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Effects of Corona Discharge upon Polyethylene

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A number of recent studies[1-3] have been concerned with the degradation suffered by organic dielectric materials, such as polyethylene, upon exposure to the phenomenon of corona discharge. In this process, the dielectric and its surrounding medium are subjected to a voltage gradient sufficient to ionize air at the dielectric interface or within voids in the dielectric, leading to a corona discharge current. This current is carried by the ionized particles produced. The maintenance of corona discharge upon or within an organic dielectric will eventually damage the material to the extent of causing electrical failure. This degradation has been ascribed variously to ionic bombardment,[1] electron bombardment,[2] ozone attack, and localized heating; the latter two arguments are generally included as contributory, rather than primary, causes.

In a recent article,[3] Nail has shown that polyethylene is degraded far more rapidly by corona discharge from a negatively charged electrode than from a positive electrode. These results, supported by theoretical arguments concerning the relative energies of the ionized particles, support the conclusion that electron bombardment is probably the chief factor involved. The purpose of the present study is to re-examine the corona discharge process in polyethylene in order to confirm, if possible, the electron bombardment hypothesis, and to inquire into the mechanism by which such bombardment degrades polyethylene.

Corona discharge has been observed to produce crystals of oxalic acid on the surface,[4] and on the surfaces of voids[5] within polyethylene. In the former study it was shown that formation of oxalic acid did not occur in the absence of either oxygen or water vapor. In these studies and in the present investigation no other oxidized fragments were noted.

In the present series of experiments, a steel sphere, maintained at 20 kv. (rms) (60-cycle alternating current), was placed in contact with a sheet of polyethylene on a grounded steel plate, resulting in a sustained corona discharge at the polyethylene–air interface. The following qualitative effects were observed:

A resinous substance formed on the surface of the polyethylene sheet directly beneath the point of contact of spherical electrode. This material gradually turned brown and embrittled on contact with air, with particular rapidity in the presence of sunlight. Sections of polyethylene removed from this area were found to have developed unsaturation to the extent of 0.1 to 0.3 mole-%. This material appears to be partially depolymerized polyethylene of relatively low molecular weight.

Surrounding this material at the center of the polyethylene sheet, was found a ring of oxalic acid crystals, of outer radius of 1.3 to 1.4 in. This radius proved independent of the time of exposure to corona discharge, but could be varied by changing the applied voltage. Such a potential dependence and time independence is appropriate to a reaction initiated by a bombardment phenomenon.

Microscopic examination of the ring of oxalic acid revealed a uniform monolayer of crystals. Except at the extreme outer edges, the density of crystals and weight of oxalic acid per unit area appeared independent of the time of exposure. The process evidently proceeds to the formation of a monolayer of oxalic acid in an area governed by the potential difference applied, at which point the formation of oxalic acid ceases. The polyethylene beneath the layer of oxalic acid was found to have suffered considerable checking and cracking.

A diagram of the experimental apparatus is included as Figure 1. In Figure 2, the range through which electrons travel in air at 760 mm. Hg is plotted as a function of potential energy, as abstracted from the experimental data of Buchmann.[6] Although the data refers to 0°C. and the present experiments were carried out at room temperature, the curve should remain adequate for purposes of approximation. From the geometry of the apparatus and the potential difference applied, an approximate maximum radius of the circle under electron bombardment may be calculated in the following manner:

In Figure 3, the voltage gradient produced by the spherical electrode is plotted against a horizontal radius along the upper surface of the poly-

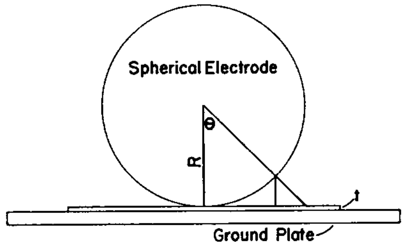

Fig. 1. Diagram of experimental apparatus.

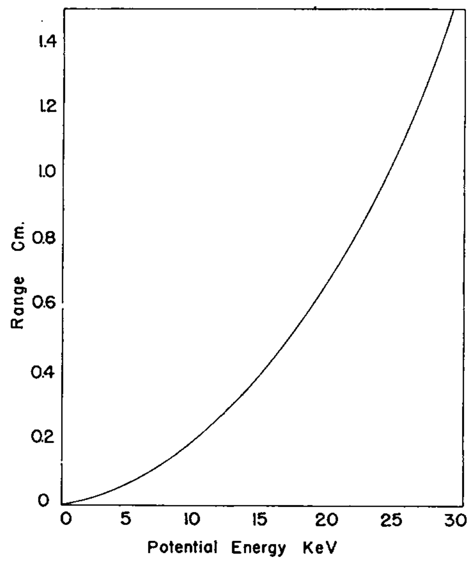

Fig. 2. Range of electrons in air.

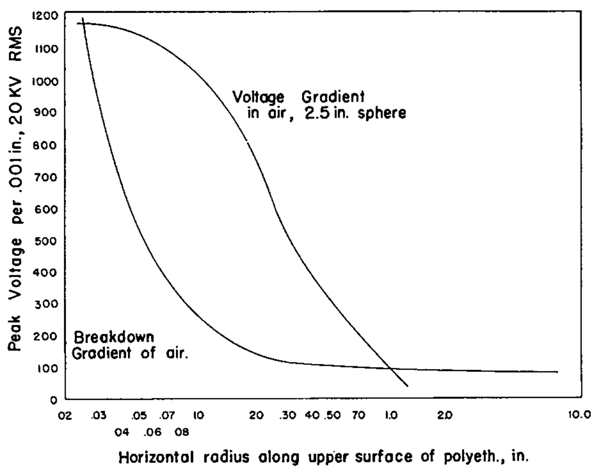

Fig. 3. Voltage gradient in air.

ethylene sheet, according to elementary physical principles:

$$V_{\text{air}} = V_{\text{sphere}} \frac{\log (\sec \theta)}{(1/\epsilon) \log (R + t/t) + \log (\sec \theta)}$$

where V is the voltage gradient, ϵ dielectric constant of the polyethylene sheet, R is the radius of the sphere, t is thickness of the polyethylene sheet, and θ the angle between the vertical radius and the radius to any point on the upper surface of the sheet. On the same graph, the voltage gradient sufficient to ionize air is plotted against the same horizontal radius.[7] The two intersections of these curves define a maximum and minimum radius wherein air will be ionized. When the rms potential difference is 20 kv., simultaneous solution yields a maximum radius of 0.9 in. It can be seen from Figure 2 that electrons produced in ionizations in this area will have a maximum range of 0.58 in. (1.48 cm.). Even with the assumption of random paths, the bombarded area cannot, therefore, have a maximum radius greater than 0.9 + 0.58 = 1.48 in.

Actually, the paths of electrons in this area will tend to follow the lines of force of the applied field, and will travel in a direction normal to the spherical electrode and normal to the ground plate beneath the polyethylene sheet. As an approximation, it will be assumed that the electrons travel normal to the spherical electrode in a straight line to the polyethylene sheet. In this case, the maximum horizontal radius will be gained by an electron produced in the air space at the maximum ionization radius of 0.9 in. traveling the maximum range of 0.58 in. in a direction normal to the sphere. Trigonometrically, this radius is 1.32 in.

Experimentally, the outer radius of the ring of oxalic acid crystals was found in all cases to be between 1.3 and 1.4 in. This agreement is taken as supporting evidence for the hypothesis that oxalic acid is formed as a result of reactions initiated by electron bombardment. If, on the other hand, ionic bombardment were the major factor involved, the extremely short range in air of the relatively heavy positive ions would establish a maximum bombardment radius of only slightly greater than 0.9 in.

Oxalic acid is hardly an expected oxidation product of the bombardment of polyethylene with an electron beam. Studies of the effects of gamma and neutron radiation on polyethylene[8] have never encountered this or similar degradation products. The chemical effects of such treatment have apparently been limited to the production of crosslinking and unsaturation. In the corona discharge process, this appears to be the sole result when oxygen and water vapor are excluded, as evidenced by the resinous, discolored area beneath the electrode, and also by studies carried out in nitrogen and carbon dioxide atmospheres.[4]

It has been suggested[9,10] that electrons produced by ionization of the polymer by incident radiation, in this case an electron beam of relatively low energy, may combine with molecular oxygen to produce the O_2^- anion. The latter, a radical ion, may be expected to hydrolyze in the presence of water vapor:

$$O_2^- + H_2O \longrightarrow OH^- + \cdot OOH$$

forming the perhydroxyl radical. It is suggested that this species may be responsible for the formation of oxalic acid through the following reaction:

$$\cdot OOH + -CH_2-CH{=}CH- \longrightarrow -\underset{\displaystyle OOH}{\underset{|}{CH}}-CH{=}CH-$$

at unsaturated sites produced by radiation-induced dehydrogenation.[8] Precedent for such reaction occurs in the autooxidation of 1-hexene, studied by Hock and Neuwirth:[11]

$$C_3H_7-CH_2-CH{=}CH_2 \longrightarrow C_3H_7-\underset{\displaystyle OOH}{\underset{|}{CH}}-CH{=}CH_2$$

The studies of Farmer[12] have shown that such vinyl hydroperoxides further decompose, destroying the unsaturated linkage. This step presumably proceeds through scission of the peroxy linkage to yield the double bond-reactive hydroxyl radical. Such a process would be expected to produce two carbon fragments as the primary oxidation product. Under the experimental conditions employed, oxidation proceeds to the fully oxygenated product, oxalic acid.

Rationalizations as to why this oxidation should be peculiar to the electron beam radiation of the corona discharge process are not at all clear. It is felt that this behavior poses mechanistic problems worthy of further pursuit.

EXPERIMENTAL

Corona Discharge on Polyethylene

A 5-kva transformer (0–65 kv. rms) was used to produce a 20-kv. (rms), 60-cycle alternating current output. This output was delivered to a stainless steel sphere, 2.5 in. in diameter, resting upon a polyethylene (Alathon 10) sheet of 0.070-in. thickness which, in turn, rested on a grounded, 14.5 in.-diameter, stainless steel disk. Both electrodes were smooth and polished. The electrodes were supported in an open, 16-in.-diameter, 12-in.-deep glass jar.

Identification of Oxalic Acid

The crystals were removed from the polyethylene sheet after periods of sustained corona discharge of from 20 to 120 hr. by extraction with boiling 50% ethanol. Evaporation led to crystallization of white solid; m.p. 100–102°C., reported 101°C.[13] for oxalic acid dihydrate; diamide m.p. 400–410°C., reported 420°C.;[13] dianilide m.p. 251–257°C., reported 257°C.[13] Oxalic acid produced in the corona discharge process has previously been well characterized.[4]

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Synopsis

Supporting evidence for the electron bombardment mechanism for the degradation of dielectric materials by corona discharge has been obtained by correlating the maximum radius of oxidized product, oxalic acid, produced by corona discharge from a spherical electrode upon polyethylene, with the theoretical range of electrons produced. Rationalizations concerning the formation of oxalic acid in the process are offered.

Résumé

On a obtenu une preuve du mécanisme de bombardment électronique au cours de la dégradation de matériaux diélectriques par les décharges en reliant à la quantité théorique d'électrons produits le rayon maximum de produit oxydé, l'acide oxalique, produit par décharge aux dépens d'un électrode sphérique sur le polyéthylène. On présente des explications rationnelles pour la formation d'acide oxalique au cours de ce procédé.

Zusammenfassung

Zusätzliche Belege für den Elektronenbombardementmechanismus des Abbaus dielektrischer Materialien durch Koronaentladung wurden durch die Aufstellung einer Beziehung zwischen dem maximalen Radius für das Oxydationsprodukt, nämlich Oxalsäure, das bei Koronaentladung von einer kugelförmigen Elektrode zu Polyäthylen auftritt, und der theoretischen Reichweite der gebildeten Elektronen erhalten. Eine Erklärung für die Bildung von Oxalsäure während des Prozesses wird gegeben.

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