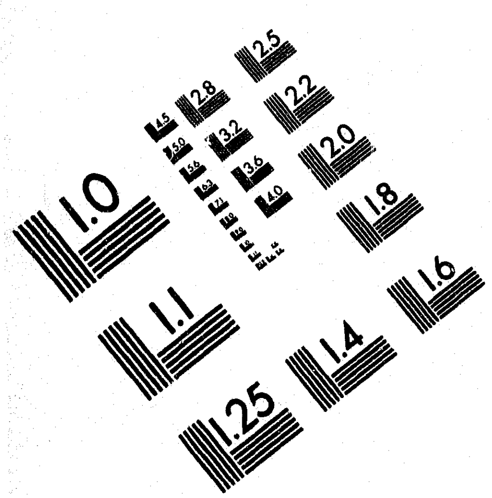
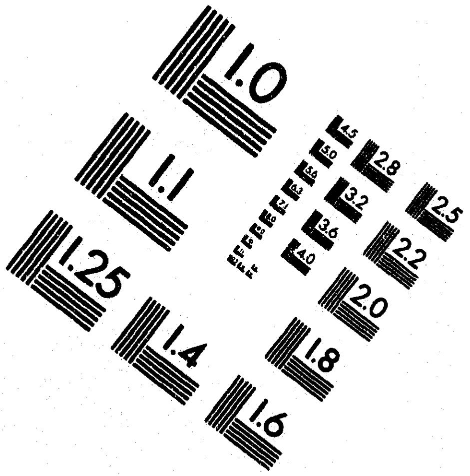
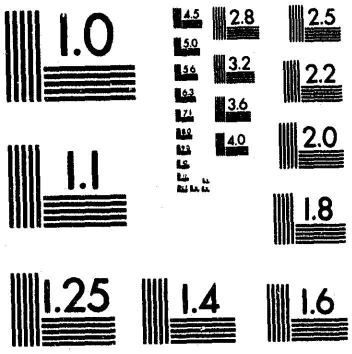


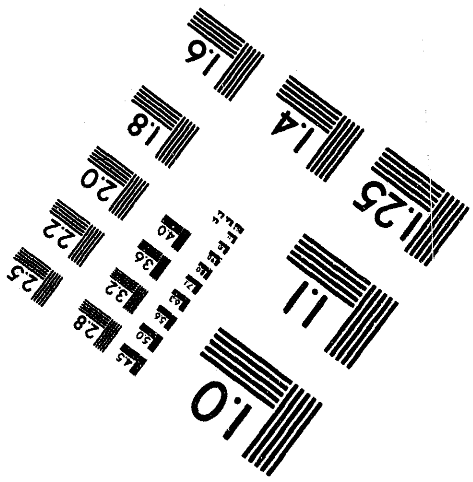
AIIM

Association for Information and Image Management

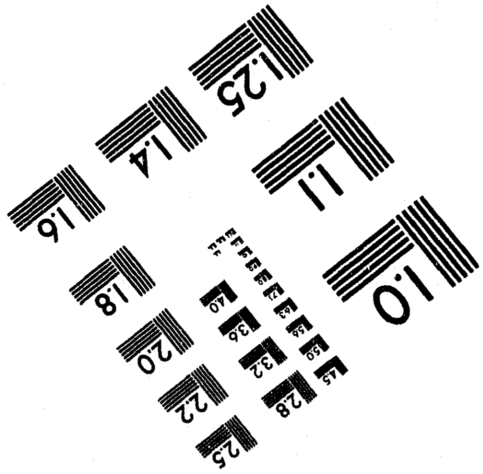
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

2

CONF-940414--4

A POSSIBLE NEW MECHANISM INVOLVED IN NON-UNIFORM FIELD BREAKDOWN IN GASEOUS DIELECTRICS[1]

Lal A. Pinnaduwage and Loucas G. Christophorou

Atomic, Molecular, and High Voltage Physics Group, Health and Safety Research Division, Oak Ridge National Laboratory, Post Office Box 2008, Oak Ridge, Tennessee 37831-6122, and Department of Physics, The University of Tennessee, Knoxville, Tennessee, 37996

I. INTRODUCTION

The electrical breakdown of gases under uniform field conditions is fairly well understood [1-3] in terms of the Townsend's breakdown theory. In most cases involving uniform fields, the breakdown voltage can be estimated via this theory using basic electron impact parameters (including electron attachment cross sections) for molecules in their ground electronic states [1-3].

In contrast, a consistent model of gaseous breakdown under non-uniform fields is not available at present although substantial progress has been made recently [1-5]. We point out the possibility that electron impact processes (in particular electron attachment processes) involving high-lying electronically-excited states [6,7] may play a significant role under non-uniform field conditions. Thus, such processes may need to be included in order to obtain a better understanding of non-uniform field breakdown phenomena.

The general, breakdown characteristics of highly non-uniform field gaps can be illustrated by that for a point-plane geometry, shown in Fig. 1 [4]. It has been found that the breakdown voltage for such a gap can be calculated by a simple streamer criterion [8] if the pressure, P, is above a critical value, P_c; for $P < P_c$, the estimated breakdown voltage is found [8] to coincide with the corona inception voltage, with the actual breakdown occurring at a higher voltage; corona discharges occur only for $P < P_c$. In other words, the presence of corona in the pressure region below P_c seems to prevent the breakdown from occurring at the predicted value.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

---

[1] Research supported in part by the U.S. Air Force Wright Laboratory under Contract No. F33625-92-C-2221 and the National Science Foundation under Contract No. CHE-9022903 with the University of Tennessee and by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

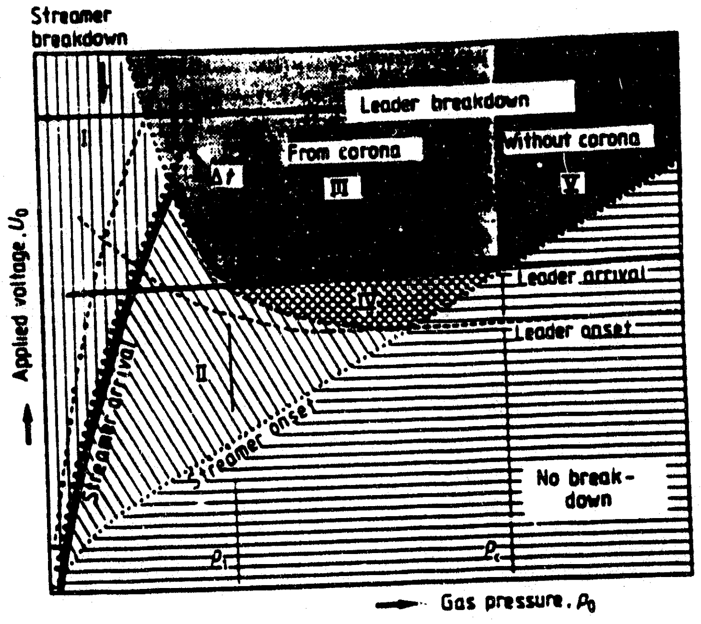


Figure 1. General breakdown characteristics for a point-to-plane gap [4].

This has led to the term "corona stabilization" to describe the enhancement in the breakdown voltage for pressures below P_c. Non-uniform field breakdown measurements in gases will be discussed in Section III.

In Section III, we will discuss the possibility that the "corona stabilization" (under both negative and positive corona) is due to the prevention of avalanche progression by attachment of free electrons to molecules in their high-lying electronically-excited states. Information on electron attachment to electronically-excited states of molecules was not available up until the late 1980's, see below.

II. RECENT DEVELOPMENTS IN ELECTRON ATTACHMENT PROCESSES

Recent basic studies on electron attachment to low-lying [9,10] and high-lying [7,11] excited electronic states of molecules indicate that the cross sections for these states can be orders of magnitude larger compared to those for the corresponding ground electronic states. In particular, electron attachment to superexcited states, SES, (electronically-excited states lying above the ionization potential, I.P., of a molecule) is an extremely efficient process. For example, it was shown [11] that while the electron attachment rate constant, k_a, is $< 10^{-12}$ $cm^3\ s^{-1}$ for the ground electronic state of triethylamine, $(C_2H_5)_3N$, (for electron energies < 1 eV), k_a is $\geq 10^{-3}$ $cm^3\ s^{-1}$ for the SES; this electron attachment to the SES of triethylamine (TEA) is more than 4 orders of magnitude larger compared to thermal electron attachment to SF_6.

Furthermore, electron attachment to SES appears to be of common occurrence in molecules. We have observed efficient electron attachment to SES in saturated tertiary amines (including TEA), nitric oxide, hydrogen, deuterium, methyl iodide, and benzaldehyde. The general requirements for this process to occur are: (i) molecules must be excited to an energy within a few eV of the I.P. where the efficiency for formation of SES is high, and (ii) at least one of the possible molecular fragments has a positive electron affinity. Of the molecules we have studied so far, only N_2 did not attach molecules in the SES; this is understandable since the nitrogen atom does not have a positive electron affinity, i.e., it does not form a stable negative ion.

In our basic studies, we populated SES of molecules via laser multiphoton excitation [11]. Resonant two-photon excitation of a molecule (via a low-lying electronic state) to an energy above its ionization threshold is schematically shown in Fig. 2. As a result of the excitation the molecule may undergo direct ionization (the excited electron coming off within ~ 10^{-15} s) or formation of a SES. A molecule in a SES may decay via preionization/predissociation (the SES lifetime is presumed to be $< 10^{-9}$ s) or it can attach a closeby electron dissociatively [11]. In our experiments, the same laser pulse provided molecules in SES and attaching electrons (via direct ionization and preionization), see Fig. 2. Since the attaching electrons and SES were produced concomitantly and in close proximity, electron attachment can occurr prior to the decay of the SES [11].

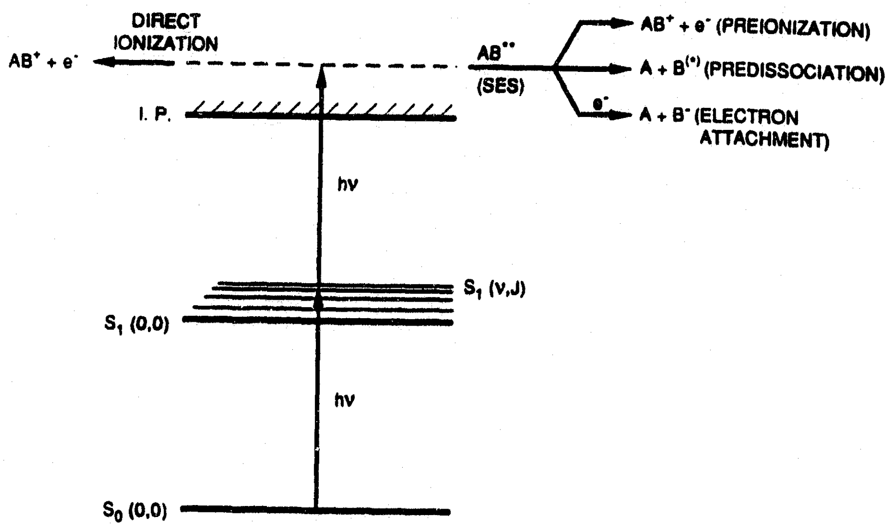


Figure 2. A typical two-photon excitation of a large molecule to an energy above its ionization potential (I.P.). This two-photon excitation will result in direct ionization or population of superexcited states (SES) of the molecule. A molecule in a SES (populated via photon absorption, electron impact or by other means) can decay via preionization, predissociation, or by dissociatively attaching a close-by electron.

Figure 3 shows our data [11] for TEA excited via the KrF (248 nm) excimer laser line; 15 microns of TEA were mixed in with 200 Torr of N_2 for the data of Fig. 3. Nitrogen was used as a buffer gas to lower the effective E/P (E = applied electric field and P = total pressure) value and hence to separate the electronic and the ionic components in the signal waveform [11]. The laser light did not affect N_2 (I.P. ~ 15.8 eV), but excited TEA (I.P. ~ 7.5 eV) to an energy ~ 2.5 eV above its I.P. via two-photon excitation. The positive ions produced via photoionization were rejected using a 3-electrode arrangement and only the negative ions and unattached electrons were detected [11]. The total signal, V_T, of Fig. 3 is the sum of the detected signals due to negative ions, V_I, and unattached electrons, V_E. Thus, V_T is proportional to the number of electrons initially produced via laser photoionization; some of these were converted to negative ions via attachment to SES. As seen in Fig. 3, at higher laser intensities almost all the electrons were converted to negative ions.

The basic electron attachment studies [9-11] have so far concentrated on electronically-excited states produced via laser excitation; however, in a corona discharge these excited states may be produced also via electron impact [6,7], excitation transfer via collisions with metastables or by light absorption.

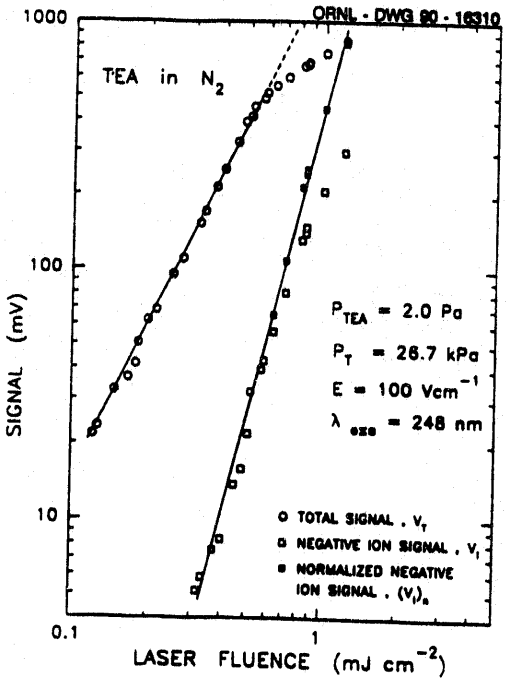


Figure 3. Laser fluence dependence of the measured total, V_T, and negative ion, V_I, signal and the normalized negative ion signal, $(V_I)_n$ [11] for TEA under the experimental parameters indicated in the figure.

III. QUALITATIVE MODEL FOR BREAKDOWN UNDER NON-UNIFORM FIELD CONDITIONS

In this section we point out that the enhancement in breakdown voltage under non-uniform field conditions (see Fig. 1) can be qualitatively explained by taking into account electron attachment to highly-excited molecules and in particular to SES, produced in the corona discharges.

1. Breakdown of Unitary, "Non-Electron Attaching" Gases

The streamer theories first proposed, independently, by Meek, Raether, and Loeb deal primarily with electron multiplication via electron impact and photoionization [12]. Implicit in these theories are two main assumptions: (i) electron multiplication must occur rapidly to produce large space charge fields, and (ii) these localized discharges produce radiation (light) which induces photoionization in front of the corona, especially for positive corona [12]. Once a critical field is reached to satisfy these conditions, breakdown ensues.

The above picture works well with unitary gases that do not attach electrons in their ground or excited electronic states: breakdown occurs almost simultaneously with the appearance of first corona. The so-called "corona stabilization region" (see Fig. 1) is absent or minimal in such gases. In both positive and negative point-to-plane gaps the absence of a significant stabilization region has been reported for He [13], Ar [13], and N_2 [13,14]. To quote Pollock and Cooper [13], "In these gases the individual streamers are able to propagate entirely across a short gap before a sufficient number of streamers form simultaneously to give burst corona, ..." . Any evidence for stabilization in these gases observed by some experimenters is probably due to the presence impurities [12]. It must be noted that for a gas at atmospheric pressure, contamination of 1 part per million corresponds to ~ 10^{13} impurity species per cm^{-3}.

Therefore, in the absence of electron attachment to excited states the first streamers formed can lead to breakdown. The above discussed gases do not form stable negative ions via electron attachment to either ground or electronically-excited states.

2. Breakdown of Electronegative Gases

When electron attachment to the ground electronic state is taken into account, the streamer criterion can predict [8] the breakdown voltage for electronegative gases under non-uniform fields for pressures above P_c, see Fig. 1. Below P_c, the estimated voltage coincides with the corona inception voltage, but the actual breakdown voltage lies at a higher value, see Fig. 1; i.e., for pressures below P_c, an additional mechanism for inducing an enhancement in breakdown voltage is present, which comes in to play with the inception of corona. We propose that the enhancement in breakdown voltage for $P < P_c$ is due to the attachment of electrons to high-lying excited electronic states of the molecules produced in corona discharges.

At the onset of the corona, localized "mini discharges" occur in the gas where electron impact induces ionization and excitation of the gas. In such mini discharges, as many excited species compared to ionization events can be produced [15]. Thus, at a total pressure of 300 Torr, the electron number density [16], and hence the excited species number densities, are in the range of ~ 10^{11} to 10^{16} cm^{-3} in various stages of discharge development. Since the electron attachment cross sections for the high-lying excited electronic states can be much more efficient (with $k_a > 10^{-3}$ cm^{-3} s^{-1} [11]) compared to ground state electron attachment, under such conditions electron attachment to these excited states can completely dominate even for a strongly electronegative gas such as SF_6 ($k_a \leq 10^{-7}$ cm^3 s^{-1} for the ground electronic state). Therefore, the stabilization of breakdown voltage under both positive and negative corona conditions can be predominantly due to the prevention of electron avalanches by electron attachment to high-lying excited electronic states.

Any electronegative molecule (i.e., a molecule which attaches electrons in the ground electronic state) should display electron attachment to high-lying excited states, provided that such states do not undergo rapid dissociation, see Section II.3. Thus, with a possible few exceptions, any electronegative gas should display the stabilization effect shown in Fig. 1. At pressures higher than P_c the loss of stabilization could be due to the shortening of the lifetime of the excited species via collisional quenching compared to the electron attachment time. It must be noted that, high non-uniformity of the electric field (e.g., sharper point) will lead to higher excited species number densities and thus small attachment times, i.e., the stabilization effect is more pronounced under higher field non-uniformity.

We also like to point that the terms electronegative and non-electronegative may have to be redefined since up to now they refer only to electron attachment to the ground electronic state of a species. A molecule which does not attach electrons in the ground state could attach electrons in the electronically-excited states, in particular the SES. For example, while TEA does not significantly attach electrons in the ground electronic state, it attaches electrons efficiently when excited to SES, see Section II.

3. Enhanced Stabilization by Additive Gases of Low Ionization Potentials

It has been shown [2, 17-23] that the stabilization effect in gases like SF_6 can be enhanced by the addition of a few percent of a gas with low I.P. for both positive and negative points in point-to-plane gaps. In these cases the highly-excited states of the additive lying both above and below its I.P. are populated by electrons with energies well below the I.P. of the main constituent (buffer gas) of the mixture; also they may be populated via energy transfer from comparatively low-lying electronic states of the main constituent, and by radiation emitted by the excited states of the main constituent. Even though the additive concentration is only a few percent, efficient excitation together with the ultra efficient electron capture can lead to efficient removal of accelerating electrons from the discharge. This is confirmed by the observed reduction in corona activity [17,18, 22] in the discharge with additives.

One of the additives used [18, 19] with SF_6 is triethylamine (TEA) where enhancement in stabilization was observed for both positive and negative points. The I.P. of TEA is ~ 7.5 eV compared to ~ 16.0 eV for SF_6. Electron attachment to ground state TEA is extremely weak (rate constant $< 10^{-12}$ cm^3 s^{-1}) for electron energies of ≤ 1 eV [11]; electron attachment data for electron energies above 1 eV are not available. However, we observed that electron attachment to laser excited superexcited states of TEA is extremely large, rate constant $> 10^{-3}$ cm^3 s^{-1} [11].

In a very recent study reported in these proceedings, Chalmers et al. [23] observed enhanced stabilization in SF_6 with different freon additives. Of the four freons studied, they did not observe enhanced breakdown only in R116 (C_2F_6). This molecule seems to be dissociating rapidly when in a SES: in both photoionization [24] and electron-impact ionization [25] studies the parent ion $C_2F_6^+$ was not observed and only fragment positive ions were observed; upon excitation to energies above the I.P., the superexcited molecule dissociated rapidly via repulsive potential energy surfaces. Evidence for the inability of C_2F_6 to capture electrons via superexcited states formed in a corona discharge comes also from a recent corona ion source mass spectrometric study [26]. In this study, ions formed in a corona discharge were extracted into a quadrupole mass spectrometer; the mass spectra of a pure SF_6 discharge and a mixture of 1% C_2F_6 and SF_6 were similar, i.e., no negative ions characteristic of C_2F_6 appeared in the spectrum of the mixture. On the other hand, a mixture of 0.5% R113 (CCl_2F - $CClF_2$) and SF_6 clearly showed Cl^- and ClF^- peaks in addition to the peaks characteristic of SF_6; this is consistent with the observed enhancement in breakdown characteristics of R113/SF_6 mixtures observed by Chalmers et al. [23].

From the discussion so far, we can make some predictions that can be tested in breakdown experiments: (i) C_2F_6 should not display a significant breakdown stabilization region (see Fig. 1) in pure form or as an additive in a mixture with other gases, (ii) even though TEA does not attach electrons in the ground electronic state, ions characteristic of TEA (possibly $C_2H_5^-$ and/or $C_2H_5N^-$) should be observable in a corona source mass spectrometric study on a mixture of TEA and SF_6, and (iii) since we have observed [11] enhanced electron attachment to the superexcited states of nitric oxide, the stabilization effect should be present in nitric oxide even though the electron attachment to the ground electronic state is extremely weak [11]. Furthermore, used as an additive, NO (I.P. = 9.6 eV) should display enhanced stabilization in SF_6 or in other gases with I.P. > 10 eV.

IV. CONCLUSIONS

We have introduced a novel concept that may lead to a better understanding of electrical breakdown in gases under non-uniform field conditions. Evidence was presented that the loss of electrons via attachment to high-lying excited electronic states of molecules could play a significant role in corona discharges, leading to the observed enhancement in breakdown voltage under non-uniform field conditions. Further basic and breakdown studies are needed to test this concept.

REFERENCES

1. Meek, J. M. and Craggs, J.D. (Eds.), Electrical Breakdown of Gases, (John Wiley, New York, 1978).

2. Christophorou, L. G., Sauers, I., James, D. R., Rodrigo, H., Pace, M. O., Carter, J. G., and Hunter, S. R., Recent Advances in Gaseous Dielectrics at Oak Ridge National Laboratory, *IEEE Trans. Electr. Ins.* **EI-19**, 550-566 (1984).

3. Christophorou, L. G. and Pinnaduwage, L. A., Basic Physics of Gaseous Dielectrics, *IEEE Trans. Electr. Ins.* **EI-25**, 55-74, (1990).

4. Pinnekamp, F and Niemeyer, L., Qualitative Model of Breakdown in SF_6 in Inhomogeneous Gaps, *J. Phys. D* **16**, 1293-1302 (1983).

5. Gallimberti, I., Breakdown Mechanisms in Electronegative Gases, in Gaseous Dielectrics V, Ed., by L. G. Christophorou and D. W. Bouldin, (Pergamon, N. Y., 1987, pp. 61-80).

6. Christophorou, L. G., Electron-Excited Molecule Interactions, Proc. of the XXth Intern. Conf. on Phenomena in Ionized Gases, (Ed., V. Palleschi, D. P. Singh, and M. Vaselli). pp. 3-13.

7. Pinnaduwage, L. A. and Christophorou, L. G., Verification of H^- Formation in UV Laser Irradiated Hydrogen; Implications for Negative Ion and Neutral Beam Technologies, *J. Appl. Phys.* (March, 1994 issue).

8. Nitta, T. and Shibuya, Y. Electrical Breakdown of Long Gaps in Sulfur Hexafluoride, *IEEE Trans. Power App. Systems* **PAS-90**, 1065-1071 (1971).

9. Christophorou, L. G., Hunter, S. R., Pinnaduwage, L. A., Carter, J. G., and Christodoulides, A. A., Optically Enhanced Electron Attachment, *Phys. Rev. Lett.* **58**, 1316-1319 (1987); Pinnaduwage, L. A., Christophorou, L. G., and Hunter, S. R., Optically Enhanced Electron Attachment to Thiophenol, *J. Chem. Phys.* **90**, 6275-6289 (1989).

10. Kuo, C. T., Ono, Y., Hardwick, J. L., and Moseley, J. T., Dissociative Attachment of Electrons to the A $^2\Sigma^+$ State of Nitric Oxide, *J. Phys. Chem.* **92**, 5072-5074; Mock, R. S. and Grimsrud, E. P., Optically Enhanced Electron Capture by p-Benzoquinone and Its Methylated Derivatives, *J. Phys. Chem.* **94**, 3550-3553 (1990); Jaffke, T., Hashemi, R., Christophorou, L. G., Illenberger, E., Baumgärtel, H., and Pinnaduwage, L.A., Photoenhanced Dissociative Electron Attachment to SO_2, *Chem. Phys. Lett.* **203**, 21-27 (1993).

11. Pinnaduwage, L. A., Christophorou, L. G., and Bitouni, A. P., Enhanced Electron Attachment to Superexcited States of Saturated Teritary Amines, *J. Chem. Phys.* **95**, 274-287 (1991); Pinnaduwage, L. A. and Christophorou, L. G., Enhanced Electron Attachment to Superexcited States of Nitric Oxide, *Chem. Phys. Lett.* **186**, 4-10 (1991); Pinnaduwage, L. A. and Christophorou, L. G., H^- Formation in Laser-Excited Molecular Hydrogen, *Phys. Rev. Lett.* **70**, 754-757 (1993).

12. Loeb, L. B., Electrical Coronas, (Univ. of California Press, Berkeley, 1965).

13. Pollock, H. C. and Cooper, F. S., The Effect of Pressure on the Positive Point-to-Plane Discharge in N_2, O_2, CO_2, SO_2, SF_6, CCl_2F_2, Ar, He, and H_2, *Phys. Rev.* **56**, 170-175 (1939).

14. Ford, R. T., Positive Point-to-Plane Spark Breakdown of Compressed Gases, *Nature* **166**, 688-689 (1950).

15. Loeb, L. B. and Meek, J. M., The Mechanism of Spark Discharge in Air at Atmospheric Pressure I, *J. Appl. Phys.* **11**, 438-447 (1940).

16. Stritzke, P., Sander, I., and Raether, H., Spatial and Temporal Spectroscopy of a Streamer Discharge in Nitrogen, *J. Phys. D* **10**, 2285-2300 (1977).

17. Weissler, G. L. and Mohr, E. I., Negative Corona in Freon-Air Mixtures, *Phys. Rev.* **72**, 249-297 (1947).

18. Farish, O., Chalmers, I. D., and Vidaud, P., SF_6 Mixtures with Enhanced Corona Stabilization, in Proc. of the 7th Intern. Conf. on Gas Discharges and Their Applications (London, 1982), pp. 223-226.

19. Lakdawala, V.K., James, D.R., and Christophorou, L.G., Effect of Ionization Processes on the Corona Stabilization Breakdown in SF$_6$ and SF$_6$-Mixtures, Proc. of the 4th Intern. Symposium on High Voltage Engineering (Athens, Greece, 1983), pp. 1-3.

20. Nelson, J. K., Modification of Corona Stabilization in Electronegative Gases by Low Ionization Potential Additives, in Gaseous Dielectrics IV, (Ed. by L. G. Christophorou and M. O. Pace, *Pergamon*, New York, 1984) pp. 175-183.

21. Chalmers, I.D., Qiu, Y., Sun, A., and Xu, B., Extended Corona Stabilization in SF$_6$/Freon Mixtures, *J. Phys. D* **L107-112** (1985).

22. Qiu, Y. Sun, A., and Kuffel, E., Improved Dielectric Strength of SF$_6$ Gas With a Trichlorotrifluoroethane Vapor Additive, *IEEE Trans. Electr. Ins.* **EI-22**, 763-768 (1987).

23. Chalmers, I.D., Farish, O., and Shelton, R. V., Insulation Performance of SF$_6$ Mixtures, in Gaseous Dielectrics VII, (Ed., by L. G. Christophorou and D. R. James, Plenum, New York, to be published, 1994).

24. Noutary, C. J. , Mass Spectrometric Study of the Photoionization of Some Fluorocarbons and Trifluoromethyl Halides, *J. Res. NBS* **72A**, 479-485 (1968).

25. Lifshitz, C. and Long, F. A., Some Observations Concerning the Positive Ion Decomposition of C$_2$F$_6$ and C$_3$F$_8$ in the Mass Spectrometer, *J. Phys. Chem.* 69, 3746-3751 (1965).

26. Sigmond, R. S. and Sigmond, T., Corona Ion Source Mass Spectrometry of SF$_6$ Gas and Mixtures, Proc. of the IXth Intern. Conf. on Gas Discharges and Their Applications (Venezia, 1988), pp. 212-214.

DATE
FILMED

8/3/94

END