Chapter X

Room temperature vulcanized Silicone Rubber coatings

Application in high voltage substations

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Abstract

Silicone rubber brought a new era in the field of outdoor insulation, providing improved performance in comparison to the ceramic materials that were traditionally employed. The primary advantage occurs as a result of the surface behavior in respect to water, with silicone rubber being able to maintain hydrophobic characteristics, in field conditions, even after the deposition of contaminants on the surface. This improved behavior is correlated to the material formulation employed, to the properties and capabilities of the base polymer and the included fillers. Room temperature vulcanized silicone rubber (RTV SIR) is one of the forms of silicone rubber implemented in outdoor insulating systems, usually in order to improve the pollution performance of ceramic insulation. This chapter is a review of the basic features and properties of RTV SIR coatings applied on ceramic insulators in high voltage substations.

Keywords:

High voltage insulators, silicone rubber, room temperature vulcanization, pollution, substations
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X.1 Introduction

High voltage transmission and distribution systems constitute critical infrastructures for the development and the prosperity of today’s society. Substations and transmission lines form a network responsible to interconnect the power generation facilities, from conventional and renewable sources, with the power consumption centers. In addition, further requirements are set, demanding the optimized operation of these installations with the highest degree of reliability and in the same time with the minimum possible cost.

For the majority of these systems, the primary insulating component is the surrounding atmospheric air. This is a choice made considering that the use of increased voltage levels is necessary in an effort firstly to reduce the correlated transmission power losses and further to improve additional features of the transmission performance, such as system stability [1]. Furthermore, the necessity of adequate insulating systems is evident and the surrounding atmospheric air has to demonstrate considerable advantages, starting from the fact that is free of charge. A significant disadvantage on the other hand, as for any gas or liquid dielectric, is it’s incapability to mechanically support the high voltage conductors. Consequently, the use of solid insulators capable of providing the required mechanical features is required [2]. Therefore an insulation system is formed combining a gas dielectric, which is the atmospheric air and solid dielectrics in the form of insulators.

The performance of the gas solid interface formed is quite critical [3, 4]. It will determine the efficiency of the insulator, in respect to the experienced service conditions and furthermore the reliability of the high voltage installation, considering that a single insulator failure, is sufficient to set an installation such as a transmission line, out of service for many hours.
A major concern for the operators of many high voltage installations is the change of the insulator surface behavior, due to the deposition of contaminants that are or can become conductive [4, 5]. It is a problem known as “Pollution of high voltage insulators” and is responsible for the majority of power outages in many transmission and distribution systems, especially those that are near the sea coast [5, 6]. Under the influence of pollution, the behavior of an insulator is degraded, resulting to a complete loss of the dielectric capability, although the applied voltage stress remains within the nominal limits.

The surface performance under pollution conditions is the comparative advantage of composite materials, and especially silicone rubber, in respect to the ceramic materials, porcelain and glass, which were traditionally employed for the manufacture of insulators [3, 7, 8]. In fact, the introduction of silicone compounds brought a new era in the field of outdoor transmission and distribution insulating systems. This change occurs mainly due to the surface behavior of silicone rubber and especially due to a property known as hydrophobicity [6-8].

Hydrophobic surfaces resist wetting, which is necessary in most cases, and especially in coastal systems, for the surface contamination to develop electrical conductivity. Consequently silicone rubber insulators demonstrate a hydrophobic surface behavior and thus a quite improved performance, in comparison to the ceramic insulators. Porcelain and glass are hydrophilic materials and therefore are vulnerable to the action of the pollution phenomenon [3].

Nevertheless, exploiting the silicone technology and especially the vulcanization process of silicone rubber, it is possible to develop an improvement for ceramic insulators also, and this solution is Room Temperature Vulcanized Silicone Rubber (RTV SIR) coatings. These coatings can be applied on the surface of a ceramic insulator and ascribe a behavior similar to silicone rubber insulators and therefore ensure an improved performance in the case of pollution [9, 10]. The coating properties, capabilities and efficiency are correlated to the formulation and the fillers incorporated, to the application conditions and procedures and certainly to the service conditions experienced [11-16].

X.2 Pollution of high voltage insulators

Pollution of high voltage insulators is a problem experienced in many outdoor high voltage installations worldwide and in most cases is the primary cause of power outages. It is usually considered as a six stages mechanism, as shown in figure X.1 [5]. The first stage is the deposition of contaminants on the insulation surface, experienced mainly due to the wind but also other mechanisms such as acid rain. The amount accumulated and the electrical behavior of the film formed, are critical for the mechanism development. Usually there are substances within the accumulated contaminants that have or may develop electrical conductivity. The second stands for the case of coastal systems, where the primary source of contamination is the sea and the majority of contaminants are sea
salts, which become conductive when diluted in water. The wetting agent is available on
the insulation surface, as the result of mechanisms such as fog, dew, condensation and
light rain. Wetting is the second stage of the mechanism and leads to the third stage,
which is the formation of surface conductivity and the flow of current, known as leakage
current.

![Diagram of the pollution phenomenon in stages]

*Figure X.1 Development of the pollution phenomenon in stages*

The flow of current unfolds a counterbalancing mechanism as far as the surface
conductivity formation is concerned. The contaminants film behaves as a resistance
distributed on the insulator surface, with a value determined by the amount of
contamination accumulated and the degree of wetting. The flow of current, through the
development of joule losses is capable of changing the degree of surface wetting and thus
the conductivity value. This change is not uniform on the surface, but it appears to be
relevant to the insulator geometry and in fact is more intense in areas with small radius
from the insulator axis of symmetry [17]. Along these areas, drying is intense resulting to
zones of increased resistance, known as dry bands. The formation of the dry bands is considered as stage four. Consequently, the initial insulating surface, where only a small capacitive current was observed, can now be considered as a series combination of electrolytic resistances, with values that vary and depend on the accumulated contamination, the degree of wetting and the joule losses experienced due to the flow of leakage current. As a result, the voltage distribution along the insulator leakage path is changed and the stress distribution is now dependent on the value of conductivity achieved. This change of the surface behavior, and further the voltage distribution that occurs, result to the application of intense stress along parts of the leakage path. Thus surface discharging appears, known as dry band arcing and this is stage five.

Dry band arcs bridge parts of the leakage path and not the complete leakage distance. Thus, they are present on the insulator surface, but a flashover is not achieved. Only under favorable conditions, and especially an optimum combination between the conductivity values of the surface film and the gas discharge, the discharge will propagate and a complete flashover will occur. These favorable conditions are not always present and usually stages 1 to 5 are experienced. In the picture of figure X.2 dry band arcing and finally a flashover on a 150 kV post porcelain insulator, during an artificial pollution test is illustrated. The considered test took place at the Talos High Voltage Test Station in Crete, Greece [18].

![Figure X.2 Flashover of a 150kV post porcelain insulator at Talos Test Station [18]](image)

X.3 Silicone coatings for high voltage ceramic insulators

It is evident from the pollution mechanism analysis, that the demonstrated surface behavior is a key factor regarding the vulnerability of an outdoor insulator to the action of the pollution phenomenon. Therefore, imparting the surface with properties that could
postpone the mechanism development is a way to increase the system efficiency and reliability. The concept of coatings for high voltage ceramic insulators is the application of an additional layer on the insulator surface, which will interfere to the pollution mechanism development and eliminate the possibility of a flashover. This is possible by reducing either the amount of contaminants on the insulator surface or the degree of wetting [3, 19].

In the first case, coatings in the form of grease have been developed, capable of encapsulating the deposited contamination and thus maintaining a clean surface. These formulations were based on hydrocarbons or silicones, with the second mostly employed, due to their increased thermal stability, which allowed them to be implemented in various climatic conditions [3]. However, the amount of contamination that could be encapsulated was limited and dependant on the amount of grease applied. Thus saturation was due to appear and when it appeared the coating replacement was unavoidable. Considering that in the case of a moderate to heavy pollution environment, the time period from the coating application until saturation was less than six months, the application of this type of coatings is time and money consuming. In addition it must be also noticed that after saturation the behavior of the saturated greased insulator is quite inferior to the ungreased ceramic insulator.

The second type of coatings is RTV SIR coatings. In this case, another path is followed. Instead of encapsulating the accumulated contamination, RTV SIR incorporates a molecule migration mechanism to impart hydrophobic properties to the formed contaminants film. In this way, surface wetting is difficult and thus the development of the pollution mechanism is postponed. In the picture of figure X.3 a section of a porcelain post insulator is illustrated, where the RTV SIR coating can be seen. The porcelain bulk is white but the surface can be detected due to its brown color and a 5 mm white coat can be seen.

It is worth mentioning that RTV SIR coatings is not a new technology. The first application found in the literature is in 1968 in the USA, were a small amount was installed in a high voltage substation of Bonneville Power Administration [3]. The improvement achieved was remarkable, however tracking and erosion problems very soon appeared. Since then, many applications can be found worldwide [6, 14-16, 19-41] and considerable improvement of the coatings performance has been achieved.

X.4 RTV SIR coatings formulation

Composite materials employed in outdoor insulating systems are usually compositions of one base polymer and a number of additives, known as fillers. Fillers aim to formulate the composition properties, according to the application requirements, starting of course from the properties of the base polymer. Consequently, for the development of a composite material, both the base polymer and the fillers included have a critical role to play. Further, depending on the anticipated service conditions, an optimum formulation
(type and amount of the base polymer and filler) can be determined. In the case of RTV SIR coatings, silicone rubber and especially polythimethylsiloxane is the base polymer implemented.

![Figure X.3 Section of a 150kV post porcelain coated with a 5mm RTV SIR coat](image)

**X.4.1 The base polymer**

Polydimethylsiloxane is the base polymer for silicone formulations employed in outdoor high voltage systems, not only in the case of coatings but also for composite insulators [3, 9, 10, 11]. It is a widely applied polymer within the silicones family [42], with remarkable and sometimes unique properties, which enable applications not only in outdoor installations but also in many technical fields [42-47]. The polymer chain is composed by silicone oxygen bonds, accompanied by two side methyl groups connected to the silicone atom, as shown in figure X.4 where the monomer unit is illustrated.

In comparison to polymer materials that have been employed in high voltage outdoor insulation systems, like EPM and EPDM, PDMS has to demonstrate considerable advantages such as:

- Low levels of surface tension (energy),
Surface hydrophobicity
Hydrophobicity recovery mechanisms,
Good dielectric properties
Resistance to thermal stress
Capability of operating within a wide temperature range, with limited changes of its physical and chemical properties
Increased resistance to the action of various environmental oriented aging mechanisms,
Chemically inactive to the action of various oxidative substances,
It is not toxic and is friendly to the environment,
Low glass transition temperature.

These properties are strongly correlated to the monomer structure and especially to the presence of the silicone oxygen bond, the weak intermolecular forces that appear within the material and the flexibility of the polymer chain [43].

![Figure X.4 Representation of the PDMS monomer](image)

**Properties of the silicone oxygen bond**

In the PDMS chain, silicone is connected to oxygen through a strong covalent chemical bond, with a bond energy that is the highest among the chemical bonds found in polymers employed in high voltage outdoor insulation, as illustrated in table X.1 [43-47]. The bond strength is responsible for polymer properties such as the thermal and environmental durability of the material. In addition there is an influence to the behavior of the side
silicone carbon bonds, which become stronger in the polymer chain. As a result, the attachment of the side methyl groups to the silicone oxygen chain, appears to be stronger in comparison to other polymers and therefore the side methyl groups are less exposed to mechanisms such as replacement reactions [42]. The reason is the electropositive silicone behavior, which attracts electrons, polarizing the methyl groups and further enforcing the attachment degree. Consequently the presence of the silicone oxygen bond in the material monomer results to the development of a strong structure, when compared to other polymers within the same application field, where the polymer chain is composed by carbon atoms instead of silicone. Nevertheless, it must be noted that the polar nature of the silicone oxygen bond, results to a material that is vulnerable to the action of hydrolysis [44], which however appears to be notable for pH values less than 2.5 or greater than 11[48].

**Table X.1** Energy of the chemical bonds usually encountered in polymers employed in outdoor high voltage systems.

<table>
<thead>
<tr>
<th>Chemical Bond</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-Si-O-</td>
<td>445</td>
</tr>
<tr>
<td>-C-H-</td>
<td>414</td>
</tr>
<tr>
<td>-C-O-</td>
<td>360</td>
</tr>
<tr>
<td>-C-C-</td>
<td>348</td>
</tr>
<tr>
<td>-Si-C-</td>
<td>318</td>
</tr>
<tr>
<td>-Si-H-</td>
<td>318</td>
</tr>
</tbody>
</table>

**Low intermolecular forces**

The levels of surface tension in a material appear to be strongly correlated to the material structure [49, 50]. Usually materials with strong chemical bonds demonstrate a surface with increased levels of surface tension, which further results to a hydrophilic behavior. In the case of silicone rubber however, despite the presence of the strong silicone oxygen bond within the PDMS monomer, the levels of surface tension experienced are considerably low, resulting to a hydrophobic surface. In fact, as illustrated in table X.2 [51], the value of surface tension experienced in the case of silicone rubber is the second lowest value, after PTFE (TEFLON).

**Πίνακας X.2** Typical surface tension values encountered in materials employed in outdoor high voltage systems and water.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain</td>
<td>366</td>
</tr>
</tbody>
</table>
This behavior occurs since the surface tension is primary correlated to the experienced intermolecular forces developing between the polymer chains. In the case of PDMS, the presence of the side methyl groups decrease the strength of interaction between the polymer chains and further limit the resulting surface tension [42, 43]. Therefore, the side methyl groups conceal the presence of the relatively strong silicone oxygen bond, resulting to a hydrophobic surface [49, 50]. In this direction the number of the side methyl groups and especially the chain flexibility act in favor of a low energy surface behavior.

### Chain mobility and flexibility of PDMS

The PDMS chains are characterized by increased levels of mobility and flexibility. They are capable of moving within the material volume and the rotation of the side methyl groups is also possible [42, 43, 51]. This remarkable mobility is very important, since it is correlated to properties such as the low glass transmission temperature (-127 °C), the low levels of surface tension and thus hydrophobicity and the capability of hydrophobicity recovery which is quite critical in the case of outdoor insulators. It is worth noticing that the energy required for the methyl groups rotation is considerably low, less than 4 kJ/mol [52], indicating that this movement is almost free. For the same rotation 14 kJ/mol [53] are required in the case of polyethylene and 20 kJ/mol [53] in the case of PTFE. Further, for polymer chains that are near the surface, the orientation of the methyl groups towards the surface occurs in the direction of minimizing the surface tension, according to the first law of thermodynamics.

The importance of chain mobility and flexibility can be further realized when comparing the behavior of silicone rubber to the behavior of PTFE. As already has been mentioned, PTFE is the most hydrophobic material among the materials employed in outdoor insulation and is more hydrophobic than silicone rubber. It is characterized however by a high glass transition temperature at 117 °C [51], which indicates that at room temperature the material demonstrates a strong solid form rather than rubber as in the case of silicone rubber. As a result in the case of a hydrophobicity loss, recovery is not possible, in contrast to silicone rubber, where recovery mechanisms are present. Consequently, although PTFE is more hydrophobic than silicone rubber and had been used for the

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>170</td>
</tr>
<tr>
<td>Epoxy Resins</td>
<td>35</td>
</tr>
<tr>
<td>EP Rubbers</td>
<td>30</td>
</tr>
<tr>
<td>PDMS</td>
<td>23</td>
</tr>
<tr>
<td>PTFE</td>
<td>19</td>
</tr>
<tr>
<td>water</td>
<td>72.3</td>
</tr>
</tbody>
</table>
manufacture of insulators during the 70s, today silicone rubber is the dominant material, mainly due its capability to maintain the surface behavior in field conditions.

X.4.2 Polymerization and crosslinking processes

The manufacturing procedure of silicone rubber is consisted of various processes starting from the production of dimethyldichlorosilane from powdered silicon and ending to the rubber formation. Polymerization and crosslinking are two processes of paramount importance in order to understand the material structure. Both are considered to increase the chains size; however they are two different processes sequentially occurring. Polymerization is a process where a big molecule is formed by appropriately connecting a number of smaller molecules (monomers). In the case of PDMS the polymerization process starts from the hydrolysis of dimethyldichlorosilane (reaction X.1) followed by condensation reactions (X.2, X.3) [45]. The molecular weight of the obtained macro molecules is determined by the polymerization conditions and can be controlled by various methods, such as the addition of active monomers (for example examethyldisilane). The polymer finally manufactured is a mixture of linear and cyclic macro molecules, which further are used to produce larger molecules by anionic or cationic ring opening polymerization of the cyclic oligomers or by polycondensation of the silanol end block linear oligomers.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} \quad \text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{HO} \quad \text{Si} \quad \text{OH} + 2\text{HCl} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{HO} \quad \text{Si} \quad \text{OH} + 2\text{HCl} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{HO} \quad \text{Si} \quad \text{OH} + 2\text{HCl}
\end{align*}
\] (X.1)

\[
\begin{align*}
\text{Cl} & \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HO} \quad \text{Si} \quad \text{Si} \quad \text{Cl} \rightarrow \text{Cl} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HCl} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HO} \quad \text{Si} \quad \text{Si} \quad \text{Cl} \rightarrow \text{Cl} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HCl} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HO} \quad \text{Si} \quad \text{Si} \quad \text{Cl} \rightarrow \text{Cl} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HCl}
\end{align*}
\] (X.2)

\[
\begin{align*}
\text{HO} & \quad \text{Si} \quad \text{OH} + \text{HO} \quad \text{Si} \quad \text{OH} \rightarrow \text{HO} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{OH} + \text{H}_2\text{O} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HO} \quad \text{Si} \quad \text{Si} \quad \text{Cl} \rightarrow \text{Cl} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HCl} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HO} \quad \text{Si} \quad \text{Si} \quad \text{Cl} \rightarrow \text{Cl} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si} \quad \text{Cl} + \text{HCl}
\end{align*}
\] (X.3)
Depending on the molecular weight, the material produced is in gas or liquid form (low intermolecular forces). In order to acquire a solid material, the development of connections between the polymers molecules that will stabilize the material structure are required. Crosslinking or vulcanization is the process followed in this direction. Two of the vulcanization mechanisms that are applied in the case of Silicone Rubber (outdoor insulation) are:

**High Temperature Vulcanization**

In High Temperature Vulcanization (HTV) the connections between the rubber macromolecules are developed between the side methyl groups, with the participation of free radicals that abstract hydrogen atoms [45, 46, 54]. This process, described by reactions X.4 and X.5 takes place at elevated temperatures ranging from 115°C to 173°C depending on the radicals used. In addition a post curing process is applied (storage at elevated temperatures) in order to remove the byproducts (volatile) of the curing process.

\[
\begin{align*}
\text{R} + \text{Si} - \text{O} - & \rightarrow \text{Si} - \text{O} - + \text{RH} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[\text{(X.4)}\]

\[
\begin{align*}
2 \text{Si} - \text{O} - & \rightarrow \text{Si} - \text{O} - \quad \text{Si} - \text{O} - \\
\text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

\[\text{(X.5)}\]

**Room Temperature Vulcanization**

There are two mechanisms for the network formation characterized as RTV [45, 46, 54]. The first is a condensation reaction of silanol groups to form siloxanes with the participation of water and drastic groups, catalyzed by acid or base, as shown in reaction X.6. The process is triggered by the atmosphere humidity and the connections are developed with oxygen atoms. Also the byproducts formed, usually alcohol.

The second mechanism involves an addition reaction between a siloxane, containing vinyl groups and a siloxane crosslinking agent with Si-H functional groups (reaction X.7). The process is catalyzed by a noble metal.
The second mechanism (two part RTV) is very specific. The crosslink density can be controlled very accurately and no byproducts are formed. However two components vulcanization requires a temperature of 60°C, which is not available in the environment (it is also remarkably lower than the 180°C for the HTV Rubber). Therefore the commercially available RTV SIR Coatings are vulcanized according to the first crosslinking mechanism (one part RTV). It is worth mentioning that the byproducts formed in this case (usually alcohol) are volatile and no influence to the material performance is observed after application.

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{HO}-\text{Si} \quad \text{O}-\text{Si} \quad \text{O}-\text{Si} \quad \text{OH} + \text{R}_n\text{Si(OR)ʹ}_n + \text{H}_2\text{O} \quad \text{catalyst} \quad \rightarrow
\]

\[
\text{CH}_3 \quad \text{R} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{R} \quad \text{CH}_3
\]

\[
\text{CH}_3 \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3
\]

\[
\text{CH}_3 \quad \text{Si} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} \quad \text{CH}_3
\]

\[
\text{R} \quad \text{Si} \quad \text{CH} \equiv \text{CH}_2 + \text{H} \quad \text{Si} \quad \text{catalyst} \quad \rightarrow \quad \text{R} \quad \text{Si} \quad \text{CH}_2\text{CH}_2 \quad \text{Si} \quad \text{R} \quad \text{R}'''''
\]

\[
\text{R} \quad \text{Si} \quad \text{CH} \equiv \text{CH}_2 + \text{H} \quad \text{Si} \quad \text{catalyst} \quad \rightarrow \quad \text{R} \quad \text{Si} \quad \text{CH}_2\text{CH}_2 \quad \text{Si} \quad \text{R} \quad \text{R}'''''
\]

**X.4.3 Formulation additives**

Various additives are used depending on the desired material improvements. For RTV SIR coatings used in outdoor insulation a typical formulation includes:

*Solvent*

Coating systems are available in the form of a liquid paint. In order to be applied efficiently, a minimum viscosity level is required. This is achieved with the use of an
appropriate solvent, which is either included from the manufacture (ready to use) or it is added at the application site [3, 9, 55].

The solvent becomes the transfer medium to the insulator surface and after application it evaporates, initiating the vulcanization process. Therefore no remains are found in the cured material. However, the rate of evaporation influences the development of the curing process and therefore different curing times can be observed for different solvents. Also roughness measurements [55] have revealed that the surface quality (appearance, smoothness etc) is also affected, thus possible effects on the coating performance can be assumed.

In the case of naphtha and 1,1,1 trichloroethane, solvents frequently used, a superior performance has been observed for the coating using naphtha. H. Deng et al.[55] compared rod insulators coated with the same material but different solvents in a salt fog chamber. For the coatings using naphtha the time to failure was found longer. Of course it must be mentioned that due to the different viscosity, (the material was applied by dipping) different thicknesses were achieved, 0.79±0.10mm and 0.50±0.10mm for naphtha and 1,1,1 trichloroethane respectively.

However, the use of naphtha is not always possible. Due to its low flash point naphtha is flammable and therefore the possibility of an accident is increased in the case of an energized application. Consequently the application of naphtha is limited only for not energized insulators. Otherwise non flammable solvents, such as 1,1,1 trichloroethane must be used.

*Tracking and erosion filler*

Tracking and erosion are phenomena observed on the material surface. Tracking is an irreversible degradation referring to the formation of conductive paths, which remain conductive even under dry conditions [56]. Erosion is also an irreversible degradation, non conducting, which refers to the loss of material [56]. Both can limit the material performance and lifetime and therefore fillers are added in the formulation, in order to improve the system durability. Alumina Trihydrate (ATH) and Silica are the fillers usually adopted and rarely magnesium oxide [57].

The cause of surface degradation is the electrical activity observed on the material surface during a period of a hydrophobicity loss. Dry band arcing can supply the material volume with energy in the form of heat, which will support the development of chemical and physical changes [58]. The addition of fillers, ATH and Silica, aims to increase the material heat conductivity [59, 60] and further decrease the amount of energy dissipated within the material volume. In addition, in the case of Alumina Trihydrate, when a material temperature of 220°C is exceeded, water is released in the form of vapor (reaction 2.8) enhancing the filler action [46].
\[
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\] 

(X.8)

The filler efficiency and the corresponding material endurance depend on many parameters. The filler type, the amount used, the particle size selected and the degree of bonding to the polymer matrix are some of them to be considered. In the case of ATH, which is the filler selected in many formulations, much research has been done in the direction of the optimum formulation that will conclude to an increased material performance and lifetime.

S.H. Kim et al. [61] investigated the influence of the ATH filler level in the coating formulation. The filler addition resulted to a decrease of the silicone fluid diffusion to the surface and therefore the hydrophobicity recovery process was decelerated. On the other hand it was shown that after prolonged dry band arcing, the coating with increased filler content performed better. The results from R. S. Gorur et al. [62] also pointed out that increased ATH levels provide higher protection levels, however coatings with lower filler levels showed faster hydrophobicity recovery. Therefore, depending on the field conditions, an optimum filler level can be set.

An optimum particle size for the ATH is also suggested. Comparisons performed between coatings of the same concentration and different particle sizes, indicated an optimum particle size of 4.5 μm [63]. In the case of smaller size, dispersion problems were observed and, on the other hand, a larger size increases the surface roughness and slows down the LMW migration.

If Silica is selected instead of ATH, the same protection levels can be achieved provided the appropriate formulation. Studies of L. Meyer et al. [59, 60, 64], R. Omranipour et al. [65, 66] and K. Siderakis et al. [12, 67], indicate that at higher concentrations (> 50%) both fillers yield similar performance. However in the case of lower amounts the ATH filler provides superior performance, due to the additional action of water release [12, 67].

It is worth mentioning however, that even in the case of optimum filler content the possibility of tracking still exists. For the ATH/PDMS system studies performed by S. Kumagai and N. Yoshimura, applying an inclined plane test, revealed that tracking is also possible, at high temperatures (>1600°C) [68, 69]. The mechanism is different since the amounts of carbon formed on the surface are limited and requires the participation of gas byproducts. However a degradation of the material performance is observed [69].

**Adhesion promoter**

Adhesion to the ceramic substrate is a very important property for a coating. In the case of a poor application a failure is possible to occur due to the stress applied from the wind. Additionally the necessity of pressurized water washing must be considered, especially in
applications where thick contamination such as cement, can accumulate on the coating surface. Adhesion problems were experienced with the early coating systems applied [3, 9, 20]. The RTV SIR coatings available today have incorporated appropriate fillers that can ensure the necessary adhesion levels, providing that the ceramic surface has been thoroughly cleaned before the coating application.

Coating colour

A coloring pigment is used to provide the coating colour, usually white, blue, grey or yellow. The selected color does not influence the material performance; however it is a useful tool in order to evaluate the application coverage and the achieved thickness. It is important to notice that depending on the selected color, different impressions about the surface condition can be induced. However, in this case no correlation of the contaminants build up with the coating performance should be done, as in the case of uncoated insulators.

Other fillers

In addition to the above mentioned, a number of other fillers are also included in the material formulation. For example crosslinking agents, condensation catalysts are used in order to enhance the material curing process.

X.5 Hydrophobicity in RTV SIR

Hydrophobicity is a surface property correlated to the material internal structure [49]. It is the result of an energy excess observed, due to an imbalance of the intermolecular forces that develop. Molecules that are near the surface are subjected to attraction forces from the molecules inside the material volume, which are not symmetrical as for the molecules that are away from the surface. This imbalance is described by the surface tension which corresponds to the amount of energy per unit surface (Joule/m$^2$) or the amount of force per unit length (N/m).

When a droplet is found on a surface two contradictory mechanisms are observed. The attraction forces between the droplet molecules, which action is in favor of the droplet surface decrease (form of minimum energy) and the surface tension in the direction of the droplet dispersion. The equilibrium usually achieved is described by the Young equation and especially the value of the contact angle $\theta$.

Silicone rubber is a hydrophobic material, demonstrating values of surface tension remarkably lower than the corresponding values of porcelain and glass but also lower in comparison to other polymeric materials as it can be seen in table X.2. This is the result of the weak intermolecular attractions observed between the Silicone Rubber molecules,
although the molecule structure (backbone) is remarkably stronger (silicon–oxygen bond), in comparison to the other polymeric materials used for outdoor insulation. In addition, the flexibility of the SIR backbone permits the orientation of the side methyl groups towards the surface, pushing the strong silicon oxygen bond away.

Hydrophobicity is the property that will provide the improved performance of a SIR coating in the case of pollution by interrupting the development of the phenomenon, since surface wetting is not achieved. However, during service, periods of hydrophobicity loss are possible to appear [70]. The accumulation of contaminants for example, in the usual case will result to a hydrophilic layer that will hide the original hydrophobic behavior. Additionally, degradation due to various stresses (electrical and environmental) will also reduce the material capability to withstand wetting. Fortunately SIR has the capability to recover hydrophobicity and restore the initial surface behavior. There are two principal mechanisms responsible for the hydrophobicity recovery [71], the reorientation of the side hydrophilic groups away from the surface, and the migration of Low Molecular Weight PDMS molecules from the material volume to the contaminants layer. In the pictures of figure X.5, surface hydrophobicity in a clean and in a contaminated RTV SIR coated surface is illustrated.

![Figure X.5 Surface hydrophobicity in a clean (a) and in a contaminated (b) RTV SIR coated surface](image)

**Reorientation Mechanism**

The inherent hydrophobic behavior of SIR and the remarkably low values of surface tension are strongly correlated to the presence of the side methyl groups in the PDMS molecule and the low intermolecular forces that exist between them [73, 74]. However, under service conditions, the substitution of these methyl groups is possible as a result of various mechanisms [58]. A typical example is shown in reaction 2.10. The substitution of the methyl groups by hydroxyl alters the initial hydrophobic behavior to hydrophilic.
This change may result to a rapid loss of hydrophobicity due to the strong hydrogen bonding forces that develop between the chains [73-75]. However, the PDMS molecules demonstrate a remarkable flexibility when compared to hydrocarbon or fluorocarbon polymers. The rotation about siloxane bonds is virtually free, since the energy necessary is almost zero. Therefore the rotation of the side hydrophilic groups to the material interior is possible, allowing the remaining methyl groups to approach the surface and decrease the demonstrated surface tension [71–75].

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} \quad \text{O} \quad + \quad \text{H}_2\text{O} \quad \stackrel{\text{heat}}{\longrightarrow} \quad \text{CH}_3 \\
& \quad \text{Si} \quad \text{O} \quad + \quad \text{CH}_4 \quad \text{OH}
\end{align*}
\]

(2.10)

**Migration of LMW molecules**

The migration of the low molecular weight PDMS (6 to 15 siloxane monomers) molecules is considered as the primary mechanism responsible for the recovery of hydrophobicity [71, 72, 75, 77]. These molecules are formed during the polymerization process. Due to their small size they are quite flexible and are not included (connected) in the crosslinked network. Consequently, considering the weak intermolecular forces observed, they are free to move within the material volume and diffuse to the surface. When a contamination layer is formed they can penetrate into the layer and change the initial hydrophilic behavior to hydrophobic. Thus, although the surface is covered by a hydrophilic film, eventually a hydrophobic behavior is achieved.

The speed of recovery and the endurance of the migration mechanism are affected from the amount of LMW molecules available. The initial population and type (linear or cyclic) depends on the polymerization process and the vulcanization that follows. Further, during service a possible loss of the LMW molecules can be assumed since they are exposed on the surface. Consequently, a probable depletion of the LMW reservoir, which corresponds to the end of the material lifetime, becomes the primary user concern, and thus the parameters that influence the diffusion process have to be considered.

**Silicone fluid - material thickness**

The amount of the LMW PDMS molecules can be increased either by the addition of silicone fluid or, in the case of a coating, by increasing the material used, thus the coating thickness.
More silicone fluid corresponds to a larger reservoir of LMW molecules, considering that the fraction of the material mass, characterized by low molecular weights, depends on the production procedure (polymerization and crosslinking). It is worth mentioning that the recovery of hydrophobicity is possible by a part (<20%) of the LMW molecules initially available [76]. Consequently this will result to a faster hydrophobicity recovery and a longer material service time [77, 78].

However, laboratory investigations revealed that the addition of silicone fluid has an adverse effect on the material performance, since the heat stress applied is enhanced [55]. This occurs due to the decrease of the material heat conductivity, since the amount of filler (tracking and erosion) in the material mass is reduced. Consequently more energy, available from the surface electrical activity, is dissipated within the material volume and therefore aging is accelerated. The same effect is observed in the case of a thickness increase [55, 78], since the heat resistance formed between the surface activity and the substrate becomes greater. Of course a minimum thickness is required in order to minimize the possibility of exposing the substrate due to erosion. Thus, an optimum thickness of 0.38 mm is suggested [55].

**Material formulation**

The molecules migration can be affected by the presence of fillers in the material formulation. Especially in the case of ATH, laboratory studies have revealed that increased filler levels correspond to decreased migration rates, mainly for two reasons [79, 80]. Firstly, the ATH particles attract the PDMS molecules and therefore the movement to the surface is more difficult. This action becomes stronger for smaller ATH particle size [80]. Secondly for a certain formulation the addition of filler corresponds to lower amounts of silicone fluid and therefore LMW molecules.

**Influence of the Crosslinking degree**

LMW molecules do not participate to the crosslinked network due to their increased mobility. Therefore crosslinking does not seem to influence their number. However there is a possible influence to the molecules diffusion to the surface. The electrical activity observed, either during periods of hydrophobicity loss (dry band arcing) or even if the surface is hydrophobic (corona along the water droplets) supplies energy to the material that can support oxidation reactions (X.10 following X.9), which finally conclude to a silica layer near the surface [72, 81, 82].
This layer impedes the LMW molecules diffusion and therefore the hydrophobicity recovery process. Additionally it must be mentioned that a possible increase of the surface tension is probable to occur due to the increase of the siloxane bonds near the surface.

*Influence of the contamination nature*

The physical and chemical properties of the contamination layer formed on the surface affect the efficiency of the migration mechanism. The LMW molecules have to penetrate into the layer and, by changing the composition, transform the initial hydrophilic behavior to hydrophobic. In fact, since the substances usually found on the insulator surface are characterized by higher surface energy, the LMW movement occurs more in the form of absorption from the contamination and less as a penetration [83]. This occurs in the direction of energy minimization and therefore the larger is the difference of the surface energy (LMW and contaminants), the more intense is the absorption observed. Also the physical structure (for example a porous material) has a role in the migration development [83, 85]. Additionally the layer thickness also affects the recovery time. Increased amounts of contamination correspond to slower hydrophobicity recovery [86].

*Amount of LMW*

The LMW molecules that have reached the surface are exposed to the environment. For example, cleaning mechanisms such as rain and wind can be assumed to be capable of removing the LMW molecules together with the surface contamination. Thus, the influence to the LMW molecules surface population must be examined.

**Wind:** The possible influence of wind to the amount of LMW molecules on the surface has been investigated by H. Deng and R. Hackam [87]. RTV SIR specimens were
subjected to an artificial wind with a speed ranging from 7.2 km/h to 7.7 km/h for a period of 20 months. No effect to the LMW content was found.

Surface wetting: various wetting mechanisms are observed in the environment (rain, fog, mist etc). The degree of influence depends on the cleaning capability, thus the amount of water deposited on the surface. For example, a laboratory comparison between water immersion and condensation wetting [88] revealed a decrease of the mass for the immersed samples thus a decrease of the LMW molecules amount. This change is enhanced when increasing the immersion time in water. H. Deng et al. measured a 16.6% mass reduction after 12 months of water immersion in a saline solution [87]. However the stress applied in the case of water immersion is remarkably higher than the observed in the environment, especially by rain, which appears to be the most alarming wetting mechanism, since it provides the largest amount of water among the environmental mechanisms. Consequently the influence of the environmental wetting to the LMW molecules population and further hydrophobicity is insignificant.

Temperature: the LMW molecules diffusion is a temperature dependant procedure. Increased ambient temperature will accelerate the molecules movement to the surface and therefore reduce the necessary recovery time [88-90].

UV Radiation: The PDMS backbone cannot be affected from the sun originated UV radiation, since the Si-O bond energy is higher than the energy supplied through UV radiation. However a reduction of the LMW molecules number is possible to occur. Chemical changes regarding the side groups can be observed, due to the UV influence [91], resulting to the attachment of the LMW molecules to larger chains [57]. Consequently UV radiation can reduce the amount of LMW molecules and therefore hydrophobicity [88, 91].

Influence of the electrical surface activity

Two forms of electrical activity may appear on the coating surface, dry band arcing during a period of a hydrophobicity loss and corona. The energy supplied in both cases can support physical and chemical changes of the material surface and thus affect the amount of LMW PDMS molecules present. The possible mechanisms initiated due to dry band arcing have been investigated by S. H. Kim et al. [58]. The chemical reactions that occur are associated with the following processes:
Scission and interchange of bonding or chains: Reduction of the chain size is observed due to scission and interchange, thus an increase of the LMW molecules amount can be assumed,
Hydrolysis of the siloxane bonds and hydrocarbon groups: Hydrolysis reactions require the presence of water, thus mist, fog or rain. In linear polymers, random chain scissions are observed leading to a rapid decrease of the molecular mass (Reaction X.9). Consequently in this case also an increase of the LMW molecules amount can be assumed.

Oxidation of hydrocarbon groups and crosslinking of siloxane bonds: Hydrolysis reactions are usually followed by oxidation of hydrocarbon groups and crosslinking of the siloxane bonds (for example reaction X.10). In this case, a number of LMW molecules are connected to the crosslinked network (cross linking) and therefore the amount of LMW molecules is decreased.

A two fold influence to the LMW molecules population occurs due to the corona stress. Depending on the conditions corona can support oxidation reactions followed by crosslinking, which will result to the formation of a surface silica layer [72, 81, 82]. In this case the amount of the LMW molecules on the surface will decrease and the migration from the material bulk will be blocked. In addition the coating surface will become brittle and hydrophilic. On the other hand scission of the Si–O bond can occur under corona stress and therefore the amount of the LMW molecules can increase [81, 92]. It is worth mentioning that UV radiation from corona discharges supplies higher energy amounts than the sun originated UV [93].

The electrical and environmental stresses observed, influence the material structure either by splitting the chemical bonds present in the PDMS molecules, or in the opposite direction by supporting the formation of additional bonds. Consequently, the amount of LMW molecules available varies during the service years depending on the loss and generation rate observed [80, 94, 95]. Further, the possibility of a mechanism attenuation is postponed and the material lifetime elongated.

**X.6 Electrical performance of RTV SIR coatings**

Leakage current and dry band arcing are the first electrical stages of the pollution phenomenon. The application of a coating aims to minimize the possibility of a flashover by suppressing the surface electrical activity from the start. The property responsible is surface hydrophobicity, which prevents wetting and therefore the development of conductivity. However as already mentioned the possibility of a hydrophobicity loss has to be considered, as a result of various mechanisms. Therefore, the capability of the coating to remain hydrophobic or regain its initial behavior in the case of a loss (hydrophobicity recovery), rise as the crucial properties, which will determine the application efficiency and lifetime.

The ability of a coating to suppress surface activity has been investigated both in laboratory and field conditions [6, 9, 10, 13, 15-16, 19-31, 35-41, 62, 96–112]. In the lab,
usually salt fog tests and rotating wheel dip tests are applied, involving various stress scenarios, (fog and dry periods, fog conductivity, test duration, electrical stress etc). Leakage current is the parameter used for the material evaluation in both cases and usually an investigation of the material condition is performed by using appropriate methods (contact angle, ESCA, FTIR etc). In the field, leakage current and material analysis methods are also incorporated for the coating evaluation.
In both cases the coating ability to suppress the surface activity is strongly correlated to the hydrophobicity recovery process. Material formulation in combination with the stresses applied and their influence to the LMW migration mechanism are the crucial parameters that determine the application efficiency and material lifetime.

X.6.1 Application of RTV SIR coatings in high voltage substations

High voltage substations have a critical role in the operation of a high voltage transmission system. A possible outage can have a great impact to the system stability and operation, in many cases greater than a corresponding outage in a transmission line, since a substation is in fact a power system node. Furthermore, pollution performance is an issue of concern for the transmission system operators, especially in the case of coastal systems.

Many maintenance methods have been implemented, in order to ensure the fault free performance of a substation, in pollution conditions [23]. Nevertheless, the application of RTV SIR coatings has been proved to be the optimum method in the case of already installed equipment for many reasons [19, 23, 39-41]. Firstly, the application of RTV SIR coatings can ensure an improved pollution performance. The improvement achieved, occurs due to the hydrophobic surface behavior which resists the development of leakage current and dry band arcing, even in the presence of contaminants [6, 9, 10, 15, 19, 39-41]. Secondly, being available in the form of paint, RTV SIR Coatings can be easily applied on insulators, regardless the profile geometry and insulator use [3, 11, 19, 39-41]. This can be quite convenient, considering that in a substation, insulators have additional roles, as for example current and voltage transformers, bushings etc, requiring many different housing sizes and thus geometries. Thirdly in comparison to silicone grease, the expected application lifetime can exceed a period of ten years, depending on the experienced conditions [3, 19, 23, 39-41]. The difference in this case is that there is no encapsulation feature but instead a hydrophobicity transfer capability is evident, sufficient to change the initial hydrophilic behavior of the deposited contamination film to hydrophobic. The elongated material lifetime further allows large scale application, at a reasonable cost. Finally, the application can take place at a time convenient for the utility and thus it can be considered as a preventive measure. Consequently, in the case of substations and especially for already installed equipment, RTV SIR coatings represent an efficient method to improve the pollution performance of the ceramic insulation.
X.7 Conclusions

Room temperature silicone rubber coatings provide an efficient solution for the improvement of ceramic insulation pollution performance, especially in the case of high voltage substations. The primary advantage is the material capability of maintaining a hydrophobic surface behavior, even in the presence of contaminants on the insulator surface, due to hydrophobicity recovery mechanisms available. The material behavior is strongly correlated to the material formulation and especially to the properties of the base polymer and also of the fillers incorporated. Further the electrical performance and the experience acquired from many applications worldwide, reveal the remarkable improvement achieved by the application of the coating. In addition the importance of the hydrophobicity recovery mechanism due to the migration of low molecular weight PDMS molecules is also evident.

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