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AGING OF FIELD-INSTALLED RTV SILICONE INSULATOR COATINGS

Christopher L. Mirley, JoAnne Ronzello, Hiro Homma*, and Steven A. Boggs
Electrical Insulation Research Center
University of Connecticut
97 North Eagleville Road
Storrs, CT 06269-3136

***Abstract*:** The silicone-based coating applied to 345 kV post insulators in a substation on the shore of Long Island Sound has depolymerized over a period of about 7 years. Studies of samples of the virgin coating, coating removed from station insulators, and coating removed from insulators which were weathered but not energized suggests that the degradation is dominated by environmental factors rather than electrical factors and is probably the result of acid rain-catalyzed depolymerization.

INTRODUCTION

In the context of outdoor, air-insulated systems, porcelain is an excellent dielectric, with adequate bulk dielectric strength and excellent surface resistance to weathering, electrical tracking, and corona attack. The primary limitations of porcelain are related to operation under heavily contaminated conditions, where the combination of the hydrophilic nature of the surface combined with conducting pollution can cause highly nonuniform grading of the insulator, dryband arcing, and surface flashover. The performance of porcelain insulators can also suffer under freezing conditions, especially when an insulator becomes coated with ice and then warms through the freezing point. Thus while porcelain has served the electrical industry well for many decades, the industry is motivated to seek insulating systems with improved performance under specific conditions, such as heavy pollution.

The application of room temperature vulcanizing (RTV) silicone rubber coatings filled with aluminum trihydrate (ATH) to porcelain insulators improves insulator performance under heavily polluted conditions. Coating performance is primarily a result of the migration of low molecular weight silicones to the coating surface, where it coats any pollution and renders even a heavily polluted surface hydrophobic. The low molecular weight silicones restore hydrophobicity to the coating after damage from heavy rain, dryband arcing, etc. Unlike porcelain, silicone-based coatings do "wear". Aging is induced by weathering, arcing, corona, erosion, etc., and silicone polymer is lost over time. Eventually the coating will come to the end of its life. Given the relatively recent use of such coatings, "life" under service conditions is not yet established, and designs are changing as a result of past service experience.

In a previous contribution [1], the authors described depolymerization of an RTV silicone coating applied to porcelain insulators of the Millstone Nuclear Generating Station operated by the Northeast Nuclear Energy Co., part of the Northeast Utilities Corporation. After roughly eight years of service, the coating had become putty-like, lost all elasticity, and cracked. This contribution presents a detailed analysis of the aged coating.

Three types of coating samples are available for analysis, viz. (i) samples from insulators which have been energized for roughly 7 years at 345 kV system voltage in the switchyard of Millstone, (ii) samples from unenergized insulators which were weathered in the same environment as those in the substation, and (iii) samples from insulators which were coated at the same time as those in the substation but stored in a protected environment. These are referred to as "energized", "weathered", and "virgin", respectively.

EXPERIMENTAL PROCEDURES

***Coating thickness*:** The thickness of RTV silicone coatings applied to the top surfaces of several Millstone insulator sheds was measured by two methods. The first method was to break a portion of the porcelain

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*Visiting scholar from Central Research Institute of the Electric Power Industry (CRIEPI), 2-1-6 Nagasaka, Yokosuka-shi Kanagawa-Ken, 240-01, insulator shed, leaving the RTV silicone coating intact. An optical microscope equipped with a calibrated optical micrometer was used to measure the RTV coating thickness. The second method was to scrape off a portion of the RTV silicone coating with a razor blade and measure the thickness of the coating using a hand-held micrometer accurate to ±0.001 mils. The two methods were in good agreement.

***Scanning electron microscopy*:** Samples from the top surfaces of the sheds were removed with a razor blade and prepared for examination with a scanning electron microscope (SEM). The samples were made conductive by applying a thin (5 nm) gold-palladium coating to the sample surface. A carbon coating was applied to the surface for chemical analysis of the sample by electron dispersive x-ray spectroscopy (EDAX), which facilitates identification of elements on the sample surface.

Water contact angle measurement: Advancing water contact angles were measured using a modified pendant drop apparatus equipped with a sessile contact angle cell. RTV silicone coating samples were taken both from the top and under sides of sheds located along the upper, middle, and bottom portion of the Millstone insulators. The RTV silicone samples were placed in the contact cell which was maintained at 30 °C under saturated water vapor conditions. A 10 μl drop of distilled, deionized water was used as the probe solvent. The datum reported for each contact angle is the average of three measurements on each drop.

Direct dynamic headspace gas chromatography-mass spectroscopy (GC/MS): RTV silicone samples removed from the upper shed surface were cut, weighed (0.5-1 mg), loaded into a glass sample tube, and heated to 200 °C for 2 min. The volatile components from the sample were collected directly onto a nonpolar (100% methyl silicone) GC column held at 35 °C. The column was then heated from 35 to 300 °C at 15 °C/min. The GC column temperature program aids in separating the volatile chemical species collected from the RTV silicone samples. The output from the GC column was subsequently passed to a mass selective detector for chemical identification. This technique provides identification and a quantitative measure of the volatile components contained in coating which can be driven off at 200 °C. In the case of RTV silicone coatings, these are low molecular weight siloxanes which contain from 3 to about 16 functional groups. All GC/MS data provided in this paper have been normalized for sample weight, so that relative peak heights of various components can be compared.

Thermogravimetric analysis (TGA): RTV silicone samples (2-10 mg) collected from a single insulator were heated from 150 to 650 °C in oxygen. The weight loss versus temperature was recorded using a Perkin-Elmer TGA apparatus. The various components of the aged and unaged RTV silicone samples were identified and quantified from the temperature at which they volatilize or oxidize.

RESULTS AND DISCUSSION

Visual inspection of the aged RTV silicone coatings: An inspection of the "energized" RTV silicone coating on three typical porcelain insulator section from the top half of two-section insulator stacks, as well as an onsite inspection of the coatings at the Millstone switchyard, indicated several interesting features. In all cases, the surfaces of the aged RTV silicone coatings had turned from pure white to a light gray color. In many instances, this gray layer had flaked off revealing a white layer underneath. This loss of the RTV coating from flaking was more severe on the side of insulators most exposed to the effects of wind and rain (the side of the insulators facing Long Island Sound). Small cracks had developed over most of the RTV silicone coating surface. Scraping the coating demonstrated that the cracks did not extend all the way through the coating. These aged, energized RTV silicone coatings had lost mechanical strength and elasticity compared to samples of the virgin material.

The worst aging of the RTV silicone coatings was on the top surface of the topmost insulator shed. Here the coating was almost completely black in color and had many cracks in the coating surface. Scrapings of these coatings revealed that the cracks extended from the surface of the coating all the way to the surface of the porcelain insulator. The mechanical strength of these blackened films was very poor as compared to virgin RTV silicone material.

***Coating thicknesses*:** Table 1 shows the thickness measurements made on the aged RTV silicone coatings from the three insulator sections removed from the station yard. Samples of the RTV coating were taken from the top surface of sheds located at the top, middle, and bottom of the insulator section. The measurements showed that the thickness of the aged RTV coating was fairly uniform from top to bottom for each insulator, except for one insulator for which the coating thickness varied from 19 to 29 mils.

Table I: Aged RTV Silicone Coating Thickness

Switchyard Insulator	Average Coating Thickness (mils)*		
	Top Shed	Middle Shed	Bottom Shed
#1	19±4	24±2	29±3
#2	21±1	23±1	24±1
#3	15±1	15±2	16±4

*Coating samples taken from top surface of each shed.

Scanning electron microscopy: SEM analysis of the RTV silicone coating taken from the upper surface of the topmost shed and a lower shed of a Millstone insulator section indicated that the coating removed from of the topmost insulator shed (which was quite dark and extensively cracked) had a rougher surface as compared to that of the coating taken from one of the lower sheds on the same insulator. Increases in the surface roughness of RTV coatings have been associated with permanent changes caused by aging [2]. As the surface roughness increases, the surface wetting area and the leakage current also increase, which can reduce coating performance.

Energy dispersive x-ray (EDAX) analysis of the coating from the upper surface of the topmost and lower sheds of a Millstone insulator section was also carried out to help identify atomic species present in the coating samples. As discussed in our earlier contribution [1], the RTV silicone coatings consist primarily of the polydimethylsiloxane (PDMS) polymer and the alumina trihydrate (ATH) filler. The EDAX data for all coating samples showed that the major atomic species present were silicon, oxygen, aluminum, representing the polymer and ATH filler components, respectively. In addition, the coatings included traces of titanium and iron which may be associated with UV-light stabilization and condensation catalysts. Potassium, calcium, and sodium were found on the surface, which are components of sea water, while the sulfur is probably from air pollution.

The ratio of ATH filler to polymer ratio was estimated by taking the ratio of x-ray peak heights for the aluminum and silicon atoms. The results indicated that for the virgin RTV silicone, Al/Si=1.1. For the topmost shed of an energized coating, Al/Si=0.3, while for a lower shed on the same insulator, Al/Si= 1.3. Clearly ATH filler has been lost from the RTV silicone coating on the topmost shed as compared with the energized coating on sheds below and the virgin material.

The SEM results confirmed the visual observations, viz., that the RTV silicone coating on the Millstone insulators has aged considerably and that the effect is worse for the coating on the topmost shed of the insulator. This was observed from the color change of the RTV silicone over time, the increase in surface roughness of the RTV coating, and the apparent loss of ATH filler. The reduced concentration of ATH filler suggests that the ability of the coating to resist dry band arcing may be compromised, and this, in turn, can compromise the ability of the coating to prevent flashover.

Contact angle measurements: Water contact angle analysis has been used to monitor changes in the hydrophibicity of RTV silicone coatings either over time or as a function of the number of simulated aging cycles [3,4]. These investigations indicate that the water repellency of RTV silicone coatings is caused by low molecular weight (LMW) PDMS polymers which migrate to the surface of the coating. Since larger water contact angles indicate a more hydrophobic surface, water contact angle measurements are used as a probe of the integrity of the LMW siloxane coating on the RTV surface.

The average water contact angle for aged RTV silicone samples taken from the top (114°±2) and underside (109°±1) of a Millstone insulator did not appear to differ appreciably. Samples from the top surface of the shed are exposed more directly to the weather than those from the underside of sheds, which are somewhat shielded, especially from rain. The large water contact angles indicate that the coatings are hydrophobic. However the water contact angle for the virgin material was greater than that of the energized RTV silicone samples, i.e., $\theta_{virgin} = 126°$, $\theta_{aged} = 110$ to $114°$. While energized, weathered, and virgin of RTV silicone coatings had hydrophobic surfaces, the greater water contact angle of the virgin material suggests a difference between the LMW siloxane layer on the surface of weathered or energized coatings relative to virgin coatings. Changes in coating hydrophobicity over time while in contact with water have important implications for coating efficacy.

Figure 1 compares the changes in water contact angle over time for RTV silicone coating taken from the upper surface of the topmost shed of an energized insulator, from the upper surface of a lower shed on the same insulator, and for virgin coating. The RTV silicone coating from the topmost shed has an initial water contact angle which is greater (132°) than that of the virgin material. The initial contact angle of the aged RTV silicone coating from a lower shed was much smaller than that for the top shed or the virgin coating. Over thirty minutes continuous contact with the water drop, the water contact angle decreased for all three samples. While the water contact angles for the virgin and top shed were still high (120°) at the end of 30 minutes exposure, the contact angle for the aged RTV silicone coating taken from a lower insulator shed dropped to 87°, indicating spreading of the water drop. The largest decrease in the water contact angle for this sample occurred within the first five minutes of exposure to water.

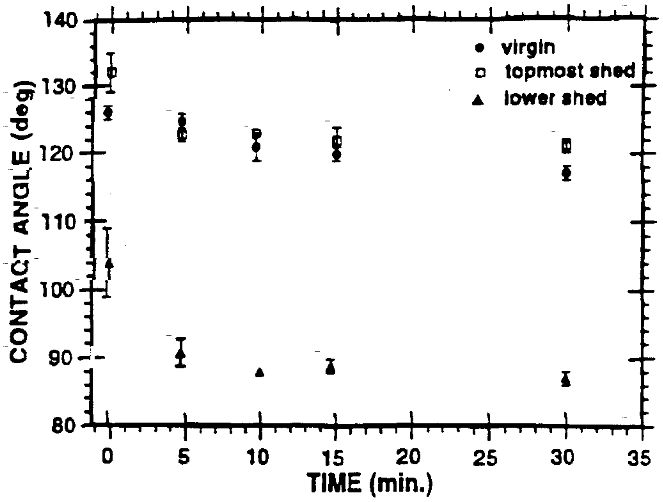

Figure 1: Water contact angle stability of virgin and energized Millstone RTV silicone coatings. T=30 °C.

These results indicate that the hydrophobic LMW siloxane coating on the majority of the Millstone insulator sheds is not stable under exposure to water. After only five minutes contact with water, the hydrophobicity decreased, which allowed the water to spread on the surface of the coating. This behavior was in contrast to that for the virgin coating for which the hydrophobicity remained essentially constant during a 30 minute exposure to water. The ability of the aged RTV silicone coatings to provide a good hydrophobic barrier appears to be compromised. The reason for this must be changes in the LMW siloxane layer present on the surface of the RTV coating, as will be discussed more fully below.

These water contact angle studies also demonstrate that care must be taken in interpreting such measurements. As was shown in Figure 1, the RTV silicone coating on the topmost shed of Millstone insulators had even higher contact angles than virgin RTV silicone material. This was in spite of the fact that the coating showed more visual signs of degradation and erosion. The higher contact angle of the coating on the topmost sheds is the result of hydrocarbon contamination deposited by atmospheric pollution rather than LMW siloxane, as will be shown more clearly in the next section.

Direct dynamic headspace GC-MS analysis: This technique is extremely well suited for gaining information about the low molecular weight components (such as additives) present in any solid polymer material. Headspace GC-MS was used to investigate chemical, concentration, and molecular weight changes in the LMW siloxane component of the RTV silicone coatings. In this technique, the sample to be analyzed is held at several hundred degrees centigrade while volatile components elute from the sample. Such volatiles are then collected, separated according to mass by a gas chromatography column, and analyzed using a mass spectrometer.

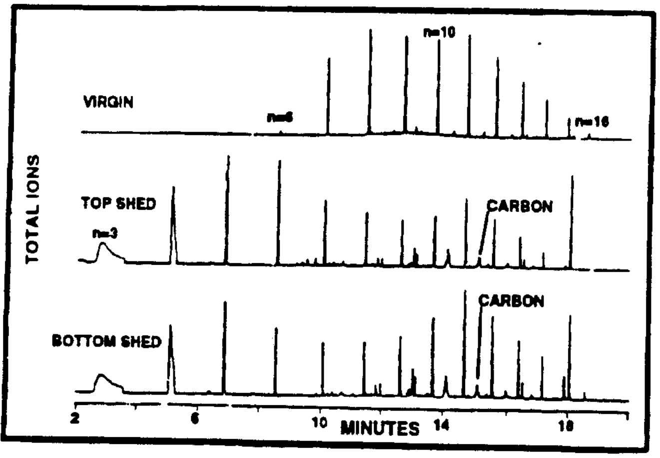

Figure 2: GC-MS headspace chromatograms of virgin and aged RTV silicone from an energized Millstone insulator, upper surface of the topmost shed and a lower shed.

Figure 2 shows a plot which compares the GC-MS traces for a virgin RTV silicone sample and aged samples removed from the upper surface of the topmost shed and a lower shed of an ener-

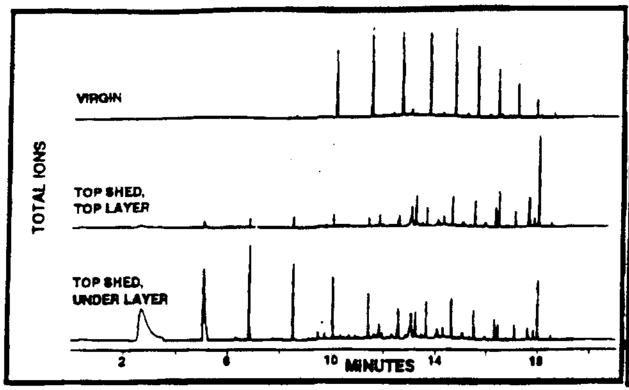

Figure 3: Headspace GC-MS chromatograms of virgin RTV silicone, top layer and underlying layer of energized RTV silicone coating taken from topmost shed of a Millstone substation

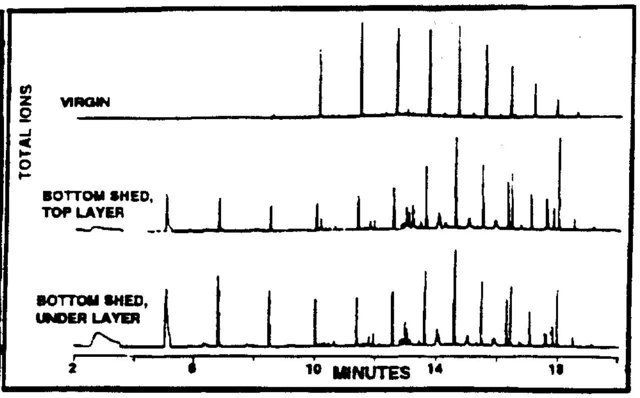

Figure 4: Headspace GC-MS chromatograms of virgin RTV silicone, top layer and underlying layer of energized RTV silicone coating taken from a lower shed of a Millstone substation insula-

gized insulator. The height or area (for n=3,4) of each peak is proportional to the relative concentration of a chemical species, as the data have been normalized to the sample mass. The mass spectrometer facilitates chemical identification of each peak present in the chromatogram. For the virgin RTV silicone sample, the leftmost peak corresponds to siloxane molecules which contain six monomer repeat units ($-(Si(CH_3)_2 - O)_n-$, where n=6), while successive peaks represent an homologous series of polydimethylsiloxane (PDMS) molecules. According to the cure chemistry of RTV coatings, the terminal groups of the PDMS molecule are most likely of -OH functionality.

Following the chromatogram from left to right, each peak represents an increase in the number of monomer repeat units by one. Therefore the siloxanes detected from the virgin RTV silicone sample have monomer units from n=6 to n=16, which represents a mass range of approximately 450-1200 g/mole (for PDMS, each repeat unit is 74 g/mole). The highest concentration of siloxane species was found to be at n=8 and n=11 repeat units, giving a bimodal distribution for the low molecular weight siloxane species. The molecular weight range of the LMW siloxane polymers determined by headspace GC-MS was in very good agreement with previously published gel permeation chromatography data of RTV coatings [2].

Since the presence of these LMW siloxane polymers on the surface is responsible for the hydrophobicity of RTV coatings, changes in molecular weight distribution and/or concentration of the LMW siloxanes are likely to affect the hydrophobic properties of the aged RTV silicone. The chromatograms for aged RTV silicone samples taken from the upper surface of the topmost shed and a lower shed from a Millstone insulator show that both the absolute mass and distribution of the LMW siloxane fraction has changed considerably from the virgin sample. The mass range of LMW siloxane polymers in the aged RTV silicone samples ranges from 222 to 1100, which corresponds to molecules with n=3-15 siloxane monomer repeat units. The highest concentration of siloxane species for both samples was at n=3 or 4 monomer repeat units as compared to the virgin RTV silicone at n=8 and 11. However the RTV silicone sample taken from a lower surface of a shed still had a sizable portion of n=11 siloxane molecules.

The shift of LMW siloxane polymers to lower masses for the aged RTV silicone samples suggests that the bulk siloxane is depolymerizing. The exact causes of depolymerization are not yet clear, but exposure of the RTV silicone coating to the weather conditions along the Connecticut shore are sufficient to initiate breakdown of the siloxane matrix [2]. Siloxanes depolymerize readily under acidic ($pH<7$) or basic ($pH>7$) conditions [5]. Under basic conditions, temperatures on the order of 250 °C are required to initiate depolymerization. Under acidic conditions, depolymerization can occur at room temperature. Given the average pH of 3.8 to 4.6 for rain water collected along the Connecticut shore of Long Sound during 1993 [6], acid-catalyzed depolymerization of the RTV silicone coating could be a major factor in their degradation over time.

If depolymerization results from acid raid, then the phenomenon progresses from the surface inward. The rate of this process is likely to depend strongly on the ability of the coating to absorb water, and this will depend strongly on the interface between the polymer matrix and filler. If the filler is not bonded to the matrix, the filler-matrix interface will be porous and capable of retaining substantial moisture. Given the large filler surface area, such interfacial phenomena could increase greatly the rate of acid-catalyzed depolymerization [5,7].

Depolymerization of the aged RTV silicone coatings and subsequent generation of very low molecular weight siloxane species is responsible for both the loss of mechanical strength and modification of hydrophobic properties. Since the depolymerization occurs from the surface of the RTV silicone coating into the bulk, the loss in mechanical properties is responsible for the flaking of the top layer of the RTV coating and eventual cracking of the coating, which leads to exposure of the underlying porcelain insulator. Both of these effects were observed with aged RTV silicone coatings on insulators at the Millstone Power Plant.

Over time, a loss of the LMW siloxanes from the RTV silicone coating is to be expected as a natural part of the RTV aging process [2]. From our headspace GC-MS analysis, the majority of LMW siloxanes generated through depolymerization of the RTV silicone coating are polymers with n=3 and 4 siloxane repeat units. Since the vapor pressure of a siloxane chain with n=4 repeat units is 130 Pa (1 mmHg or 0.02 psi) @ 23 °C (the vapor pressure of water at the same temperature is 2810 Pa), these LMW siloxane species are lost from the surface of the RTV coating by evaporation and therefore provide little long lasting hydrophobic protection. Note that the majority LMW siloxanes in the aged RTV silicone are of n=3 repeat units, which has an even higher vapor pressure. Also, very low molecular weight siloxanes are soluble in water, so that whatever LMW siloxanes do not evaporate are easily washed away. Thus the depolymerization of the coating does not appear to generate useful LMW siloxane species.

This effect is clearly demonstrated in Figures 3 and 4, which show the GC-MS chromatograms for material taken from the exposed surface and the underlying surface (adjacent to the porcelain) of RTV silicone samples taken from the topmost shed and a lower shed of an energized Millstone insulator. While the surface layer of the RTV silicone coating from the lower shed showed a diminished concentration of siloxane species with n=3 to 7 monomer units compared to the layer underneath, the top layer of RTV silicone from the topmost shed showed very little siloxane polymers from n=3 to 16.

The hydrophobicity of the RTV silicone coating taken from the topmost shed was due to the presence of carbon contamination deposited on the RTV coating from atmospheric pollution. GC-MS analysis showed that peaks detected in between those for the siloxane molecules were mainly caused by C_{20} to C_{30} hydrocarbon chains. These contaminants were present on all of the aged RTV silicone samples tested but most concentrated on samples taken from the topmost sheds of the Millstone insulators.

Thermogravimetric Analysis: Typically, two weight loss plateaus were observed for each sample, at the temperatures indicated in the Figure captions. Close examination of the TGA curves indicates that more than one component is lost from the RTV silicone coatings for each drop in weight. By taking the derivative of the slopes of the TGA curve, a profile is developed that shows individual loss peaks versus temperature. This eases identification of multiple components lost in the same temperature range. The area under each peak is proportional to the percent weight loss for that component. Figures 5-7 show the TGA curves along with their derivatives for the virgin RTV silicone sample and the two aged samples. The derivative curves indicate that at each weight loss peak, at least two components from the RTV silicone samples are being volatilized at the same time, thereby giving a total of four loss peaks.

TGA of the alumina trihydrate (ATH) filler indicates that the water was lost at an onset temperature of 275 °C. GC-MS data show that the LMW siloxane components are driven off at 200 °C. Therefore the first weight loss peak in the RTV silicone TGA derivative curves is probably LMW siloxane (450-1200 g/mole) followed by loss of water from the ATH. Identification of the remaining two loss peaks was carried out by performing TGA on a sample made by combining linear PDMS at molecular weights of 3000 (5.4% by weight) and 10,400 g/mole (48.6% by weight) with ATH filler to give a mixture of 54% polymer and 46% filler. Figure 8 shows the TGA curve and its derivative for this sample. The first weight loss peak is caused primarily by removal of water from the ATH filler, with a smaller peak at 225 °C which is probably caused by loss of some low molecular weight linear PDMS present in the 3000 and 10,400 MW samples. The next two peaks are caused by loss of the 3000 MW PDMS followed by pyrolization of the 10,400 MW PDMS. While the weight loss peaks for the combined PDMS and ATH mixture did not occur exactly at the same temperatures as those for the RTV silicone samples, the derivative curves were qualitatively of the same

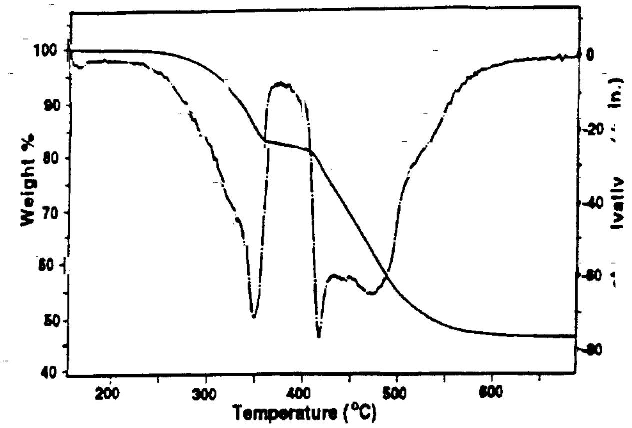

Figure 5: TGA curve (solid line) and its derivative (dot-dashed line) for virgin RTV silicone in oxygen atmosphere. 150-650 °C, at 20 °C/min. An onset temperature of 292 °C is associated with a 15% weight loss, while an onset temperature of 409 °C is associated with a 31% weight loss. The residue is 54% of the initial weight.

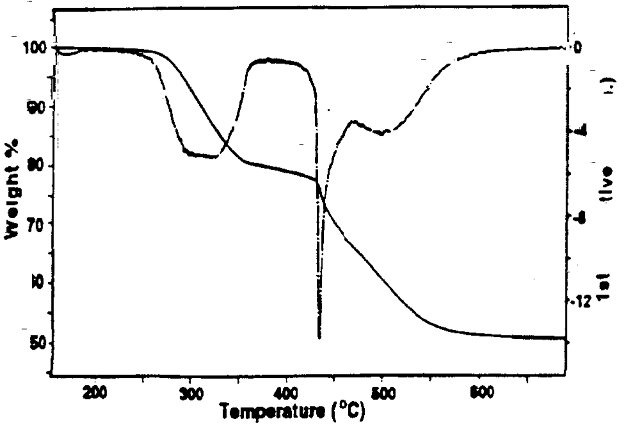

Figure 6: TGA curve (solid line) and its derivative (dot-dashed line) for energized RTV silicone from the top surface of the topmost shed of a Millstone insulator in oxygen atmosphere. 150-650 °C at 20 °C/min. An onset temperature of 270 °C is associated with a 18% weight loss, while an onset temperature of 390 °C is associated with a 24% weight loss. The residue is 58% of the initial weight.

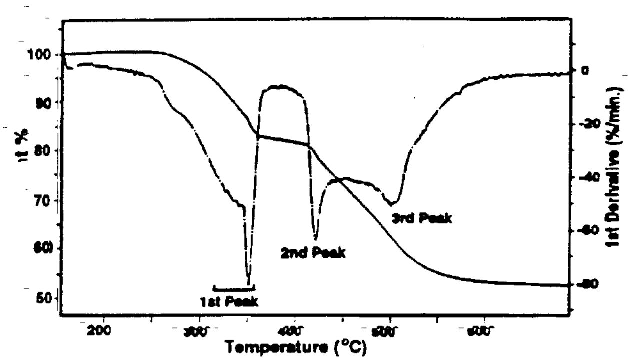

Figure 7: TGA curve (solid line) and its derivative (dot-dashed curve) for energized RTV silicone from lower shed of Millstone insulator in oxygen atmosphere 150-650 °C at 20 °C/min. An onset temperature of 292 °C is associated with a 16% weight loss, while an onset temperature of 390 °C is associated with a 25% weight loss. The residue is 59% of the initial weight.

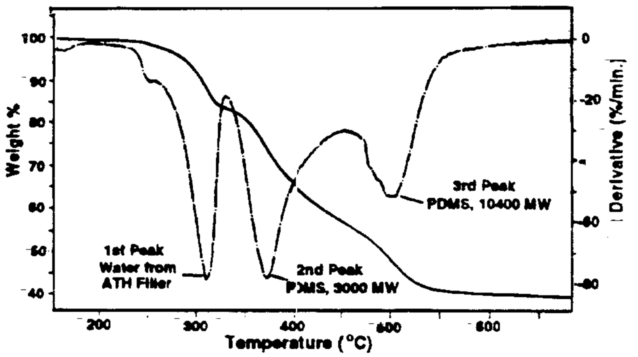

Figure 8: TGA curve (solid line) and its derivative (dot-dashed line) for mixture of linear PDMS (MW=3000 and 10,400, 54% by weight) and ATH filler (46% by weight) in oxygen atmosphere. 150-650 °C at 20 °C/min. siloxane and hence a loss of bulk siloxane due to depolymerization.

shape and relative position. Therefore identification of the weight loss peaks and comparison of aging effects for the RTV silicone coatings was based on the data for this synthetic PDMS -ATH mixture.

Comparison of the derivative TGA curves for the virgin RTV silicone and the energized RTV silicone removed from the topmost shed of a Millstone insulator indicates that the weight loss for the water peak and the peak corresponding to pyrolization of the siloxane matrix for material from the topmost shed both decreased drastically relative to the virgin material. The decrease in the water peak was consistent with the SEM results that showed a loss of ATH filler content for the sample, while the decrease in the siloxane matrix peak was consistent with the GC-MS results showing depolymerization of the RTV silicone coating. Alternatively, the lower water peak is also consistent with a loss in hydration level for ATH as a result of dry band arcing. The TGA curve of the RTV silicone sample removed from a lower shed surface of the Millstone insulator also showed a smaller peak for the siloxane matrix.

Electrical Aging vs. Environmental Aging: Figure 9 compares GC/MS analysis for RTV silicone coating aged in the station yard at 345 kV and the same coating as applied to an insulator which was weathered at the same site but not energized. The degree of depolymerization is very similar, which suggests that the primary degradation mechanism is dominated by environmental factors rather than electrical aging. This is consistent with the observation that the coating has aged quite uniformly along the insulator (with the exception of the top shed) and that top surfaces of sheds have depolymerized to a greater degree than the bottom surfaces, which are much more protected from exposure to rain.

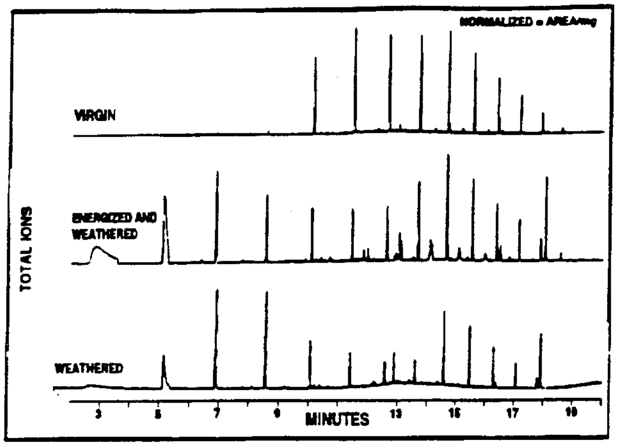

Figure 9: GC/MS analysis for RTV silicone coating aged on a station insulator at 345 kV and coating applied at the same time to an insulator which was weathered (unenergized) at the same site.

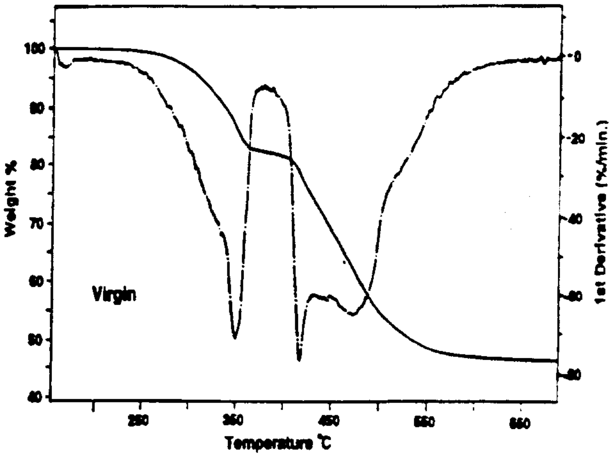

Figure 10: Thermogravimetric data for virgin RTV sample to provide a reference for comparison with Figures 11 and 12.

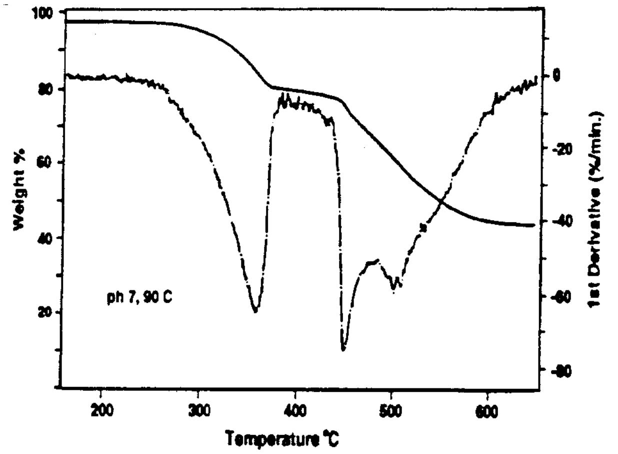

Figure 11: Thermogravimetric data for RTV silicone coating aged for one month at 90 °C in water buffered to pH = 7. Degradation relative to the virgin sample of Figure 10 is minimal.

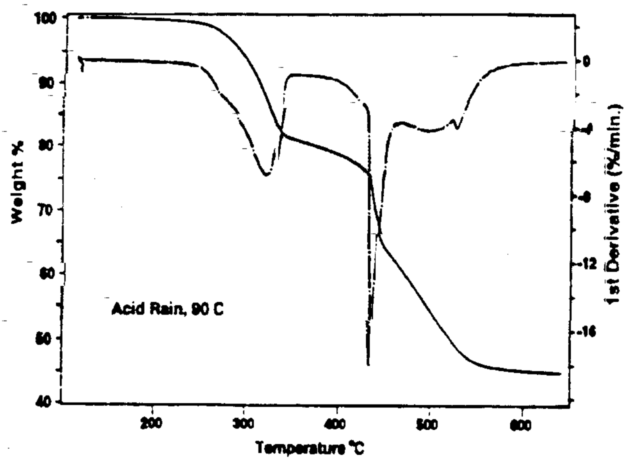

Figure 12: Thermogravimetric data for RTV silicone coating aged for one month at 90 °C in artificial acid rain water (adjusted to pH = 3.9 with HCl). Severe degradation has occurred which is similar to that of the top shed of field-aged coatings (Figure 6).

ARTIFICIAL AGING

Figures 10 - 12 show TGA analysis of virgin RTV silicone coating and the same coating aged artificially at 90 °C in water buffered to pH = 7 and artificial acid rain (water adjusted to pH = 3.9 with 0.1 Molar HCl). As can be seen from these figures, the pH = 7 water (Figure 11) had little effect on the coating, while the "acid rain" (Figure 12) had a very large effect. The severe degradation caused by the artificial acid rain environment appears to be very similar to the degradation of the topmost shed of field aged insulators, as can be seen by comparing Figure 12 to Figure 6. These data provide a reasonable basis for suggesting that much of the degradation is environmental in nature and is probably related to the acid rain exposure along the Connecticut coast of Long Island sound.

CONCLUSIONS

1. Visual onsite inspection of RTV silicone coatings applied to the porcelain outdoor insulators at the Millstone Power Plant showed that the coatings had turned from white to light grayish color after being subjected to 345 kV system voltage and exposure to weather conditions for a period of 7 years. On many insulators, the gray layer had flaked off completely, exposing a white layer underneath it. Cracks had developed in the RTV silicone coatings of all energized insulators. Three complete 345 kV insulator sections from the Millstone switchyard were sent to the University of Connecticut for analysis, and further samples were taken from insulators in the field. For all three insulators, the RTV silicone coating on the top shed was almost completely black in color and had many deep cracks which extended to the surface of the porcelain insulator. Most of the original mechanical strength and elasticity of the RTV silicone coatings had been lost.

2. Thickness measurements of the aged RTV silicone coatings from Millstone showed some variability, which is typical for spray application. The average RTV silicone coating thickness was 21±2 mils, consistent with the manufacturer's recommendations.

3. Analysis of RTV silicone by headspace gas chromatography-mass spectroscopy was used to determine changes in the low molecular weight (LMW) polydimethyl-siloxane (PDMS) fraction of the RTV coatings. These mobile siloxane species provide the hydrophobic surface, which is the basis of RTV coating efficacy. The results showed that virgin RTV silicone contained a LMW siloxane fraction from 450-1200 g/mole (corresponding to $n=6$ to 16 monomer repeat units) with a significant portion in the 600 to 800 g/mole range ($n=8$ to 11 monomer repeat units). The aged RTV silicone coatings removed from energized and weather-aged (but unenergized) Millstone insulators contained a LMW siloxane fraction from 200-1200 g/mole (corresponding to $n=3$ to 16 monomer repeat units) siloxane fraction with significant portion in the 200-400 g/mole range ($n=3$ to 5 monomer repeat units). The downward shift in the mass range and distribution of LMW siloxane species for the aged RTV silicone coatings is attributed to depolymerization of the PDMS matrix. Although the exact cause of depolymerization is not certain, we believe that the process is acid-catalyzed by acid rain along the Connecticut shoreline near the Millstone Power plant. Rain samples collected along the Connecticut shore line during 1993 ranged in pH from 3.8 to 4.6 [6]. The lower mass siloxane species ($n=3$ and 4) generated through depolymerization of the RTV silicone coating do not provide long-term hydrophobic barrier as a result of the relatively high vapor pressure and water solubility of these species. Shrinkage of the coating caused by depolymerization has resulted in loss of mechanical integrity, cracking of the coating, and, in some locations, exposure of the underlying porcelain insulator. The susceptibility of the coating to attack by acid rain is likely to depend on the ability of moisture to penetrate and reside in the polymer composite, which is likely to be a strong function of the bond between the filler and polymer matrix [7]. Depolymerization is also enhanced by the presence of moisture in the absence of oxygen [5].

4. SEM-EDAX analysis of the aged RTV silicone coatings confirmed the conclusions from the visual inspection that the coatings on the topmost shed surface of the Millstone insulators were degraded to a greater extent than the coatings on lower sheds surfaces. The Al/Si ratio was found to be 1.1 to 1.3 for the virgin RTV silicone and aged RTV silicone from lower shed insulator surfaces. For the topmost shed coating, Al/Si =0.3 indicating a loss a ATH filler. We believe that the surface layer of the topmost shed is some form of silicate with carbon surface contamination from pollution.

5. Thermogravimetric analysis of the RTV silicone coatings showed a decreased water loss peak from the ATH filler in the topmost shed surface. This could indicate either a loss of ATH filler level, as confirmed by SEM-EDAX measurement, or a loss of hydration in the ATH filler from dry band arcing. A loss of bulk PDMS from aged RTV silicone coatings as a result of depolymerization was also observed from the TGA data.

6. Water contact angle measurements of the RTV silicone surfaces showed that both the virgin and aged coatings from Millstone had good hydrophobicity. However, the absolute values of the water contact angle for the virgin material and the coating from the topmost shed of the Millstone insulators were greater than that for the coatings from the lower shed surfaces. On the basis of GC-MS data, the hydrophobicity of the RTV silicone coating from the upper surface of the topmost insulator shed can be attributed to

atmospheric hydrocarbon contaminants deposited on the coating rather than to attributes of the RTV silicone coating. Water contact angle stability tests showed that over a 30 minute time period of continuous exposure to a water drop, energized RTV silicone samples taken from upper surface of lower sheds exhibited spreading behavior during the first five minutes of exposure. Virgin RTV silicone samples and energized RTV silicone samples from the topmost shed on the insulators also showed decreases in the water contact angle over time but remained quite hydrophobic to water during 30 minutes of continuous exposure.

7. Comparison of RTV silicone coating taken from insulators energized in the station yard with coating taken from unenergized insulators at salt monitoring station on the same site indicate that the weathered, unenergized coatings have depolymerized to a similar degree to those which have been energized. The primary difference between the two is degradation of the topmost shed, which is much greater for energized insulators than for weathered, nonenergized insulators. We therefore believe that weather-related environmental factors dominate the degradation process, which is consistent with the fact that the insulators have degraded fairly uniformly, although to a slightly greater degree on the side facing Long Island Sound.
8. Artificial aging of the coating for one month in 90 °C water buffered to pH = 7 caused very little degradation of the coating. Similar aging in artificial ocean water (slightly basic) had a similar result. However, aging in water adjusted to ph 3.9 with0.1 Molar HCl resulted in severe degradation of the coating which appears to be very similar to the degradation of the coating on the topmost sheds of insulators aged along the Connecticut coast of Long Island Sound, where the rain water is of similar acidity.

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Christopher Mirley was graduated from Tufts University in 1982 and 1985 with a B.S and M.S. in chemical engineering. From 1982 to 1987, he worked at the Polymer Science Division of the Army Materials and Technology Laboratory, Watertown, MA., and from 1987 to 1989, Dr. Mirley worked for the Transdermal Research and Development Group of CIBA-GEIGY Pharmaceutical Division, Ardsley, NY. Dr. Mirley completed his Ph.D. in Polymer Science at the University of Connecticut in 1994 and is presently a post-doctoral fellow with the Electrical Insulation Research Center.

JoAnne Ronzello was graduated from Central Connecticut State University with a B.S. in chemistry. She also holds an Associates degree in electrical engineering. Prior to joining the University of Connecticut about a decade ago, Ms. Ronzello was employed by Chandler-Evans Corp. as a materials laboratory technician. In her capacy at EIRC, she manages the dielectrics laboratory on a day-to-day basis and performs electical and chemical analysis on dielectric materials.

Hiro Homma was graduated from Rikkyo University, Tokyo in 1987 and received his M.S. degree in engineering physics from the University of Tsukuba in 1989. Since 1989, he has been with the Functional Materials Group, Central Research Institute of the Electric Power Industry (CRIEPI) Tokyo, Japan, where he has been engaged in research on polymer insulating materials as related to composite insulators. Presently, Mr. Homma is a visiting scholar at the Electrical Insulation Research Center, University of Connecticut. Mr. Homma is a member of the IEE of Japan and the Physical Society of Japan.

Steven A. Boggs (F) was graduated from Reed College and completed his Ph.D. at the University of Toronto. His employment experience includes 12 years with the Research Division of Ontario Hydro during which he carried out research in the areas of solid dielectrics and gas-insulated substations (GIS). He was elected a Fellow of the IEEE for his contribution to the technology of GIS. In 1987, he joined Underground Systems, Inc. where he was Director of Research and Engineering. In 1993, he became Associate Director of the Electrical Insulation Research Center and a Research Professor of Materials Science at the University of Connecticut. Dr. Boggs is also an Adjunct Associate Professor of Electrical Engineering at the University of Toronto, a voting member of the IEEE Substations Committee, a Contributing Editor to IEEE Electrical Insulation Magazine, and a member of the Program Committee of the Conference on Electrical Insulation and Dielectric Phenomena.