

VOLTAGE STABILIZING ADDITIVE ASSESSMENT IN POLYETHYLENE INSULATION

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ABSTRACT

Experimental screening of voltage stabilizing additives has been conducted using the needle-plane geometry in a voltage-step protocol to failure. Excellent performance of both the fused aromatic additive family and other claimed voltage stabilizing additives has been demonstrated; however, the correlation of performance with general concepts based upon ionization potential and electron affinity appears to deteriorate outside of the fused aromatic family. The "molal field stability" (MFS) parameter is compared to that of similar compositions as reported by others using different test geometries. The results are discussed with regards to the degradation mechanism and the practical utilization of voltage stabilizing additives.

KEYWORDS

Voltage stabilizers, electrical tree retardants, breakdown strength.

INTRODUCTION

In the early 1960s some of the first patent applications were filed on the use of organic additives, referred to as voltage stabilizers, to improve the resistance of polyolefins to electrical breakdown [1-4]. It was recognized that the electrical breakdown of polyolefins occurred at well below the theoretical breakdown strength, and the root cause for this behavior was suggested to be the presence of small contaminants, defects and voids within the material. The electrical breakdown mechanism was described as the result of damage to the polymer matrix done by the impact of high-energy electrons and/or ions in the high-field regions in the vicinity of the flaw. (An excellent review of concepts for electrical breakdown mechanisms has been provided by Eichhorn [5].) So called "voltage stabilizing" additives were considered to interfere with this high-energy process to absorb energetic electrons and/or quench ionized polymer resulting from high-energy impact, so as to result in substantial increases in electrical breakdown strength (but still below the theoretical breakdown strength) or in the lifetime of the polymer exposed to a given electrical stress.

In some of the earliest work to enhance electrical breakdown strength and voltage endurance of polyolefins, the addition of hydrocarbon oils, which include substituted aromatics or halogenated aromatics, was found to provide a means to increase electrical breakdown strength by 50% or more [1]. Extensions of this concept were exploited in further developments by Simplex Wire with use of halogenated aromatic compounds such as dibromoanthracene [4]. While the compatibility and solubility of the solid voltage stabilizing additives within polyolefins was limiting and potentially detrimental if a crystalline additive "defect" was formed, the Simplex work enabled the utility of a broader range of voltage stabilizing additives [3] and the incorporation of the additives into polyolefins through liquid aromatic carriers [4].

The concept of electron donating and electron accepting nature of the voltage stabilizing additives proposed by Simplex is similar to the correlations between the needle-test characteristic voltage performance and the electron affinity and ionization potential of various polycyclic aromatic species described by Ashcraft, and later included in the previously mentioned review of Eichhorn [5]. Ashcraft noted that the most effective additives evaluated by Eichhorn were aromatic compounds, and particularly those having amine or nitro functionality. However, it was also noted that many of the most effective additives have a tendency to migrate out of the polyethylene. With anthracene also near the top of the list in Eichhorn's earlier work, Ashcraft focused on evaluation of several additional polycyclic aromatic additives. While fused aromatics provide an excellent means for voltage stabilization, the high melting points and poor compatibility within the polyolefin posed barriers to effective utility. Also in the mid 1970s, an approach was patented by Kureha Kagaku Kogyo Kabushiki Kaisha to functionalize pyrene with several short chain alkyl groups in an effort to improve compatibility with polyolefins and thereby yield a more permanent voltage stabilizing property [6].

Despite the promising performance of polycyclic aromatics, these materials have not realized success as voltage stabilizers in a commercial application. Alternative approaches have emerged which seem to have originated from the observations that acetophenone, a byproduct of the crosslinking reaction when using dicumyl peroxide as a free-radical initiator, has excellent voltage stabilizing characteristics. Of course, acetophenone is also volatile and will diffuse out of a manufactured cable. A logical progression from acetophenone to more recent voltage stabilizer concepts is described within US Patent 6,696,154 [7]. Namely, ketones or alcohols of aliphatic and/or aromatic molecules were proposed as voltage stabilizing additives or mixtures (EP-A-89490 and EP-A-111043), including acetophenone and benzophenone. Then in later work, carboxylic acids or esters of diaryl ketones as voltage stabilizers were disclosed (DE 2,709,139), such as benzophenone-2-carboxylic acid. These molecules are similar to byproducts of the peroxide crosslinking reaction and were considered to have minimal impact on the crosslinking chemistry. Other functionalized benzophenone derivatives were later disclosed as voltage stabilizing additives, including hydroxy, alkyloxy, alkyl, aryl and halogen functionality (JP 47-28042). The work within US Patent 6,696,154 described a further class of functionalized benzophenones.

Significant effort has been dedicated towards the identification of molecular properties which define a good voltage stabilizer within the aromatic family of additives, and the concepts of electron affinity and ionization potential have been brought forward again by Kisin and co-workers [8]. However, these concepts have not been extended into a comprehensive description which includes