SURFACE STUDIES OF DIELECTRIC MATERIALS USED IN SPARK GAPS*

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Abstract

Dielectric materials commonly used as insulators in spark gaps (Lexan, Nylon, Lucite, Macor, Boron Nitride, Delrin and G-10) have been exposed to the by-products of arcs in three different spark gap experiments. The first was a 60 kV, 0.05 Coul/shot spark gap using copper-tungsten or graphite electrodes at various pressures of N_2 or SF_6 gas. The second was a 5-30 kV, 4-25 kA, .1-.6 Coul/shot, unipolar, pulsed spark gap using graphite, copper-graphite, copper-tungsten, brass, and stainless steel electrodes in N_2 gas or air. The third was a 45 kV, 180 joule/shot surface discharge switch. Surface analysis of these insulators indicates that most become coated with a thick layer of electrode material depending upon the type of gas, electrode, and insulator material used, and the conditions of the arc. However, Lucite insulators inserted in the second spark gap using graphite electrodes and air showed no indications of deposited electrode material on the surface but did show small particles of graphite imbedded in the surface. The self-breakdown voltage (V_{sb}) statistics for spark gaps with insulator inserts show significant deviations from the V_{sb} statistics for spark gaps without insulator inserts, which may be due to deposits of insulator material onto the electrodes.

Introduction

The purpose of this study is to investigate the chemical and physical processes that lead to degradation of insulator materials used in high voltage spark gaps, and to determine how these processes vary with different combinations of electrode material, filler gas, insulator material, and spark gap operating parameters. Various insulating materials were exposed to the by-product of discharges in three different, high power, spark gaps. The synergism between the electrode, gas and insulator materials used in the spark gap can be very important in repetitively operated gaps. Each successive arc induces chemical, mechanical and thermal processes which affect all parts of the gap. These processes depend on the materials in the gap and the gap operating parameters, such as peak current, repetition rate, charge transfer, etc.

Experimental Arrangement

The Mark I spark gap, shown schematically in Figure 1, was used to expose Lexan and Blue Nylon insulators to 5000 shots each in a spark-gap-switched, critically damped, RC circuit.[1] The insulators were inserted as 6" x 6" x 1/4" flat plates located 1.5 cm from the 5 cm diameter hemispherical electrodes and were subjected to discharges in either 2 atmospheres of N_2 gas or SF_6 gas with either graphite or K-33 (tungsten-copper composite) electrodes. The spark gap selfbreaks at 40-45 kV and switches approximately 1 kJ of energy in 2 μs at a maximum rep-rate of 2 pulses
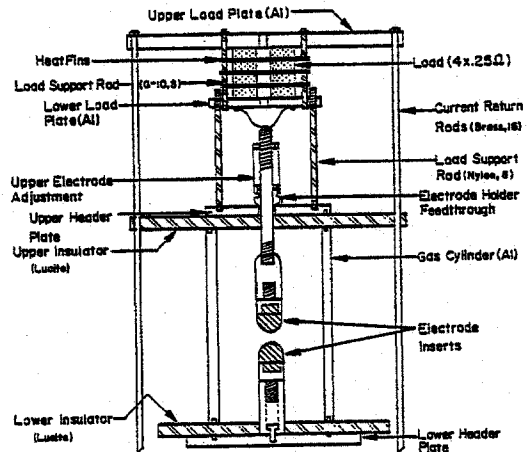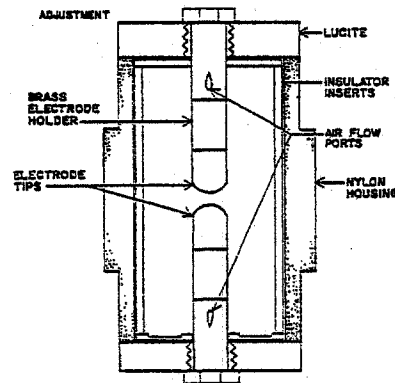
Fig. 1. Mark I Spark Gap.

Fig. 2. Mark II Spark Gap.

per second. The maximum current in the spark gap is 50 kA with a charge transfer of about 0.05 Coul per shot.

The Mark II spark gap, shown schematically in Figure 2, was used to expose Lucite insulators to 50,000 shots from an unipolar discharge.[2] The insulators were inserted as cylinders, located 6.25 cm from the discharge region between two 2.5 cm diameter hemispherical electrodes, which were graphite, copper-graphite composite, two different tungsten-copper composites (K-33 and Elkonite), or stainless steel. The spark gap normally operates at a voltage of less than 30 kV and switches 9 kJ of energy in 25 μs at a maximum rep-rate of 5 pulses per second, a maximum current of 25 kA and a maximum charge transfer of 0.6 Coul per shot. The chamber is continuously flushed so that one chamber volume flows through every 5 seconds with either air or N_2 gas, while the pressure is maintained at 1 atmosphere absolute.

A surface discharge switch, shown schematically in Figure 3, was used to expose Blue Nylon, Lucite, boron nitride, and Delrin insulators to 10,000 shots

from a "gliding" discharge across the insulator surface.[3] The switch operates at 45 kV in the ambient atmosphere (lab air) and transfers 180 joules per shot at a rate of 1.2 pulses per second. It was observed that after a few shots the switch stopped multichanneling. However, when an air jet of "dirty" lab air was blown across the surface of the insulator the sample continued to multichannel until the air jet was turned off. This phenomenon may be due to an accumulation of surface charge which deters multichanneling and the air jet somehow manages to alter this distribution of surface charge so that multichanneling can still occur.[4]
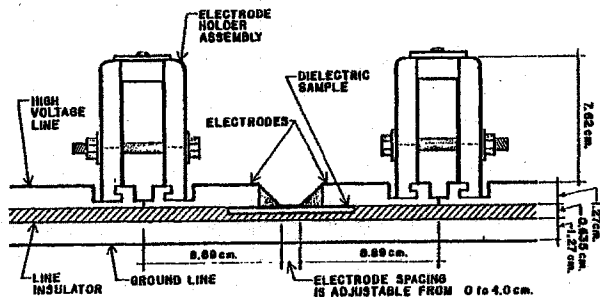

Fig. 3. Surface Discharge Switch.

After exposure to the by-products of these arcs the insulators were visually examined for any gross features such as crazing, metal vapor deposition, cracks, or large particles and then studied with several surface analysis techniques including Electron Spectroscopy for Chemical Analysis (ESCA),[5] Scanning Electron Microscopy (SEM),[6] and X-Ray Fluorescence (XRF).[7]

Results

Insulators Exposed in Mark I

Analysis of an unexposed Lexan insulator with ESCA shows the surface to be composed of 86% carbon and 14% oxygen which is the proper stochiometry for Lexan ($C_{16}O_3H_{18}$). This sample exhibited negative surface charging when exposed to the x-ray beam used in the ESCA spectrometer (as observed by the negative shift in the binding energy of the C_{1s} line). This phenomenon is rare in ESCA[8] but does occur for polymers such as Lexan which have an aromatic benzene ring.

A Lexan insulator exposed to 5000 shots in the spark gap with graphite electrodes in 2 atmospheres of N_2 also exhibited negative surface charging in the ESCA spectrometer. The ESCA spectrum for this particular sample shows that the surface carbon decreased to 49.5% and the surface oxygen increased to 35.1%. The C peak is considerably broadened compared to the virgin sample, probably due to C-N or C-O bonding, since nitrogen and oxygen are seen on the surface. However, the resolution of this peak is not adequate to identify the specific bonds. Resolution is a severe problem when ESCA is applied to polymers. It is possible to determine that the C, O, and N is bonded but not always possible to identify the bond unambiguously. Figure 4 is a Scanning Electron Microscopy (SEM) micrograph of this sample showing microparticles (the largest is 2 microns in diameter) embedded in the surface. Since the analysis area of ESCA is a 4 mm diameter circle, these microparticles cannot be identified using ESCA because they are too few and too small. The use of XRF to determine the composition of these particles gave an indeterminate result as it would if these microparticles are carbon from the graphite electrodes.

Another Lexan insulator was used with 2 atmospheres of SF_6 and graphite electrodes. ESCA scans of this sample show extremely small amounts of carbon and oxygen compared to the virgin sample, but large amounts of aluminum and fluorine. In addition, the surface no longer accumulates a negative surface charge but instead exhibits positive charging. The Al_{2p} peak shows a shift in the binding energy which corresponds exactly to AlF_3, and the Al to F ratio in the spectrum is almost exactly 3:1. Figure 5 is an SEM micrograph of this sample showing a heavy coating of powdery material on the surface. An x-ray dot map showed that this powder contains aluminum. Obviously, the AlF_3 masks the polymer surface which explains the positive surface charging. The aluminum on the surface was the result of arcing between the electrode and the aluminum electrode holder which liberated metallic aluminum. The aluminum then reacted with the fluorine in the gas to form AlF_3 which subsequently deposited inside the spark gap.[3] The arcing between the electrode and the aluminum holder was subsequently corrected.
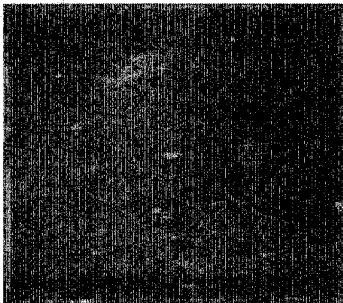

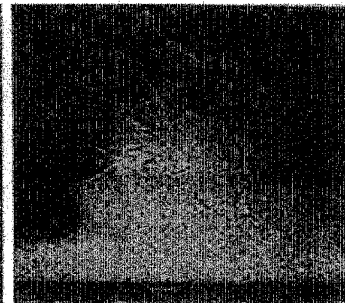Fig. 4. SEM micrograph of Lexan used in Mark I with graphite electrodes and N_2 gas. Bar length is 10 microns.

Fig. 5. SEM micrograph of Lexan used in Mark I with graphite electrodes and SF_6 gas. Bar length is 10 microns.

For a Lexan insulator exposed to 5000 shots with 2 atmospheres of N_2 and K-33 electrodes, the ESCA spectrum shows that the surface of the sample is covered with a very thin layer of copper and tungsten. The C_{1s} peak shape indicates more than one form of carbon bonding. The copper and tungsten peaks indicate that the tungsten exists as an oxide, but the copper is pure metallic copper. Figures 6 and 7 are

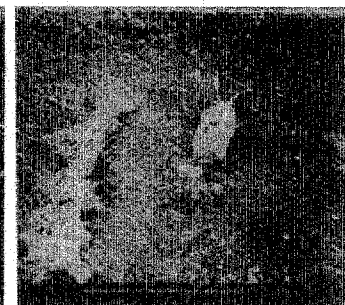Fig. 6. SEM micrograph of Lexan showing copper particles. Bar length is 100 microns.

Fig. 7. Magnified view of a portion of Fig. 6. Bar length is 100 microns.

micrographs of the surface showing a thin, discontinuous layer and some 10 to 100 micron size particles. X-ray dot maps on several particles show mainly copper on a tungsten background. This may mean that the copper and tungsten are deposited on the insulator at similar rates,[9] but the tungsten, which has a rapid rate of reduction compared to copper, is oxidized by the oxygen in the spark gap in the form of water.

(Most polymers will absorb from 3% to 8% by volume of water.) This process yields a deposited layer of copper covered with tungsten oxide and the copper does not oxidize even after the insulator is removed from the spark gap.[1]

ESCA analysis of Lexan insulators after 5000 shots in 2 atmospheres of SF_6 with K-33 electrodes shows an increase in the tungsten (from 4% to 13.3%) present on the surface, compared to the previous situation in N_2. There is also a large decrease (from 85.7% to 22.5%) in the carbon on the surface. However, this may be attributed to masking of the constituent carbon of the Lexan by the coating of copper and tungsten. SEM micrographs of the surface reveal powdery material, which x-ray maps indicate to be some form of copper. These dot maps cannot be used to determine the bonding; however, fluorine is also observed (using ESCA) on the surface. The conclusion is that this powder is a copper fluoride. ESCA data on the copper gives an ambiguous answer, but the F_{1s} peak shape indicates either a copper fluoride or a carbon fluoride.

Similar experiments were performed using a Blue Nylon insulator. ESCA on the virgin sample shows 78.1% carbon, 11.5% oxygen, 5.2% nitrogen and 5.2% silicon. The usual composition of nylon is $C_6H_{11}ON$ which would give 12.5% nitrogen. Blue Nylon is cast, not extruded as are most of these polymers. This casting process leads to a larger percentage of cross-linking in the polymer and consequently a higher tensile strength. Most likely the silicon is a constituent of a mold released used in the manufacturing process. For a Blue Nylon insulator used with graphite electrodes and 2 atmospheres of N_2, the ESCA spectrum shows no nitrogen after 5000 shots. Probably the surface is covered with a thin continuous layer of carbon which masks the nitrogen. Since the electrodes are graphite and Blue Nylon is a carbon based material it is very difficult to verify this hypothesis with ESCA.

The Blue Nylon insulator exposed to 5000 shots with graphite electrodes and 2 atmospheres of SF_6 is also covered with a powdery substance. Figure 8 is an SEM micrograph of this surface. The ESCA spectrum of this sample indicates a large concentration of aluminum (8%) and fluorine (12%). The Al_{2p} peak positions indicate the form is AlF_3, which is consistent with results discussed above. SEM micrographs and aluminum x-ray dot maps support this result. The C_{1s} peak also indicates some form of CF bonding on the surface.
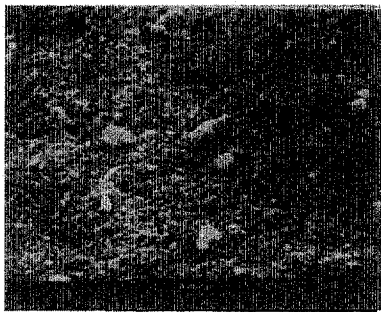

Fig. 8. SEM micrograph of a Blue Nylon insulator, used in Mark I with graphite electrodes in 2 atmospheres of SF_6 for 5000 shots.

ESCA on the Blue Nylon insulator used with K-33 electrodes and 2 atmospheres of N_2 shows reduced surface carbon (from 78% to 47%) and increased oxygen (11.5% to 15%) and silicon (5.2% to 6%). The data indicate no copper or tungsten on the surface. The SEM micrographs also indicate no copper or tungsten. This difference, compared to results with the Lexan insulator, could possiblybe due to the silicon, which

modifies the surface so that metal vapor will not adhere to the surface. Data for Blue Nylon with K-33 electrodes and 2 atmospheres of SF_6 are similar to that with K-33 electrodes and N_2. Thus, the lack of metal films on the surface is not related to the gas used.

Analysis of the electrodes used in these experiments indicates that the surfaces of the electrodes are significantly affected by the presence of an insulator. In particular, when a Blue Nylon insulator is used with either graphite or K-33 electrodes, silicon is found on the electrode surfaces after operation. Using SEM and XRF it was determined that the silicon appeared on the surface in a nodule structure.[1] These nodules could cause local electric field enhancement and lower the self breakdown voltage. This was observed when Blue Nylon insulators were used in the gap. Also, the standard deviation of the self-breakdown voltage (V_{sb}) distributions is larger in these systems and there is a larger number of dropouts, (breakdown events with voltages considerably lower than the mean breakdown voltage).[1] When Lexan insulators are used in this gap with graphite electrodes and N_2 gas, the V_{sb} distributions become narrower, giving a smaller standard deviation from the mean, than without an insulator present. The SEM micrographs of the graphite surface indicate contamination with some sort of insulating material, which could increase the electron emission from the surface. This could cause a V_{sb} distribution with a lower mean value and possibly a smaller standard deviation.

Insulators Exposed in Mark II

In the Mark II gap the Lucite insulators are cylinders concentric with the electrodes, with the insulator wall located 6.25 cm from the discharge. When graphite was used as the electrode material with air flowing through the gap, the Lucite showed no visible (naked eye) signs of electrode material coating but there were signs of crazing on the insulator in the region nearest the discharge. Surface analysis using ESCA showed no apparent change from a virgin sample. The SEM micrographs reveal a low density of microparticles on, and embedded in, the surface. A typical area, 1000 microns by 1000 microns, contained 39 particles, four of which measured about 10 microns in diameter. This is consistent with the ESCA data if the particles are assumed to be graphite. Since ESCA analyzes a large area (2 to 4 mm diameter) the low density of graphite particles would not produce a significant increase in the carbon percentage detected (71% for virgin Lucite). Figure 9 shows a typical SEM micrograph. Note that the large particles appear to be stuck on the surface while most of the smaller ones are embedded in the surface as if the Lucite melted on impact.

In contrast, the combination of a Lucite insulator, flowing N_2 gas, and graphite electrode used for 50,000 shots produced a heavy coating of carbon on the Lucite. Visual inspection shows the coating to be some tenths of a mm thick, with easily discernible cracks. The ESCA data show a significant increase in the surface carbon (90%) compared to a virgin sample (71%), indicating a pure carbon coating on the surface.

Apparently, when flowing air is used with graphite electrodes the oxygen in the air combines with the carbon to create CO_2 and/or CO gas. Consequently, the Lucite insulator then receives no carbon coating.

The ESCA data for Lucite used with N_2 and copper-graphite shows a surface layer of copper which is oxidized. There is also a large concentration of adsorbed nitrogen. The oxygen probably comes from the disassociation of H_2O in the chamber.

Figure 10 is an SEM micrograph of Lucite used with air and copper-graphite. This micrograph shows a granulated deposit on the surface. ESCA on this surface showed carbon present, but no copper. Either there is no copper on the surface (which is doubtful) or it is masked by a hydrocarbon layer.
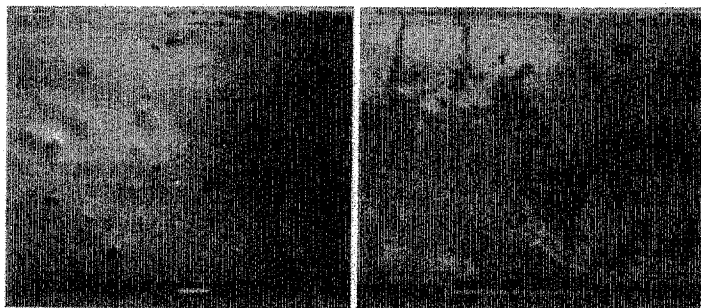

Fig. 9. SEM micrograph of Lucite used in Mark II with graphite electrodes and air for 50,000 shots. Bar length is 100 microns.

Fig. 10. SEM micrograph of Lucite used in Mark II with copper-graphite electrodes and air. Bar length is 1000 microns.

Lucite insulators were used with K-33 and Elkonite electrodes. Both are tungsten-copper composites in approximately the same relative ratios, (66% tungsten, 33% copper). For both of these the gas was N_2 and both were exposed for 50,000 shots. Both insulators are coated with tungsten and copper. In both instances the copper is oxidized and the tungsten is in the form of tungsten-nitride. The Lucite insulator used with K-33 has 6% copper and 4% tungsten on the surface, but on the Lucite insulator used with Elkonite there is 3% copper and 3% tungsten. The concentration of nitrogen on the insulators is also different for the two combinations, 33% and 10% for K-33 and Elkonite, respectively. Perhaps these differences arise because the K-33 is formed by sintering tungsten and infiltrating molten copper, whereas in Elkonite the tungsten and copper are mixed together in molten form.

The ESCA data on a Lucite insulator used with stainless steel and N_2 indicated that the surface is coated with a thin layer of Cr, Fe and Ni in relative concentrations of 1.6%, 2.0%, and 1.4%. However, visual inspection of the insulator showed no signs of coating or damage.

Surface Discharge Switch

Visual inspection, with the naked eye, of a boron nitride substrate used in this switch showed signs of a considerable amount of erosion along its surface. The surface had large black tracks bridging the gap between the electrodes. There were deposits of copper colored material along the insulator, where the edges of the electrodes were located. Surface analysis (ESCA) indicated that the boron nitride structure was not altered but did show a large concentration of carbon and oxygen on the surface, neither of which is a constituent of boron nitride.

When Delrin, Blue Nylon, and Lucite insulators were inserted as substrates in the surface discharge switch, each of them showed a large amount of erosion in the regions where discharges occurred. Surface analysis of these insulators using ESCA indicates that these insulators are all coated with a hydrocarbon layer. Whether this hydrocarbon layer is the result of the interaction of the arc with the surface or the interaction of the arc with the surrounding atmosphere, or both, is not known. The only noticeable difference is that, on Blue Nylon, there is also a deposit of metallic copper and copper oxide whereas on

Lucite and Delrin there is no detectable concentrations of copper. The selfbreak field for these insulators remained about the same, 9.7 kV/cm, 10.2 kV/cm, 10.3 kV/cm, 9.3 kV/cm for Blue Nylon, Lucite, Delrin, and boron nitride, respectively, for 10,000 shots.

Summary

From the studies on insulators used in the Mark I and Mark II spark gaps it is obvious that the dominant damage mechanism is surface coatings of evaporated electrode material. This would eventually lead to failure through insulator flashover. The micropart- icles found embedded in the surface of all the insulators probably cause insulator material to be injected into the gap. Such material may be the cause of the observed differences in the self-breakdown voltage distributions for gaps with Blue Nylon and Lexan insulators.

No evaporated carbon coating was found on a Lucite insulator when air was used as the filler gas. Carbon microparticles were found embedded in the surface and the surface exhibited crazing which is one sign of radiation damage, perhaps due to U-V from the discharge.

In the surface discharge switch it appears that plasma chemistry in the air leads to a hydrocarbon coating on the insulator surface which, after a few hundred shots, makes all the surfaces look the same. No significant differences in breakdown voltage or number of channels were observed for Lucite, Delrin, Blue Nylon, or boron nitride. However, the polymers exhibit significantly more erosion than the boron nitride.

References

[1] L. B. Gordon, M. Kristiansen, M. O. Hagler, H. C. Kirbie, R. M. Ness, L. L. Hatfield, and J. N. Marx, IEEE Transactions on Plasma Science PS-10, 286 (1982).

[2] A. L. Donaldson, R. Ness, M. O. Hagler, and M. Kristiansen, Proc. of the Fifteenth Power Modulator Sym.,Baltimore, MD (1982).

[3] D. Johnson, M. Kristiansen, and L. L. Hatfield, Proc. of the Conf. on Electrical Insulation and Dielectric Phenomena, Amherst, MA (1982).

[4] Private communication with Charlie Martin during his visit to Texas Tech University in May, 1981.

[5] D. T. Clark and W. J. Feast, J. of Macromolecular Sci.-Revs. of Marcromolecular Chemistry C12, 191 (1975).

[6] O. C. Wells, Scanning Electron Microscopy, (McGraw Hill Book Company, New York 1974).

[7] L. S. Birks, Electron Probe Microanalysis (Wiley-Interscience, New York 1971).

[8] C. D. Wagner, in Applied Surface Analysis STP 699, edited by T. L. Batt and L. E. Davis (ASTM, Philadelphia, PA 1980).

[9] Personal Communication with Ken Rahocki, Dennis Dimiduk, and Larry Matson at Wright-Patterson Air Force Base, Dayton, Ohio in Nov. 1981.