as sulfate chain ends arising from persulfate initiator in the polymerization recipe.

Styrene homopolymers have been synthesized with sulfate end groups and shown to have as low conductivity as the copolymer. Polymers with sulfate end groups and (NH_4) cation have shown low but erratic conductivity and polystyrenes having end groups of moderate polarity have lower dielectric charging prior to irradiation and some reduction in post-irradiation conductivity. Methods are proposed for development work to exploit these possibilities for improving plastic insulators.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification