LASER-EXCITED FLUORESCENCE PROBES FOR SURFACE
FLASHOVER STUDIES OF THE INSULATOR CELCON

by

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CHAPTER I

INTRODUCTION

1.1 Significance of this Study

Electrical insulation plays a crucial role in many high-voltage applications. It is found in power transmission lines, accelerators, pulsed power devices, and satellites. Insulator breakdown, whether bulk or surface, can lead to the failure of these devices, costing money and time. In the case of satellites, there are additional difficulties in getting access to the device. Consequently, there is much interest in research leading to early detection of imminent breakdown, and to better understanding of the breakdown process.

Standard electrical techniques applied to insulator damage studies include measurements of breakdown voltage, resistivity, and insulator charging. Electron microscopy is used to detect structural damage, and electron spectroscopy is used to determine the nature of chemical changes. Infrared spectroscopy and neutron activation analysis are also utilized.

There are many elements involved in creating conditions favorable for breakdown. Contributing processes include mechanical, electrical, and thermal

stress, exposure to ultraviolet radiation, and the diffusion of contaminants into the insulator from its surroundings.

Because of the large number of contributing factors, there have been difficulties in developing a good understanding of the breakdown mechanism. Most of the techniques used to study breakdown are sensitive to only one or a few of the effects of the processes mentioned, and therefore yield incomplete information.

To study breakdown mechanisms successfully, a technique is needed with good spatial resolution for the detection of flashover tracks and other small features. Surface and bulk charge probe capabilities, the ability to determine the size and quantity of bulk structural defects, and the capability to determine the chemical nature of the damage are also desirable. Fluorescence probes potentially have these capabilities, and also high sensitivity, a virtue of fluorescence techniques generally. Probes sensitive to polymer free volume and polarity are widely used in the testing of polymer microenvironments [1]. In addition, pH and voltage sensitive probes are well established in biological research. In this investigation, the diagnostic capabilities of laser-excited fluorescence probes applied to insulator breakdown are explored.

In the proposed technique, fluorescent dyes are used to “highlight” specific areas on a damaged insulator. When observed under laser excitation, certain areas of the insulator display either quenched or enhanced fluorescence. Using

spectroscopic techniques and knowledge of fluorescence mechanisms, the nature of the physical and chemical changes that occur on the surface of the insulator during flashover can be deduced. In addition, the fluorescence quenching/enhancement pattern differs from dye to dye, permitting one to choose the probe most sensitive to the particular phenomenon of interest. Although the focus here is on surface damage, bulk damage features can also be examined.

1.2 Background Information on Electrical Breakdown

This investigation is concerned primarily with damage due to surface breakdown of insulators in a simulated space environment. In an actual space environment, insulators are subject to additional kinds of stress, such as thermal and mechanical, which also affect the insulator's holdoff capability. These additional effects were not considered in this study.

Most researchers [2,3,4] agree that insulator breakdown starts with emission of electrons and negative ions from the triple junction- -where the insulator, electrode, and vacuum meet. It is also generally accepted that flashover occurs through an ionized channel in gas desorbed from the insulator surface. At 10^{-4} torr, the electron mean free path is about one meter. Our samples were flashed over at even lower pressures of about 10^{-5} torr, at which an electron would be very likely to cross our 5 mm gap without a collision if the pressure in the sample vicinity was the same as the pressure in the rest of the vacuum

chamber. However, due to outgassing from the insulator, the pressure near the sample surface is considerably greater than in the rest of the chamber, and the conditions are more favorable for breakdown.

The mechanisms of electron propagation and multiplication, and of gas desorption, have been the subject of much debate [4]. One of the most widely accepted theories was proposed by Kofoed [5,6], who showed experimentally that electrons and negative ions are produced at the triple junction, and proposed that the impact of these electrons on the anode or insulator produces X-rays. These, in turn, cause emission of more electrons from the cathode, and so on, until conditions which will support breakdown are reached.

Another theory, proposed by Fryszman [7], states that electrons emitted at the cathode strike the insulator near the anode, causing secondary electron emission and leaving a net positive charge on the area. This area of positive charge gradually extends toward the cathode, where the resulting field enhancement leads to further electron emission and breakdown.

These and most other breakdown theories have points in common, including an electron cascade along the insulator surface, or a secondary electron emission avalanche, and surface charging which affects further development of the electron cascade [4].

Other factors affect the samples as well. Keeping samples in vacuum tends to “dry” them, by desorbing substances that were in the insulator, which may

include water and air, as well as materials introduced into the plastic during the manufacturing process. “Dry” samples tend to have a higher flashover voltage, possibly because much of the desorbed gas near the insulator surface has diffused away. This process is fairly slow, however, and since our samples are in the vacuum chamber for only about an hour, most of which is spent pumping down the chamber, the effect on the samples is negligible.

Another significant phenomenon, corona discharge, has been observed in the cloud of gas surrounding the cathode. It is a source of UV radiation, which can break polymer bonds on the surface of the insulator, weakening the holdoff capabilities, and possibly changing the bulk and surface properties of the polymer enough to cause changes in the dye fluorescence.

1.3 Background Information on Fluorescence

1.3.1 Definition of Fluorescence

Fluorescence can be defined as emission produced when a molecule makes a transition between states of the same spin multiplicity. It is a very rapid process, on the order of nano- or picoseconds, and is distinct from phosphorescence, emission produced in a transition between states of different multiplicity, which is comparatively much slower.

An electron is usually excited from the zero vibrational level of the ground state S_0 to one of the vibrational states of the first singlet state S_1 . It rapidly

loses its excess vibrational energy by relaxation to the zero vibrational state of S_1 , de-excites further to one of the vibrational states of S_0 , and then to the zero vibrational state of S_0 . In the de-excitation process, $S_1 \rightarrow S_0$, a photon is emitted and observed as fluorescence, as illustrated in Figure 1.1.

Consequently, the absorption spectrum shows the vibrational spacing of the S_1 state, and the fluorescence spectrum shows the vibrational spacing of the S_0 state. When these are similar, mirror symmetry is seen between the absorption and fluorescence spectra.

The rotational levels of molecules are too closely spaced to be resolved in a room temperature spectrum. Vibrational and electronic levels can be resolved in some molecules since they are about 0.1 eV apart and several eV apart, respectively. However, many complex organic molecules, like our dyes, have a much more complex pattern of vibrational levels, causing the transitions between the various levels to make up one broad band in the fluorescence spectrum [10]. In addition, differences in the microenvironment of the dye molecule can cause shifts in the fluorescence spectrum and thus contribute to the blurring of the vibrational structure.

1.3.2 Stokes Shift

Stokes law states that the wavelength of fluorescence is always longer than the wavelength of the exciting light. An electron can be excited to any

Figure 1.1: The excitation and de-excitation process, showing fluorescence and phosphorescence, as well as some non-radiative transitions.

vibrational level, but before it returns to the ground state, it loses the excess vibrational energy. Since fluorescence is emitted only during de-excitation from the lowest vibrational level of the excited state, it takes more energy to excite an electron than will be emitted via fluorescence. The only transition that absorption and emission may possibly have in common is between the lowest vibrational levels of the ground and first excited states, and these coincide for only some molecules. Therefore, the fluorescence spectrum appears at longer wavelengths than the absorption spectrum.

Solvent effects also contribute to the Stokes shift. The dye molecule has a certain dipole moment, which changes, usually increasing, when the molecule is excited. If the solvent molecules also have a dipole moment, they change their configuration to lower the energy of the dye molecule. This is called solvent relaxation and its results are illustrated in Figure 1.2. When our samples are dyed, the solvent promptly evaporates, but a similar relaxation can be expected to take place within the polymer microenvironment of the dye.

1.3.3 Fluorescence Lifetimes

The fluorescence lifetime is the average period of time a fluorophore remains in the excited state, or the time it takes for the intensity of fluorescence to fall to $1/e$ of its original (maximum) value. A change in the lifetime of a substance

Figure 1.2: Solvent relaxation and Stokes shift. The upper diagram shows the change in energy when an excited molecule undergoes relaxation. The emission energy is decreased, causing a shift to longer wavelengths. The lower diagram illustrates the effects of the Stokes shift on the emission spectrum.

generally corresponds to a change in the fluorescence quantum yield: a high quantum yield is associated with a longer lifetime.

The intensity versus time plot approximates an exponential decay curve, but sometimes there are multiple components, caused by impurities, concentration effects, and variations in the microenvironment of the fluorophore. In addition, our insulator fluoresces at wavelengths near those of some of the dyes, contributing additional components. Nevertheless, the fluorescence lifetime is a significant quantity, since changes in the lifetime of a substance can reflect changes in its surroundings- -in this case, the insulator.

1.3.4 Complexes Formed by Fluorescent Dyes

Fluorescence can come not only from individual dye molecules, but also from complexes formed when the dye molecules combine with each other or with molecules of the surroundings.

An excimer is an excited dimer formed from one excited and one ground state fluorophore. This is a transient configuration, which rapidly splits into two ground state molecules, releasing some of the energy as fluorescence. Generally, the energy state of the excimer is less than that of a single excited molecule, therefore, the excimer fluorescence exhibits longer wavelengths than fluorescence from single molecules.

Other possibilities include the mixed excimer, composed of two different solute molecules, and the exciplex, a molecule of solute bound to a molecule of solvent. Ground state dimers and higher order aggregates also occur, each contributing different wavelengths to the fluorescence spectrum and a different lifetime.

1.3.5 Factors Which Affect Spectra

A chromophore is a molecule or part of a molecule which determines the characteristic absorption of a substance (i.e., its color). An auxochrome is a substituent atom or group of atoms which, when added to the chromophore, causes a spectral shift in the the absorption band. If the shift is toward longer wavelengths it is called bathochromic, and if it is toward shorter wavelengths it is termed hypsochromic [9].

Steric hindrance or intramolecular crowding can also produce a spectral shift. Similarly, concentration effects change the fluorescence spectrum and the fluorescence yield.

1.3.6 Fluorescence Mechanisms of the Probes

1.3.6.1 Molecular Rotors

Several of the dyes used, including Eastman Yellow, which belongs to a group of dyes known as [p-(*N,N*-dialkylamino)benzylidene]malononitriles, and rhodamine 6G (rh6G), belong to a group of dyes known as molecular rotors.

They are characterized by one or more groups attached to the rest of the molecule by a single bond, about which they can rotate. Rotation is a mechanism which enables non-radiative de-excitation to take place, and it can cause fluorescence quenching by providing an alternate de-excitation pathway for the excited molecules. Fluorescence quenching can be reduced if the rotation of the group is somehow hindered, for example, by increasing the rigidity or decreasing the free-volume of the surrounding polymer matrix, thereby preventing molecular relaxation. This property has been utilized to study both static and dynamic changes in the polymer free-volume as a function of different parameters [1].

1.3.6.2 Twisted Intramolecular Charge Transfer States

Molecules which have two moieties, a donor and an acceptor, connected by a single bond about which they can twist, can form twisted intramolecular charge transfer (TICT) states [11]. In rhodamines, for example, TICT formation occurs through rotation about the N-aryl bonds (See Figure 1.3).

Many TICT states are nonluminescent, and undergo rapid non-radiative de-excitation, resulting in fluorescence quenching. This is a particularly important factor in choosing laser dyes, where the maximum quantum yield is desirable. One way TICT state formation can be avoided is by choosing dyes that are not likely to form them. For example, compare the structures of rh6G

Rhodamine 6G

Rhodamine 101

Figure 1.3: Rhodamine 6G and Rhodamine 101.

and rhodamine 101 (rh101) in Figure 1.3. Rh6G is free to rotate about the N-aryl bond, and forms TICT states. In rh101, on the other hand, the corresponding group is prevented from twisting by “bridging”- -holding it rigid with several other bonds.

Factors which affect TICT formation include solvent parameters such as viscosity and polarity, and solute parameters, such as the ground state twist angle, the rotating volumes, molecular shape, and flexibility. TICT fluorescence is quenched by inorganic ions, although polar solvents can enhance it. Increase in molecular rigidity increases fluorescence efficiency in fluid solution, since the resulting coplanarity of the rings allows interaction of the separate electron systems [10]. In polymers, free-volume effects are especially important.

CHAPTER II

EXPERIMENTAL PROCEDURE AND APPARATUS

2.1 Sample Preparation

Fluorescence probes can be used with a variety of insulators, but in this study we concentrate on Celcon. The structure of Celcon is shown in Figure 2.1. It is a widely used insulator, and a good light scatterer for the incident laser light, which facilitates fluorescence observations. Although it does have some inherent fluorescence, it is weak compared to that of the dyes. The insulator samples are $7.6\text{ cm} \times 6.4\text{ cm} \times 0.3\text{ cm}$ pieces, cut from a $61.0\text{ cm} \times 122.0\text{ cm}$ sheet. The Celcon is obtained from Regal Plastics, in Dallas, Texas. One side of each sample is sanded with progressively finer grades of sandpaper, ranging from grit 180 to 1500, in order to remove residues from the manufacturing process and ensure a uniform surface.

The samples are washed with methanol and placed on a grounded aluminum plate attached to the inside wall of the vacuum chamber, and two circular stainless steel electrodes, 1.9 cm in diameter, are placed on the top of the insulator. Figure 2.2 shows the dimensions of the electrodes and their placement

Figure 2.1: The structure of the insulator Celcon.

on the sample, and Figure 2.3 shows the sample mounted on the flashover apparatus.

When the sample is in place, the tank is closed and evacuated, using a Varian SD 700 mechanical roughing pump to about 100 mtorr, and a Varian Model 0184 diffusion pump to bring the vacuum down further. Figure 2.4 shows a block diagram of the vacuum system set up for electrical stressing. Technical details and specifications of the vacuum system can be found in John Smith's dissertation [13].

After the desired pressure (about 10^{-6} torr) is reached, high voltage is applied using a Hipotronics HV DC power supply, which has a maximum output voltage of 120 kV. One electrode is connected to ground, and the other to a high voltage of negative polarity through an $8 \text{ M}\Omega$ resistor chain. Voltage is applied for five minutes, except in experiments investigating the effects of stress

Figure 2.2: Sample and electrode dimensions.

Figure 2.3: Sample prepared for flashover.

Figure 2.4: Block diagram of the vacuum system.

duration, in which the interval is varied. The vacuum chamber is then backfilled with nitrogen and opened, and the samples are taken out.

The samples are dyed with a 5×10^{-5} molar fluorescent dye solution in methanol, using a chromatography sprayer. Rh6G and Eastman Yellow are used most frequently, but rh101, Crystal Violet, Basic Fuchsin, 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylamino-styryl)-4H-pyran (DCM), and Merocyanine 540 (m540) are also used. Structural diagrams of rh6G and rh101 appear in Figure 1.3, while those of the remaining dyes are shown in Figures 2.5 and 2.6.

2.2 Measurements

Once the samples are dyed, they are ready to be examined under argon-ion laser excitation. The lasers used include Spectra Physics Models 171 and 162-3, and Coherent Innova 90. The optimal excitation wavelengths and fluorescence wavelengths differ for each dye. Samples dyed with rh6G are excited with 5145 Å laser light. A Corning colored glass long wavelength pass filter that cuts off at 5300 Å is used to filter out the laser light but allow observation of the fluorescence. Eastman Yellow samples are excited with either the 4579 Å line, and observed using a filter that cuts off at 4700 Å, or with the 4880 Å line, using a filter that cuts off at 5300 Å.

Eastman Yellow

Merocyanine 540

DCM

Figure 2.5: Structural diagrams of Eastman Yellow, m540, and DCM.

Figure 2.6: Structural diagrams of Crystal Violet and Basic Fuchsin.

Methods of examination include visual observation, surface charge measurements, *in situ* spectra, fluorescence intensity profiles, and fluorescence lifetime measurements.

2.2.1 Visual Observations and Photography

Visual observations and photographs of the fluorescence enable us to examine and compare qualitatively the patterns of fluorescence enhancement and quenching. With some dyes, even the spectral shifts are clearly evident. This is typically the first kind of observation made on any new samples, since it provides a quick overview of the fluorescence pattern. Photographs provide a record of the whole fluorescence pattern, especially of the details, such as flashover tracks, not readily apparent from spectra and intensity scans.

For visual observations and photographs, the laser light is channeled through a fiberoptic cable with a dispersive lens on the end, so that it illuminates the entire sample. Observations are made by selecting safety goggles with a filter which cuts out the laser wavelengths but passes most of the fluorescence, as seen in Figure 2.7. Similarly, photographs are taken by placing a suitable filter on the camera lens.

2.2.2 Surface Charge Measurements

During the process of electrical stressing, strongly charged regions form on the insulator. To determine whether these charged areas have an effect on the

Figure 2.7: Visual observation of a sample under laser excitation.

dyes, some of which have charged chromophores, surface charge is measured and compared to the fluorescence patterns.

Surface charge measurements are made using a Monroe Electronics Model 171 electrostatic field meter, set up as shown in Figure 2.8. The field meter actually measures the electric field due to the sample, which is directly proportional to the charge on the surface of the sample. The probe does not come in contact with the sample surface, but is mounted on a translational stage about 0.3 cm above the surface and is scanned over the stationary sample along one of the directions shown in Figure 2.9.

2.2.3 Spectroscopy

Different areas of the insulator exhibit varying degrees of spectral shifts. To allow quantitative comparison of these shifts, spectra are taken at different sites on the insulator, shown in Figure 2.9. Usually, they include the cathode location, the corona damage region between the electrodes, and a spot away from the corona and the electrode areas, expected to have been affected minimally. As discussed in the introduction, spectral shifts can be indicative of chemical changes in the insulator, but they can also be the result of concentration effects or aggregate formation.

Each *in situ* fluorescence spectrum is taken at a single point on a sample. As shown in Figure 2.10, the laser light exciting the dye is chopped with an EG&G

Figure 2.8: Charge probe setup.

Figure 2.9: Directions of charge probe measurements and intensity scans are shown in the two upper diagrams, while the bottom one shows the locations at which *in situ* spectra are taken.

Figure 2.10: Spectroscopy setup.

Princeton Applied Research Model 125A light chopper. The fluorescing spot is focused on the entrance slit of the GCA/McPherson 0.3 meter scanning monochromator, and the laser excitation is filtered out using a Corning colored glass cutoff filter appropriate for the wavelengths of fluorescence and excitation, as discussed previously. A Thorn EMI 9785B photomultiplier tube at the monochromator output is connected to an EG&G Princeton Applied Research Model 1112 photon counter/processor through an EG&G PARC Model 1120 amplifier/discriminator. The output from the photon counter is recorded on a strip chart recorder as the monochromator scans across wavelengths around a fluorescence peak.

Alternately, spectra of dyes in solution are taken by replacing the insulator sample with a capillary tube containing the dye solution. Everything else remains the same.

2.2.4 Fluorescence Intensity Profiles

The contrast in fluorescence intensity between the electrode and corona regions can be quite dramatic. To measure the change in fluorescence yield between locations, a fluorescence intensity profile is taken.

Fluorescence intensity profiles record the intensity of the fluorescence at a single wavelength, usually corresponding to the fluorescence intensity maximum, along a line on the sample. The setup is similar to that used for fluorescence

spectra, but the sample is mounted on a translational stage which moves the sample across the laser beam. The beam traces a line on the sample surface and the intensity of fluorescence along this line is recorded on a strip chart recorder. Intensity profiles are measured along the same orientations as the charge probe readings, shown in Figure 2.9.

2.2.5 Fluorescence Lifetime Measurements

The dyes used are organic compounds, known for having broad and featureless spectra; consequently, the information that can be extracted from spectroscopy is limited. However, fluorescence lifetime measurements can provide additional information. Most importantly, they can be used to determine whether the changes in fluorescence intensity are due to dye concentration effects, or a probe-surface interaction.

Fluorescence lifetime measurements are made using the phase modulation method with the setup shown in Figure 2.11. A spot on the sample, corresponding to the *in situ* spectra sites (Figure 2.9), is excited with a laser beam modulated sinusoidally using a Quantum Technology Model 19HP electro-optic modulator driven by a variable frequency signal generator. This causes the emission to be modulated similarly, and to lag behind the excitation by an angle ϕ . The fluorescence is detected using a Jarrel-Ash scanning monochromator with a 9781R Thorn EMI photomultiplier tube. An EG&G

Figure 2.11: Lifetime measurement setup.

50 MHz Model 5202 lock-in amplifier is used to determine the phase difference between the excitation and the fluorescence. The lifetime τ is determined from the phase difference ϕ or demodulation m using

$$\tan \phi = \omega \tau \quad (2.1)$$

$$m = \frac{B/A}{b/a} = [1 + \omega^2 \tau^2]^{-1/2}, \quad (2.2)$$

where ω is the modulation frequency, B/A is the relative amplitude of the variable portion of the emission, and b/a is the relative amplitude of the variable portion of the excitation. For a more detailed explanation of this method, as well as for a derivation of the mathematics, see Lakowicz [14].

CHAPTER III

RESULTS AND DISCUSSION

A sample that has been flashed over in vacuum at 35 kV and dyed with Basic Fuchsin is shown in Figure 3.1. It was excited with 4880 Å and photographed using a colored glass filter which transmits the fluorescence but cuts off the laser excitation wavelengths. The dark circle is the cathode area of contact, and the dark semicircle below is the anode location. The bright area surrounding the cathode site is the corona damage region, and the dark uneven lines between the electrodes are flashover tracks. Similar patterns were observed with rh6G.

This pattern of fluorescence quenching and enhancement raises several questions about the significance of different features and the processes responsible for the changes in fluorescence.

3.1 Cathode Area

The first question is: why is the cathode fluorescence quenched relative to the corona? Rh6G intensity profiles were taken at 5720 Å according to the procedure outlined in Section 2.2.4. The results, shown in Figure 3.2, suggest that the effect is not so much quenching of the fluorescence at the electrode sites, as enhancement in the corona region. The fluorescence at the electrode sites is

Figure 3.1: A damaged sample as seen under laser excitation. This sample was flashed over at 35 kV for 5 minutes and dyed with Basic Fuchsin.

Figure 3.2: Fluorescence intensity profiles of rh6G samples. The lower plot shows in more detail the profiles of the 25 kV and 10 kV samples.

comparable for all samples regardless of stressing voltage; it is the corona region fluorescence that is enhanced as higher voltage is applied. These comparisons are made relative to the areas near the edges of the sample, which have not been affected nearly as much as the corona region. Relative to the solution quantum yield, the fluorescence is indeed quenched to various degrees, over most, if not all, of the insulator.

The same effect is observed with Crystal Violet and Basic Fuchsin, as shown in Figure 3.3. The Basic Fuchsin profiles were taken at 5880 Å, and the Crystal Violet, at 5720 Å, which correspond to their fluorescence peaks. Neither of these dyes shows as much variation with voltage as rh6G; Crystal Violet, in particular, shows little response below 35 kV.

3.2 Corona Region

The next question that comes to mind might be: what is the origin of the fluorescence enhancement in the region surrounding the cathode? There are two main indications of corona effects: changes in fluorescence intensity and spectral shifts. Several interrelated factors--UV exposure, stressing voltage, and duration of stress application--seem to be responsible for much of the variation in corona fluorescence.

Figure 3.3: Fluorescence intensity profiles of Crystal Violet and Basic Fuchsin samples.

3.2.1 UV Effects

The area in question coincides with the corona discharge region, and ultraviolet (UV) radiation is emitted in the process. Since it is known that UV can damage the insulator by breaking the polymer bonds, the effects of UV exposure were investigated.

To isolate the effects of UV from those of electrical stressing, samples were irradiated inside a glove box equipped with a UV source. The box was filled with argon gas to provide an inert atmosphere, as an alternative to vacuum. Electrodes were placed on the sample surface, but not connected to a voltage source, in order to duplicate the shielding from UV that they provide during electrical stressing. After being exposed for approximately 24 hours, the samples were dyed with either rh6G or Eastman Yellow.

Visual observations show fluorescence enhancement in the area exposed to UV, and little fluorescence in the area that has been shielded. Comparison of the UV-stressed samples in Figures 3.4 and 3.5 to the electrically stressed sample in Figure 3.1 shows that the two effects resemble each other closely. These results seem to indicate that the fluorescence enhancement in the corona discharge region is due at least partly to UV exposure.

The UV-stressed sample dyed with rh6G (Figure 3.4) shows a lighter region around the edge, where the shielding electrode was apparently moved partway through the stressing cycle. This area, which received less UV exposure than the

Figure 3.4: Photograph of UV-irradiated sample dyed with rh6G.

Figure 3.5: Photograph of UV-irradiated sample dyed with Eastman Yellow.

outlying areas, exhibits an intermediate amount of enhancement, indicating that the UV effect is cumulative with time.

3.2.2 Voltage Effects

When a series of samples stressed at different voltages, ranging from 10 kV to 35 kV, is examined, it is found that the enhancement increases with stressing voltage. A sample stressed at 10 kV and dyed with rh6G shows almost no contrast between the corona and the cathode areas, a 22 kV sample has noticeable corona fluorescence enhancement, more prominent in the area between the electrodes, and a 35 kV sample shows a dramatic increase in fluorescence yield in the corona region. This is illustrated in the intensity scans in Figures 3.2 and 3.3. In addition, Table 3.1 gives the ratio of fluorescence intensity on the corona to that on the cathode at various voltages, for the dyes previously discussed. The values for rh6G, Basic Fuchsin, and Crystal Violet were obtained from intensity profiles presented earlier. The values for Eastman Yellow were obtained from intensity scans taken at 5500 Å, the fluorescence peak for the electrode and side areas. The corresponding Eastman Yellow plots appear in Figure 3.6.

Clearly, the enhancement is voltage-dependent. This dependence could be the result of more intense corona discharge, and therefore higher-energy irradiation, in regions of greater electric field strength. Also, note that the

Table 3.1: Ratio of fluorescence intensity in the corona region to the intensity in the cathode region.

	rh6G	Eastman Yellow	Basic Fuchsin	Crystal Violet
35 kV	24	1.5	4.7	1.7
25 kV	-	1.4	-	-
22 kV	2.3	-	1.9	1
10 kV	1.2	0.9	1	1

corona to cathode ratio for Eastman Yellow at 10 kV is less than one. This effect will be discussed in the following section. The variations in sensitivity of different dyes are also apparent from the table.

3.2.3 Dye Sensitivity

When the duration of the stressing is extended, the dyes become more sensitive to damage caused by lower-voltage stressing. To determine the effects of prolonged low-voltage stress, 10 kV was applied to a sample for twenty-four hours. At this voltage, flashover does not occur, although after the sample was dyed with rh6G, enhanced fluorescence was observed in the corona region.

On samples stressed for only five minutes, no distinct changes in intensity were observed visually, and only a minimal increase was detected with fluorescence intensity profile measurements (Figure 3.2). The corona region fluorescence enhancement at long stress durations may be a UV effect. In the UV stress investigation, discussed in Section 3.2.1, less enhancement was seen on

Figure 3.6: Intensity profiles of Eastman Yellow samples. Substantial variations with fluorescence wavelength and stressing voltage can be seen.

samples irradiated for shorter periods of time. While a five-minute exposure to the corona discharge at 10 kV may not cause damage severe enough to affect the fluorescence significantly, the cumulative effects over a period of twenty-four hours result in more extensive damage.

In contrast, Eastman Yellow-dyed samples show substantial variation in fluorescence, even on samples stressed for only five minutes at 10 kV. This is evident from the 10 kV intensity profiles in Figure 3.6 and photographs in Figures 3.7 and 3.8. The dark line down the middle of each sample is the result of dye degradation which occurred during the process of taking multiple intensity scans.

Although the 10 kV sample in Figure 3.7 exhibits no corona effect, the electrodes are distinctly brighter than the surrounding area. The 35 kV sample in Figure 3.8 also has bright electrodes, but the cathode is surrounded by an even brighter corona region. The bright corona area on the 35 kV sample and the bright region surrounding the shielding electrode on the UV-stressed sample in Figure 3.5 suggest that the fluorescence quantum yield increase is due to UV exposure.

3.2.4 Spectroscopy

In addition to appreciable changes in fluorescence yield, visual observations indicate substantial spectral shifts. Spectral shifts were particularly noticeable in

Figure 3.7: Photograph of an Eastman Yellow sample that has been stressed at 10 kV.

Figure 3.8: Photograph of an Eastman Yellow sample that has been stressed at 35 kV.

the corona region of Eastman Yellow samples, especially between the electrodes. The electrode locations appeared pinkish orange, while the inter-electrode area was a greenish yellow. This, of course, does not show up on the black and white photographs, but *in situ* spectra were taken in an effort to characterize these spectral shifts, using the procedure described in Section 2.2.3.

In situ spectra of 10 kV and 35 kV Eastman Yellow samples are shown in Figure 3.9. Even at 10 kV, a slight blue shift is noticeable in the corona region; at 35 kV, this shift is considerable. A slight shift in the side spectrum can be seen at 35 kV. This is probably a corona effect, less pronounced than between the electrodes because of the weaker electric field in that area.

As a result of the spectral shifts, the fluorescence enhancement pattern of Eastman Yellow samples is strongly wavelength-dependent. Intensity profiles of Eastman Yellow samples were taken at various wavelengths ranging from 5150 Å to 6500 Å. From the representative plots shown in Figure 3.6, we see that on 10 kV samples the corona is brighter than the electrodes only at wavelengths shorter than 5500 Å; at longer wavelengths, the electrodes become substantially brighter than the corona. Samples stressed at 25 kV have a brighter corona for most of the range of the fluorescence spectrum, with the electrodes slightly brighter at wavelengths above 6500 Å. The corona is brighter than the electrodes for all wavelengths up to 6500 Å on the 35 kV sample.

EASTMAN YELLOW 10 KV IN SITU SPECTRA

EASTMAN YELLOW 35 KV IN SITU SPECTRA

Figure 3.9: *In situ* spectra of 10 kV and 35 kV samples dyed with Eastman Yellow.

Consequently, when all wavelengths are viewed, the electrode areas on 10 kV Eastman Yellow samples actually appear brighter than the corona region. Photographs of a 10 kV sample and a 35 kV sample, shown in Figures 3.7 and 3.8, illustrate this effect.

In situ spectra of a rh6G-dyed sample appear in Figure 3.10. Spectral shifts on rh6G samples are much smaller than on Eastman Yellow samples, although a slight blue shift can be seen in the corona region. More noticeable is the difference between the *in situ* spectra and the spectrum of the dye in solution, indicating that just depositing the dye on the insulator changes it somewhat.

3.2.5 Fluorescence Lifetimes

Fluorescence lifetimes were measured, as described in Section 2.2.5, on the cathode, corona, and side locations. There was variation with modulating frequency, indicating possible multiple lifetimes, but a general trend was observed for both rh6G and Eastman Yellow. The corona lifetimes tended to be measurably shorter than the cathode lifetimes, suggestive of a chemical probe-interaction in the corona region. These results are somewhat puzzling, however, since an increase in fluorescence yield is usually associated with a longer lifetime.

Figure 3.10: Spectra of rh6G *in situ* and in solution.

3.3 Flashover Tracks

Another significant feature is the rather strong fluorescence quenching along the flashover tracks between the electrodes, as seen in Figure 3.1. This sample was dyed with Basic Fuchsin, but different dyes give dramatically different results.

Samples dyed with DCM have particularly interesting flashover tracks. The fluorescence in the middle of the track is comparable to that of the surrounding corona, while the edges exhibit quenched fluorescence.

Conversely, on a sample dyed with Eastman Yellow, the fluorescence of the flashover tracks cannot be distinguished from the corona. However, when an Eastman Yellow sample is examined in room light under a microscope, the flashover tracks are noticeably lighter than the surrounding area, indicating that, while there is no change in the wavelength or intensity of fluorescence, the area is not unaffected.

From these observations, it is apparent that the flashover tracks differ markedly from the surrounding corona. It is proposed that surface charge is dissipated during flashover, leaving the flashover tracks electrically neutral. It should be noted that, while most dyes behave similarly (i.e., exhibit enhanced fluorescence) in the corona region, their reactions to the flashover tracks are completely different. This is another example of the variations in sensitivity among dyes.

3.4 Other Factors

In Section 3.2.1, we saw how exposure to UV from the corona discharge can affect the fluorescence. This raises the question: are there additional factors, not directly associated with flashover, that can also affect the samples? Prolonged exposure to vacuum changes the insulator's flashover characteristics, possibly changing the nature and extent of damage, and the polar solvent used with the dyes can neutralize the surface charge, which may affect the dyeing process. Both of these can have an effect on the observed fluorescence.

3.4.1 Effects of Vacuum

Since the electrical stressing is done in a vacuum of about 10^{-5} torr, it is necessary to determine whether the vacuum itself has any effect on the fluorescence. A sample is placed in the vacuum chamber, on the flashover stage with electrodes on top, as if to be flashed over, but voltage is not applied. The chamber is evacuated and the sample is kept in vacuum for forty-eight hours. After the sample is taken out, it is dyed with rh6G and examined under laser excitation.

The fluorescence was observed to be uniform over the surface of the sample, indicating that exposure to vacuum has no direct effect on the fluorescence. As was noted in Section 1.2, however, prolonged exposure to vacuum desorbs various substances from the insulator, affecting breakdown characteristics. Since

some fluorescence features are voltage-dependent, exposure to vacuum can be said to affect the fluorescence indirectly. However, when undergoing flashover, our samples were in vacuum for only about an hour, which is not sufficient to make a noticeable difference. Therefore, vacuum effects were not great enough to be significant in this study.

3.4.2 Effect of Methanol on Surface Charge

During electrical stressing, a considerable amount of charge is built up on the surface of the insulator. Some of our dyes (e.g., rh6G and m540) have a net charge, making them potential voltage-sensitive probes; however, the solvent used for the fluorescent dyes--methanol--is a polar molecule and can neutralize the surface charge on the insulator. This experiment was done to determine the extent of charge neutralization.

Samples were flashed over at 35 kV and washed with methanol using a wash bottle. Charge probe readings were taken before and after washing, using the method described in Section 2.2.2. Figure 3.11 shows a decrease of at least 50% of the original charge after washing.

It has been proposed that the surface charge built up on the insulator during stressing affects dyes with charged chromophores. No apparent trends were observed, however [12]. Therefore, neutralization of the surface charge may not

Figure 3.11: Profiles of surface charge on flashed-over samples before and after washing with methanol.

significantly change the dyeing patterns or fluorescence characteristics of the probes.

3.5 Discussion of Results

This investigation was done primarily as a feasibility study for the fluorescence probe technique. From the responses of the dyes to the various stressing conditions, it appears that this technique has considerable potential.

Sensitivity to changes in voltage is demonstrated by corona region fluorescence enhancement seen with rh6G, and by spectral shifts observed with Eastman Yellow. The corona region fluorescence quantum yield also depends on the duration of applied voltage. Furthermore, the degree of quenching at the electrode sites may be voltage-dependent.

Careful examination of the rh6G sample in Figure 3.12 reveals that the cathode fluorescence is quenched to a greater degree than the anode fluorescence. Because high contrast film was used, and because photographs often lose considerable detail in reproduction, this may not be readily apparent from the photograph. This effect suggests that shielding from UV is only one of several factors that determine the amount of fluorescence quenching on the electrode sites.

Differences in fluorescence yield between the cathode and anode sites also can be seen in the photographs of Eastman Yellow samples in Figure 3.13. At 25 kV

Figure 3.12: Sample dyed with rh6G.

Figure 3.13: Eastman Yellow samples showing the difference in quantum yield between the anode and cathode.

the cathode is bright but the anode is not discernible, while at 35 kV the anode is distinctly visible and brighter than the cathode.

A hypothesis that this is due to interaction of the insulator with the electrode material was discounted after the same effect was observed with both brass and stainless steel electrodes. It was also proposed that the electrodes prevent outgassing from the area of contact, causing the microenvironment there to differ from that in unshielded areas. A set of electrodes was hollowed out to a depth of 1 mm, and a channel was drilled from this cavity to the outside, to allow desorbed gases to escape. No difference was observed between samples made with these and with standard electrodes.

At present, the reason for this variation in electrode-site quenching is unknown, but it is clearly more than simply a UV shielding effect. The Eastman Yellow intensity profiles suggest that this effect may be voltage-dependent.

Considerable differences were observed among dyes in the degree of fluorescence enhancement and the amount of spectral shift in the corona region. Also, various dyes were found to exhibit different levels of sensitivity to stressing voltage and flashover track damage.

The dissimilarities in dye response may be due to differences in fluorescence mechanisms of the dyes. For example, molecular rotors are sensitive to changes in polymer free volume: if the free volume is decreased significantly, the fluorescence of such a dye increases measurably. The action of the UV may cause

polymer bonds to break in the corona region, and then reform in a configuration which decreases the free volume of the insulator.

As discussed in Section 1.3.6, rh6G is a molecular rotor, while the corresponding groups of the rh101 molecule are inhibited from rotating by additional bonds; thus we expect the range of rh6G fluorescence intensity to be much greater than that of rh101. For example, in Figure 3.14, the difference in fluorescence intensity between the corona and electrode on the rh6G sample is substantially greater than the difference on the rh101 sample. The overall fluorescence intensity of the rh101 sample is lower than that of the rh6G sample, but the relative amount of fluorescence quenching for rh101 is also smaller.

Whatever their causes, differences among the probes can be very useful. Various aspects of the breakdown process could be studied individually by choosing probes that respond chiefly to the particular phenomenon of interest. Also, when testing an insulator that has suffered an uncontrolled failure in the field, several complimentary dyes could be used to pinpoint the cause of the breakdown.

By providing a selection of probes, this technique combines sensitivity and versatility. It has the potential to become an important tool for both laboratory insulator studies and field applications. In addition, as indicated by the variations in Eastman Yellow fluorescence between the cathode and anode, this technique may help discover and explore entirely new breakdown phenomena.

Figure 3.14: A photograph of a rh6G sample (left) and a rh101 sample (right).

Furthermore, since these probes are capable of detecting effects due to sub-breakdown voltages, they have potential as indicators for impending breakdown.

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