AGEING AND DEGRADATION MECHANISMS OF SILICONE POLYMERS USED FOR OUTDOOR ELECTRICAL INSULATION

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Abstract: Silicone is an organic material largely used in outdoor electrical insulation. Performances and results have shown to be largely depending upon chemistry and applications. It is used either in the form of silicone rubber moulded over a fiberglass core in composite insulators or as a coating over ceramic insulators in overhead line or substation applications.

Corona activity has been identified in the last fifteen to twenty years as a major threat for silicone rubber, and besides the erosion pattern often visible in such cases there are other signs of degradation of the polymer. Progressively, experts have pointed out the necessity to be more stringent in the evaluation of maximum acceptable stress levels allowed on silicone housings [1]. Among the typical degradation seen on the housing material, whitening and hardening of the silicone compound in its structure after exposure to corona and the acidic by-products remain incompletely described even today. This paper will provide some keys explaining the chemical degradation of silicone rubber under electrical stress with correlations to field reports and actual chemical investigations on failed composite insulators.

Likewise, silicone coatings on ceramic insulators which are being used for their hydrophobic properties can be degraded over time. Ageing tests on samples covered with silicone coatings of various chemistries are presented. The main degradation patterns are described in this paper as well as field results from actual insulators returned from service. Based on numerous observations and testing, an ageing classification chart is proposed combined with the hydrophobicity of the material and recovery considerations. Periodic Soxhlet analyses over years of field observation described in this work are supporting this evaluation.

1 INTRODUCTION

While mentioning material selection criteria, many utilities simply call for silicone rubber when describing the rubber housing of a composite insulator. This is by far insufficient and field experience as well as laboratory ageing tests has shown how complex silicone rubber selection can be with respect to the expected performances. Among all parameters, ageing and pollution performance are the drivers but taken separately they can be highly misleading or even in contradiction with each other.

Silicone for overhead transmission lines is being used mostly in the two conditions described in this paper. Either it is used as rubber housing for covering the fiberglass rod or a composite insulator or as a coating over a traditional ceramic insulator (toughened glass or porcelain insulators).

2 GENERAL PROPERTIES

Hydrophobicity is the main reason for using silicone in contaminated environments. However, silicone can lose temporarily or permanently this property and then becomes much more sensitive to erosion (figure 1). Under severe and maintained stress conditions, (including the simple effect of electric field below the visible corona inception level [2]) erosion can lead to the destruction of the insulator.

Figure 1: Left: erosion at shank near the fitting. Right: erosion between sheds.

Only rest times can reinstate the hydrophobicity. This phenomenon is described as the recovery process which duration varies as a function of the chemistry of silicone but also on the inhibition process. Under certain circumstances this recovery never happens and the silicone material will progressively be destroyed. The dynamics of this recovery are also a function of the fillers added to the silicone compound. Promoters of pure silicone such as LSR (Liquid Silicone Rubber) bet on the ability of silicone to avoid this temporary loss of performance. Field experience as well as laboratory tests show however that this is not always the case, which is why the addition of ATH (Alumina Tri Hydrate) is often considered as a must even if the addition of ATH can slightly reduce the speed of recovery [9]. Figure 2 shows a comparative ageing test between LSR and ATH filled silicone. This test was performed in clean fog conditions with 200 µS/cm water conductivity.

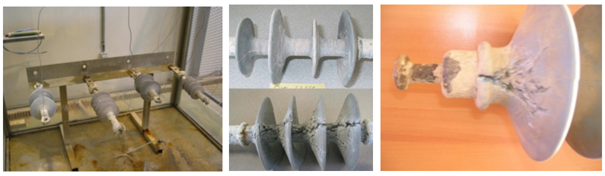

Figure 2: Left: clean fog erosion test chamber Center: ATH filled silicone (top) and LSR (bottom) after 2000h in the chamber. Right: LSR eroded in coastal environment after less than 5 years in service (Morocco).

The transfer of hydrophobicity to the pollutant covering the insulator through the migration over the contaminant of the LMW fluid (Low Molecular Weight) is one of the keys to the performance under pollution. The speed of transfer is also a function of the chemistry as shown in figure 3.

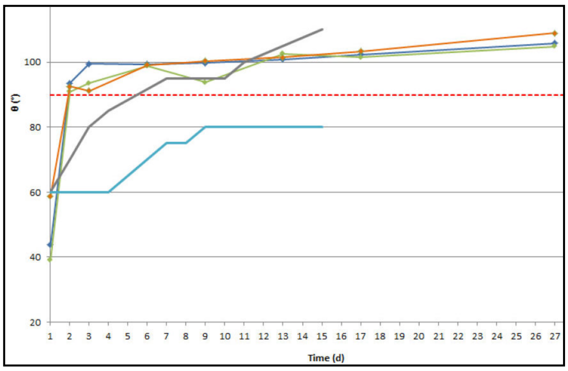

Figure 3: example of evolution of contact angle as a function of transfer time for various chemistries of silicone used for coatings.

As a consequence, it is never possible to completely wash a silicone surface since the embedded pollutants remain in the skin of the silicone as shown in figure 4 where silicone is compared to EPDM for which there is no transfer.

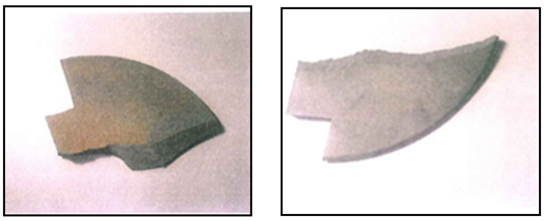

Figure 4: shed sections of composite housing after 10 years in semi desertic conditions after washing Left: silicone (brown aspect is the result of embedded dust). Right: EPDM.

Overall the selection of optimum silicone chemistry is a matter of balance between hydrophobicity, transfer and recovery time. Experience from the field and in the laboratory has clearly demonstrated that the truth is somewhere in the middle of these properties and none of them can be considered as sufficient by itself.

3 SILICONE IN COMPOSITE INSULATORS

3.1 Ageing observation

The erosion phenomenon can be slowed down or reduced to a certain degree with ATH fillers (keeping in mind that some environments will still be harsh enough to degrade even these compounds). Other ageing mechanisms have been seen but not clearly explained yet. In some cases the silicone has become brittle with an increase in hardness. When bending sheds, such cracks can propagate easily through what appears to be a mineral layer. Over time these changes can lead to open cracks in the rubber housing resulting in a complete failure of the insulator. Figure 5 describes such degradations found in service and initiated from acids on the surface of the silicone.

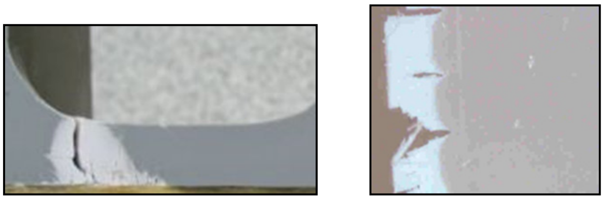

Figure 5: degradation resulting from acid attack. (Left: 345kV USA coastal application, nitric acid less than 10 years in service. Right: 230V petrochemical environment, sulphuric acid attack, Saudi Arabia after 7 years in service).

3.2 Chemical investigation

Research performed in the Sediver R&D Centre has provided interesting information on this topic. Among many tests performed, different chemistries of silicone compound have been screened under acid resistance tests. Acids such as nitric acids found as the by-product of corona but also in some agricultural environments where fertilizers are being sprayed by air, or sulphuric acid (industrial or agricultural by-products) can challenge the integrity of a composite silicone housing through different mechanisms.

Findings from the field have shown that some silicone rubbers filled with ATH can increase their hardness by more than 20% depending on their chemistry, sometimes in less than 5 to 7 years. This “white layer” was identified through ESCA technique as a rich silica layer resulting from the depolymerisation of the silicone itself as shown in figure 6.

While originally the silicone housing was made with a compound defined by 83% PDMS (Poly DiMethyl Siloxane) and 17% of silica added for mechanical strength, the measures on the chemistry of the unit removed from the field shows a reduction of the PDMS at 71% and an enrichment of mineral silica at 29%.

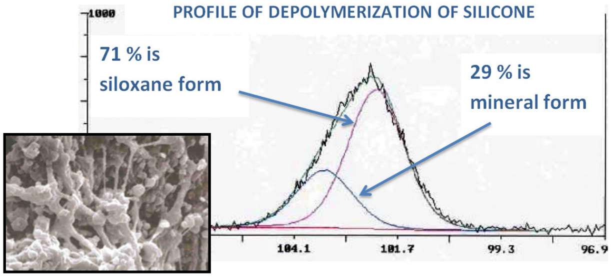

Figure 6: Left: 5000x MEB picture of aged silicone rubber with polymer damaged under sulphuric acid attack (back from the field after 7 years). Right: data from ESCA analyses showing the depolymerisation of silicone under acid attack.

Laboratory tests produced on a large variety of silicone compounds have shown that the nature and type of ATH can have a large influence in the dynamics of the destruction of silicone under acids. While all silicone rubbers are damaged under such tests, time to destruction and magnitude of the damage differ. Figure 7 shows examples of different silicone chemistries and their condition after a similar time of exposure to an acidic environment (Sediver R&D procedure). Today a large variety of silicone compounds is being used covering the entire spectrum of fillers and polymers. Such failures are more and more commonly found in service.

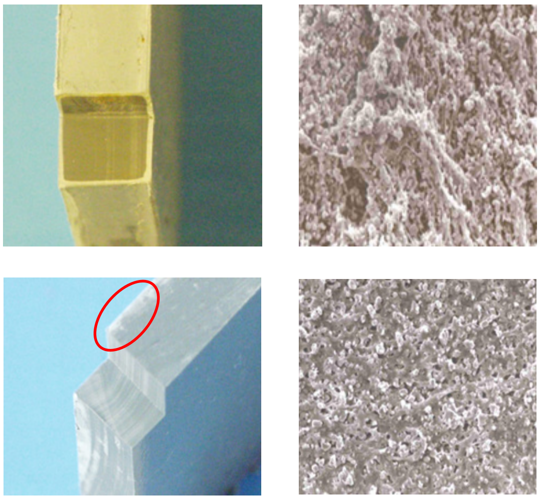

Figure 7: comparison of the damage of acids in two different chemistries of silicone housing based on the type of ATH being used in the composition of the rubber. Top: silicone with untreated ATH and associated MEB. Bottom: Silicone with a specific type of treated ATH with still a skin effect but less than previous case and associated MEB.

3.3 Consequences

Based on these results it appears necessary to produce more stringent testing criteria to describe the typology of silicone rubber for the use of overhead transmission lines, and current standards do not provide an appropriate selection criterion for the differentiation of materials.

An interesting property pointed out during this research work was the possible increase of hydrophobicity of the surface of silicone rubbers which had been chemically degraded. Figure 8 is describing the evolution of this property over the years of service in an environment where the polymer was progressively destroyed.

Hydrophobicity can therefore not be considered as a valid criterion of good condition during the inspection of a line using silicone polymer insulators and maintenance crews should be cautious when making a diagnostic of a polymer insulator. Only a physical inspection after removing the insulators can help making such an assessment.

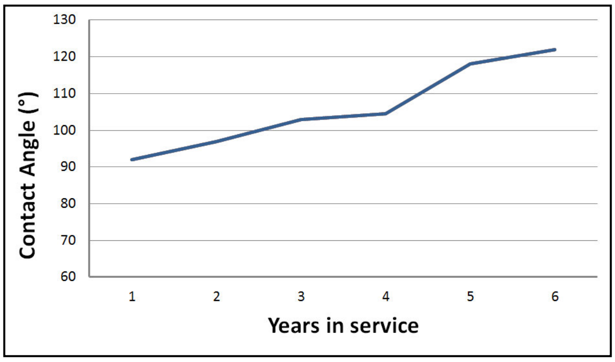

Figure 8: Increase of hydrophobicity as a function of acid related depolymerisation on a 230kV silicone unit monitored over years of service.

4 SILICONE COATED INSULATORS

Silicone coating over ceramic (toughened glass or porcelain insulators) offers a hydrophobic condition similar to composite housings but while erosion, degradation or reduction of hydrophobicity might occur [3],[4], the consequences are completely different.

The ageing of silicone coating has been studied simultaneously in laboratory tests, test stations and in the field.

4.1 Laboratory testing

The ageing of coatings was studied from two directions. On one side the degradation mechanism of various coatings was defined through ageing chambers, and simultaneously chemical changes in coatings were established.

4.1.1 Ageing chambers

Like for silicone rubber used in composite insulators, coatings can be made with silicone containing various fillers for increasing the resistance to erosion or none at all. (quartz or ATH fillers are commonly used among manufacturers). As an example (among a large diversity of test protocols established for accelerated ageing tests) interesting results can be found from a 2000h multi-stress test (figure 9) combining UV, rain, salt fog, humidity, voltage on a weekly cycle performed according to a specification from TERNA (Italy) [7] A clear discrimination appears between various coatings including coatings made with different types of ATH (figure 10).

Like for composite insulators, a better definition of the chemistry of coating will help selecting the best performer and this test was found to be a good method for ranking ageing resistance of coatings.

Figure 9: 2000h multi-stress ageing test

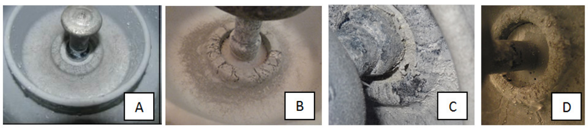

Figure 10 : Samples after 2000h ageing test. A: polymer 1 ATH type a – B: polymer 2 ATH type b – C: polymer 2 ATH type c – D: polymer 2 quartz filler

4.1.2 Chemical evolution

Among the key factors leading the hydrophobicity of silicone the presence of low molecular weight fluid (LMW) is a determinant factor. Soxhlet extraction test (figure 11) provides an interesting assessment method to determine the amount of the LMW fluid left in a sample of silicone. This gives a good indication of the hydrophobic transfer and recovery dynamics.

Such tests have been performed on coating samples from units (top and bottom) removed from service. What appears through the results is an initial decrease of the level of LMW fluid. After several years in service an asymptotic trend appears showing a stabilization of the LMW fluid ratio (figure 11). This can be considered as a good criterion for establishing the longevity of a silicone coating. Very recent tests (still in progress as we write these lines) are showing the active presence of LMW fluid even after 20 years in very harsh contamination conditions combining a desertic and marine environment.

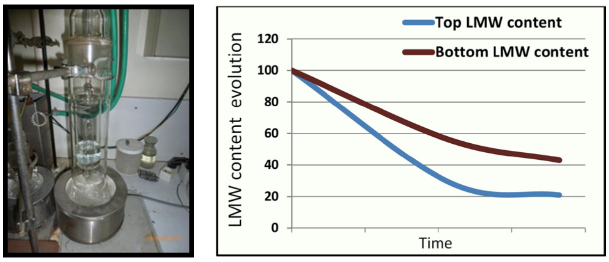

Figure 11: Soxhlet extraction test and level of LMW fluid as a function of years of service.

4.1.3 Test station evaluation

Silicone coated insulators have been installed in a variety of test stations around the world. Among those, samples installed in Koeberg (RSA) have shown how a coating can be aged after 5 years in operation in very harsh conditions. Pollution levels up to ESDD=1mg/cm² were recorded with no flashovers during the five years of evaluation. Silicone composite insulators were tested simultaneously as shown in figure 12. Erosion is important on the composite and meets all the conditions for being removed despite still being hydrophobic overall. Comparatively and while the silicone coated glass insulator shows also areas of erosion, especially around the pin, the hydrophobicity is globally preserved (reduction near the pin and still very good all around the insulator skirt). In the current condition of these insulators, and unlike the polymer insulator there is no operational risk since the pollution performance is preserved and the erosion only opens the surface to normal glass underneath.

Figure12: condition of the insulators after 5 years in the test station (USCD= 66mm/kV) (*)

(*) USCD: Unified specific creepage distance corresponds to the creepage distance per phase-ground voltage).

4.1.3 Field reports

The excellent performance of silicone coating has been established in the field worldwide [5] with millions of insulators including more recently in DC [6].

Thanks to a partnership with several utilities, SEDIVER has initiated a monitoring of the performance of coated insulators in the field. As of today what appears clearly from strings removed after more than a decade of observation is a partial reduction of hydrophobicity near the pin where the highest electrical field is concentrated (figure 13) with the presence of sporadic dry band arcing over time especially under extreme contamination conditions.

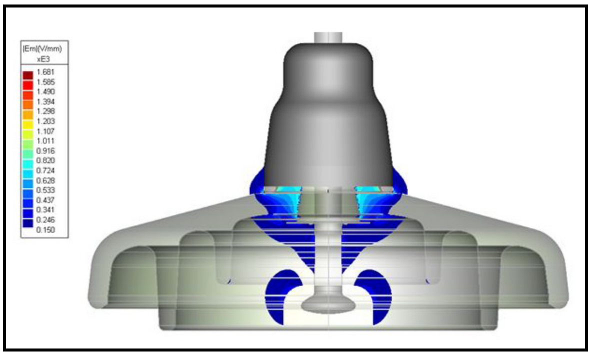

Figure 13: Typical electric field distribution on a coated toughened glass insulator

What matters here is the distribution of the ageing of the coating along a string. For polymers insulators any damage, erosion or reduction of hydrophobicity along the core can lead to an acceleration of the ageing resulting at some point in time in a failure. For a silicone coated toughened glass insulator there is no such critical condition since underneath the coating there is a non-organic material like toughened glass which is immune to the environmental conditions.

Ageing considerations for silicone coatings over toughened glass insulators are based on three sets of criteria [8]:

- Hydrophobicity (IEC 62073)
- Location along the string of the erosion/damaged coatings (figure 14)
- Level of erosion as per SEDIVER CE erosion class classification (figure 15)

The combination of these criteria has shown in the field that most likely coated insulators located in the bottom section of a string can be classified in an erosion class type CE2 or CE3, with a hydrophobicity between WC2 and WC5 depending upon location on the surface (mostly reduced near the pin) but insulators above the first section from the bottom of the string remain almost unaffected by service conditions with respect to the above mentioned criteria.

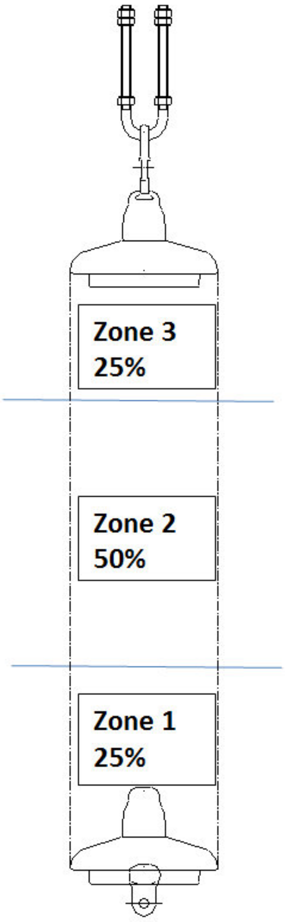

Figure 14: string zone identification

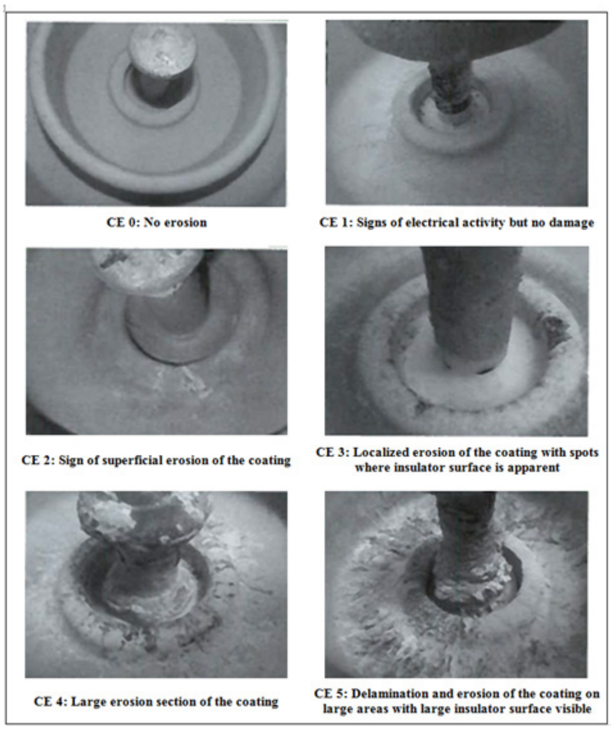

Figure 15: SEDIVER coating erosion classification chart

5 CONCLUSION

The complexity of silicone requires that testing and evaluation method go beyond the existing screening methods. Specifications asking for a silicone housing without any description more precise than the existing standard tests open the door to potential severe ageing mechanisms and potential failures as can be seen in the field today.

The mechanism of degradation of some silicone rubbers have been explained through an aggression of the polymer itself by acids and it is established that the nature of the fillers have an important role in this process. Such ageing mechanisms are currently not assessed in standardized criteria for the selection of polymers while actually the consequence on the insulator performance can be dramatic.

Silicone coatings display a different pattern even if the material can age with some similarities compared to traditional housings, mainly hydrophobicity fluctuations and erosion. However, there is much less risk using silicone as a coating given the resilience of the mineral dielectric substrate underneath especially when using toughened glass. Tests such as a 2000h ageing multi-stress test can help differentiate material strength against erosion, and an evaluation of hydrophobicity coupled with the SEDIVER coating erosion classification chart can provide an effective guidance in the monitoring of such insulators.

The end of life of silicone coatings can also be established through classical means like recovery time, hydrophobicity…with an additional tool measuring the variation of LMW fluid in the coating thanks to the Soxhlet extraction method.

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