SILICONE COMPOUNDS FOR HIGH-VOLTAGE INSULATORS: COMPOUNDING SILICONE RUBBER

PART 1 0F 2 (SERIES)

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INTRODUCTION

This paper is part one of a two-part series; it discusses the basic question "What is silicone rubber?" In answering that question, it will be shown that there are differences in the basic structure of silicone rubber and that not all silicone is the same.

This discussion also covers the compounding of silicone polymer into silicone rubber; it describes how the proper selection of ingredients and their mixing are critical to making a silicone compound suitable for high-voltage insulators. **Since silicone rubber is a mixture of ten or more ingredients — and the actual silicone polymer is about 30-percent base — selection of ingredients is crucial to achieving a product with a long service life in the harsh environments seen by electrical insulators.**

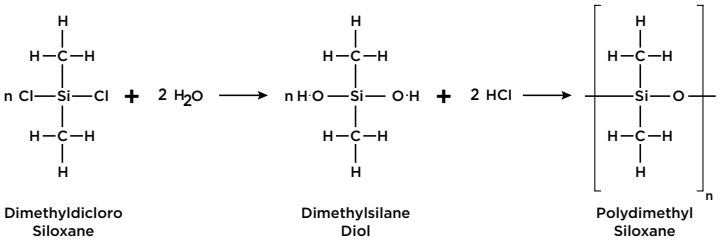
Part two in this series is dedicated to the testing of silicone rubber compounds for the high-voltage insulator market.

WHAT IS SILICONE RUBBER?

Silicone rubber is a synthetic, or man-made, compound known for its weatherability and ability to maintain useful properties over a wide range of temperatures. **Silicone rubber is an electrical and thermal insulator. It is resistant to oxidation, has low surface energy, and resists degradation from ultraviolet (UV) radiation. These properties make silicone rubber a good choice for electrical insulators**.

The properties of silicone rubber come from the structure of the polymer. Heat stability and resistance to oxidation and weathering are derived from the strength of the siliconoxygen bonds.[1] A flexible polymer chain gives low surface energy (hydrophobicity) and low temperature flexibility.[2] Organic (containing carbon) side groups attached to the silicon atoms allow for crosslinking and tailored applications (i.e., increased heat resistance, solvent resistance, increased strength, decreased compression set, increased arc track resistance, or increased cure rate[3]).

A polymer is composed of very large molecules that contain atoms arranged one after another in a chain-like manner, with each link of the chain being the same basic unit. The word polymer is Greek for "many parts;" thus, polysiloxane is many siloxane units. The chain-like arrangement repeats in regular cycles, so the structure can be written as repeating segments (Figure 1). The segments are identical, with the number of repeating units indicated by the letter "n."[4] When "n" is small (low molecular weight), the polymer exhibits low physical properties, and in some cases, it may be a liquid. As "n" increases (molecular weight increases), the polymer's physical properties are improved.[5] Silicone rubber polymer chains are between 3,000 and 10,000 monomer units in length.[6]



[**Figure 1**] Polymerization of Dimethyl Siloxane

The raw material for silicone rubber is sand, which is converted into elemental silicon by heating with carbon. Conversion to chlorosilanes is by the directprocessing of methyl chloride and elemental silicon, which gives a mixture of compounds that must be distilled to separate the dimethyldichlorosilane. Once separated, dimethyldichlorosilane is processed with water to form the dimethylsilane diol. The dimethylsilane diol condenses to form methyl siloxanes that are then polymerized to form the polydimethylsiloxanes that are used to make silicone rubber.[7] This silicone rubber is now ready for compounding directly into silicone rubber formulations as gum stock, or it is put into base stock, which is then used for compounding.

Dimethylsiloxanes can be modified by changing the carbon groups attached to the silicone. Each modification is done to gain specific properties for the base rubber. **This allows for tailored silicone rubber for each application, such as oil resistance, extreme low temperature flexibility, low compression set, transparency, etc.**

As shown in Figure 1, silicone rubber contains a repeating silicon-oxygen backbone and has organic methyl groups attached to a significant portion of the silicon atoms by silicon-carbon bonds.[8] **Silicone rubber is neither organic nor inorganic.[9] Silicone rubber is classified as an organo-silicon compound.[10] This is due to the very important bond between carbon (organic) and silicon (inorganic).**

COMPOUNDING

In the field of polymer technology, rubber compounding is a complex subject. The compounder's ability to select and combine polymers and additives to obtain a mixture that will develop the necessary physical and chemical properties can take years to master.[11]

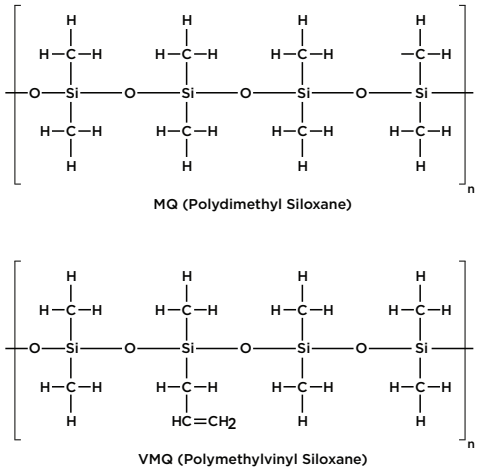
Silicone rubber can be composed of silicone gum, silicone base, reinforcing fillers, extending fillers, additives, curing agents, and special purpose materials. **The proper choice of ingredients will result in a compound tailored specifically to the end-product needs**. Low compression set, high temperature use, low temperature flexibility, solvent resistance, high-voltage electrical insulation and arc track resistance all require specific selections of raw materials.

SILICONE GUM

Silicone gum (gum stock) is the pure silicone polymer. It is composed of an alternating silicon-oxygen backbone. Common in high-voltage insulators are MQ (dimethyl siloxane) and VMQ (methylvinyl siloxane), as shown in Figure 2.[12] Although they appear to be quite similar, they do give very different properties to the silicone rubber compound. MQ is the standard silicone rubber, which must then be modified to make the VMQ. VMQ is useful for accelerating the cure and increasing the flexibility of the cured rubber. Although both MQ and VMQ are gum stock — which is the raw material for the silicone base — they may also be directly added to a silicone rubber compound.

SILICONE BASE

Silicone base (base stock), often referred to as "silicone rubber," is considered a raw material for silicone rubber compounds. Base stock is a mixture that may contain one or more silicone gums, extending fillers, reinforcing fillers, low molecular weight silicone fluids, structuring agents, and additives. Structuring agents are additives put into the silicone base to reduce "crepe hardening." Crepe hardening is the property of silicone rubber compounds to harden over time, before the rubber has been cured.



[**Figure 2**] Structure of MQ (Dimethyl Siloxane) and VMQ (Methylvinyl Siloxane)

FILLERS

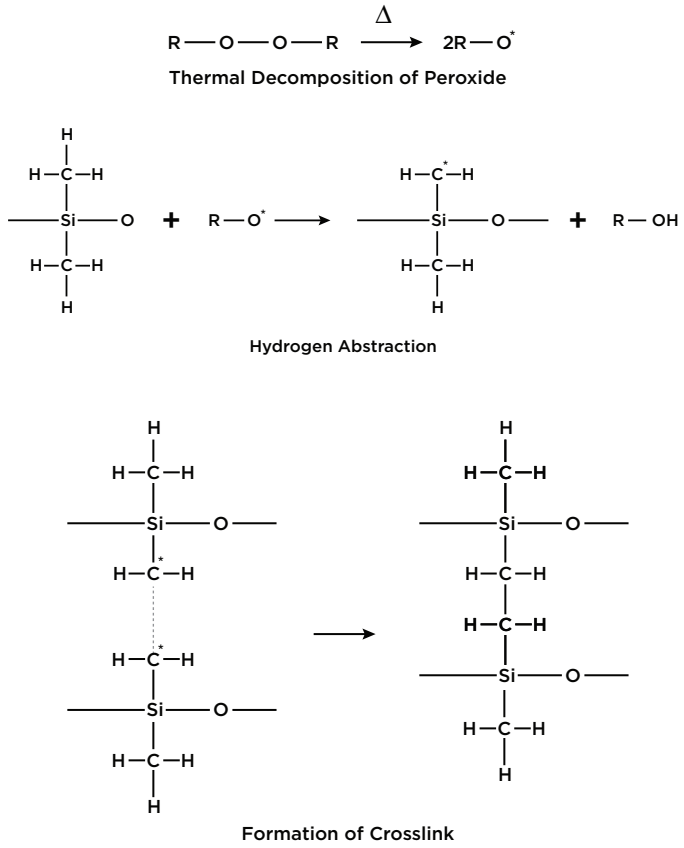
There are two types of fillers: reinforcing and extending. The reinforcing type can be used to improve tensile strength, modulus, tear strength and abrasion resistance. Common silicone rubber reinforcing fillers are fumed silica, aerogel silica and carbon black. The extending filler is a semi-reinforcing or non-reinforcing material. It may be used to impart some desirable property and also extend the formulation. Common extending fillers are ground quartz, titanium dioxide, clay, whiting, alumina trihydrate (ATH), and zinc oxide.

SPECIAL PURPOSE ADDITIVES

Special purpose additives are used for a specific purpose, which is not normally required in the majority of rubber compounds. Examples of such additives are antifungal agents, blowing agents, colorants, re-odorants, structuring agents, and hydrophobicity enhancers. ATH is used in nearly all insulator compounds to impart a high resistance to electrical tracking and to act as a flame retardant.

VULCANIZING AGENTS

Vulcanizing agents are ingredients used to cause a chemical reaction, resulting in the cross-linking of elastomeric molecules. Through chemical cross-linking, silicone rubber compound is converted from a soft putty-like material to a solid temperature-stable material. There are many types of vulcanizing or curing agents used. Organic peroxides are the most widely used for high-voltage insulation. Vulcanization in silicone rubber forms bonds between the carbon side chains; therefore, all crosslinks are carbon-carbon bonds. Crosslink reactions for both MQ (Figure 3) and VMQ (Figure 4) are shown. The MQ reaction has three discrete steps. The reaction for VMQ shows two discrete steps. The termination step — elimination of free radicals — has been omitted. The reactions shown have good agreement with experimental observation.[13]



[**Figure 3**] Three-step crosslink reaction for peroxide cure of MQ

PROCESSING AIDS

Processing aids are added to a rubber compound to help mold flow and release, as well as aid in the mixing of the compound. These ingredients can reduce mixing time, increase mixing

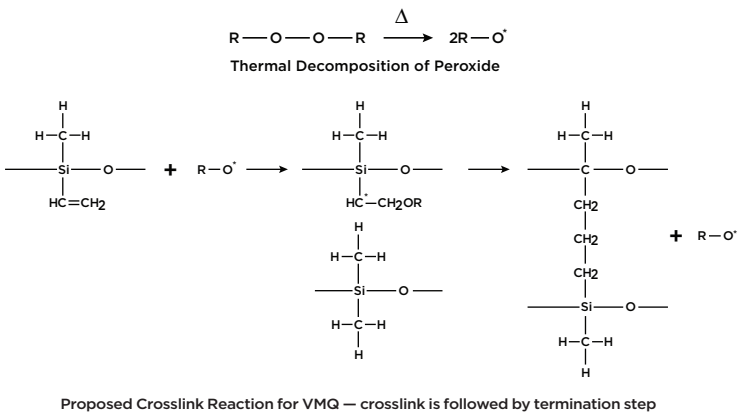
efficiency, and reduce the tendency of the compound to stick to the processing equipment.

COUPLING AGENTS

Coupling agents provide a chemical bond between the filler and the elastomer. For electrical insulators, the coupling agent is a bridge between the ATH and the polymer. These additives can greatly improve the electrical properties, modulus and tensile strength.

PLASTICIZERS AND SOFTENERS

Plasticizers and softeners are used either as an aid to mixing (lower viscosity) or to provide flexibility at low temperatures. Many ingredients in this group may also be considered as processing aids. Silicone rubber compounds usually use low molecular weight silicone fluids for plasticizers. If one were to think of the silicone rubber gum stock as a long chain, low molecular weight silicone fluid would just be a shorter chain made out of the same material. Low molecular weight silicone fluid can be added to the base stock or directly to the silicone rubber compound.



[**Figure 4**] Two-step crosslink reaction of VMQ using organic peroxide

SUMMARY

This paper has given a brief explanation of many different types of materials found in silicone rubber compounds. Considering all the different materials available, it should become apparent that no two silicone rubber compounds are the same. It is also important to understand that the selection of ingredients used in the compound directly affects the performance of the rubber; therefore, controlling the compound formulation is the only way to ensure that the material will have consistent performance over time.

In all aspects of the rubber production, from selection of raw material, to mixing and testing of rubber compounds, to manufacture and testing of insulators, Hubbell Power Systems (HPS) continues to build on the Ohio Brass foundation: pioneering the use of polymer insulators, developing test methods for polymer insulating compounds, and developing insulator test methods.

Silicone rubber compounds have several great inherent characteristics, such as a high degree of hydrophobicity, high resistance to ultraviolet energy, and high resistance to heat. **A silicone rubber compound for high-voltage applications needs to be developed through detailed and comprehensive analysis of its properties and behavior under conditions similar to those encountered in the field**. Please read Section Two of this publication series on silicone compounds to learn how HPS tests its materials to ensure the highest level of performance and durability in its products.

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