

# Conference Paper



## THERMAL STABILITY OF DIELECTRIC FLUIDS

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## THERMAL STABILITY OF DIELECTRIC FLUIDS

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### ABSTRACT

The thermal stability of dielectric fluids in electrical equipment is generally governed by reactions with other materials and with impurities that cannot be avoided. Mineral oils are susceptible to metal catalyzed oxidative degradation, involving a peroxide intermediate. Suitable inhibitors can be used to decrease the rates of this process. Both oxidative and pyrolytic degradations are considered for silicone dielectric fluids. Ascarrels are basically stable thermally where they are presently used, provided they are properly purified and other materials present do not react with them. Thermal ratings of sulfur hexafluoride depend upon reactions of the gas and its electric discharge products with the solids in a device, and an adsorber can be used to remove reactive products.

### INTRODUCTION

This paper discusses the thermal stability of some dielectric fluids with regard to their practical use. These fluids are mineral oils, silicones, ascarrels and the gas, sulfur hexafluoride, whose operating temperatures are in the range of 100°C and higher. Continuous demands to increase the operating temperatures of electrical equipment has generated considerable effort on this subject. A general view of its significance and ramifications is first presented here, in the Introduction. This will serve as the basis for dealing subsequently with the various individual dielectrics.

Knowledge of thermal stability characteristics, specifically aging, of dielectrics determine how individual ones may be used in various applications, where one may not be used, and means by which a dielectric is improved. The essential criterion for acceptability on the basis of thermal stability is that the physical and dielectric properties are not impaired by chemical reactions during reasonably long periods of operation at the expected maximum temperature. Aging consideration, in fact, sometimes enforce a compromise of electrical or of physical properties in choosing a dielectric. It is noted that electric discharge effects should not be confused with thermal effects, since both may occur during a functional aging test of a dielectric.

Investigations of thermal aging of a dielectric fluid usually follow this sequence. First, conditions, especially temperature levels, that cause significant degradation are established. This information is often sufficient to decide on the use of a specific dielectric. There are a number of ASTM tests which, with some modifications where necessary, may serve this purpose. As interest in a dielectric grows, its rates of

degradation as a function of temperature are obtained to determine its useful life under various operating conditions.<sup>2</sup> These rates are generally based on a simple criterion such as a single physical, chemical or dielectric change. Finally, detailed studies are made to determine the significant chemical reactions and their rates that occur during degradation under various conditions. Only mineral oils, of the fluids discussed here, have been subjected to all these stages of investigation. The present status of knowledge of thermal degradation of the other fluids is relatively meager.

For the most part, interest in the aging of a dielectric fluid is concerned with degradation effects of one or more other materials to which it is exposed in an electrical device. Examples of these materials are water, oxygen, metals, solid insulators, and dissolved impurities such as ionizable or reactive compounds and salts of metals. Some react directly with the dielectric, as oxygen for example, and others, such as copper salts, may catalyze degradation. In contrast to pyrolytic degradation of a dielectric fluid, where only its own molecules are involved in the reaction, these unavoidable reactants generally cause the thermal stability to decrease. Therefore, most aging studies of dielectric fluids do not include pyrolysis as a single factor.

A characteristic of a degradation process of a dielectric fluid is that this is often due to only small amounts of reactant and ensuing products. The reacting materials noted above are generally present in low concentration in the fluid or a very small part of it is exposed to them as in the case of a reacting metal. Degradation products at concentrations of parts per million have been found to cause substantial increases in the dissipation factor of dielectrics. Examples of such impurities are hydrolyzable chlorine in chlorinated diphenyls<sup>3</sup> and carbonyls<sup>4</sup> in transformer oil. This fact, that reactants and products involved in the degradation of a dielectric fluid are in small amounts, presents certain problems in pinpointing causes of degradation. It may be difficult to determine the nature of these materials, or even whether the fluid itself was degraded. The source of the deleterious effects may be decomposition or reaction products of an impurity, where the dielectric itself is not involved. Likewise, problems are encountered in attempting to elucidate effects which may be due to very small amounts of catalyst.

However, once a deleterious reactant and/or product is known, then often advantage can be taken of its small concentration to improve the

thermal stability of the fluid. This is achieved by use of an additive or suitable purification, or both. A small amount of a substance that specifically reacts with a harmful reactant can be added to remove it or change it to a relatively innocuous form. There is some leeway in choosing an additive as it need not have as good dielectric properties as the fluid itself because it is used in low concentration. An additive that reacts with a reactant is known as an inhibitor, and one reacting with the products is called a scavenger. The purification process of a dielectric fluid is often designed to remove materials that are capable of degrading easily, as well as those that impart poor dielectric properties to it in their original form.

The factors contributing to the thermal stability of a dielectric fluid in an electrical device can be conveniently summarized under two main categories. One deals with degradation effects and the other with means to upgrade the thermal stability. Degradation effects are related to:

- The reaction of the fluid with materials from which it cannot be isolated, such as oxygen and metals, and
- Catalytic effects due to certain impurities.

Increased thermal stability is achieved by:

- Purification.
- Inhibitors, and
- Scavengers

#### INDIVIDUAL DIELECTRICS

##### Mineral Oils

Specially purified and fractionated mineral oils are used extensively in transformers, cables, capacitors, and circuit breakers of high power ratings. Their maximum operating temperature for continuous service where they do not have severe reactions with the other components of the device has usually been rated at 105°. These oils are mixtures whose major constituents are aliphatic hydrocarbons, aromatics and naphthenes. Much attention has been devoted to their thermal stability to assure prolonged function of the equipment in which they are used. There are a number of conflicting conclusions about influences on their thermal stability. This occurred probably because of differences in composition, impurities, fractionation and purification of the oils studied, and use of various criteria for thermal stability. However, at this point, some of the effects of degradation of these oils in electrical equipment as well as a number of the factors that affect this process are fairly well understood. This is based on studies of transformer oil, which will be emphasized here.

Thermal stability considerations of a mineral oil invariably deal with its reaction with oxygen

and the catalysis of this reaction with copper and iron. Here, moisture is particularly harmful, and great care is taken to exclude it. Exposure to copper and iron cannot be avoided in most electrical devices. The final products of this reaction are acid, sludges (insoluble acids and soaps),<sup>5</sup> water and carbon dioxide. Their deleterious effects include lowering the insulating quality of the oil, deterioration of paper or pressboard barriers and corrosion of conductors and casing. Sludge can also obstruct flow of the oil that is necessary to dissipate heat.<sup>6</sup> There are ASTM tests for acid<sup>7</sup> and for sludge<sup>8</sup> formation in transformer oil. Besides their use in quality control, these tests have been the experimental basis for various thermal stability studies of mineral oil.

The discussion of the degradation process, here, is based principally on a review and two specific studies of the degradation of mineral oil dielectrics. The review is the proceedings of a symposium on insulating oils that was held in 1958 at the Institution of Electrical Engineers under the chairmanship of Gosling.<sup>9</sup> One of the studies was made by Molchore and Mills,<sup>4,10,11,12</sup> who made careful analysis of intermediate products of the degradation and also controlled the composition of the oil. The other is by Jell, Stuart & Ross<sup>13</sup> who emphasized details of oil composition in developing their conclusions.

The degradation of a mineral oil, according to oxygen uptake, generally proceeds kinetically as follows.<sup>9,9</sup> First there is an induction period, next the rate becomes autocatalytic, then it is constant, and finally the rate of oxygen uptake decreases. The deleterious effects in the oil become evident in the last two stages. The inhibition stage is diminished by the presence of soluble copper or iron.<sup>6, 9, 10</sup> A meaningful mechanism of this process must deal effectively with the autocatalytic phenomenon.

The course of the degradation of the oil has been shown to be associated with the production and concentration of a hydroperoxide intermediate. It is the basis of the following series of free radical reactions that have been proposed. The oil is designated as RH, and R·, RO<sub>2</sub>· and RO· are free radicals.

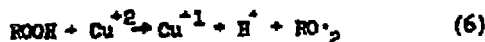


These reactions would account for the inhibition stage. The autocatalytic stage that follows is explained by a number of reactions, where the hydroperoxide decomposes to regenerate free radicals and thereby propagates a free radical chain. One such reaction could be a unimolecular decomposition of hydroperoxide.<sup>13</sup>



However the evidence points to a catalytically induced free radical chain, with copper or iron

catalyst. It has been proposed<sup>9, 11</sup> that soluble copper ions react as follows with hydroperoxide.



Also a series of reactions was suggested where hydroperoxide reacts with copper oxide, on the surface of copper, to form soluble complexes which decompose to free radicals. Soluble copper has been shown to be effective at concentrations of less than 200 parts per billion causing auto-catalysis and an increase in dissipation factor.<sup>4, 10</sup> The inhibition period decreases with increasing concentration of copper.<sup>6, 9</sup> This mechanism and associated effects probably also apply for catalysis by other metals such as iron. The auto-catalytic reaction is kept in check, from becoming explosive, by terminating reactions where free radicals combine to form non-reactive products.

Melchiorre and Mills<sup>4</sup> claim that catalysis with copper is enhanced by nitrogen and sulfur impurities that occur in the oil. They suggested that these impurities promote solubilization of copper. However, Jezl, Stuart and Ross<sup>13</sup>, and others maintain that the sulfur compounds act as inhibitors to the oxidation.

The final products, mainly acids and sludge, are formed during the last two stages of the oxidation, when the rate of oxygen uptake is constant and then decreases. Acids are derived from the aliphatic hydrocarbons in the oil, and the sludge, largely insoluble acids and carboxylic salts, from the aromatics.<sup>6, 9, 13</sup> The mechanism for formation of these materials must be very complicated, and it involves decomposition of hydroperoxide, whose concentration decreases during this period, and various reactions of the oxygenated free radicals.<sup>13, 14</sup>

From the above it can be seen that deterioration of a mineral oil can be inhibited by deactivating hydroperoxide, the free radicals, or the metal catalyst. Each of these modes of inhibition will be discussed, as well as purification as means to increase the thermal stability of a mineral oil.

Mineral oils for electrical applications are generally purified by successive extractions with sulfuric acid; but hydrogenation and solvent extraction are also used. Various studies have shown that the sulfuric acid process can be applied to a limited extent.<sup>6</sup> The first few extractions achieve increased stability. However, when they are continued beyond a certain point, where the aromatic content of the oil begins to be significantly diminished, the oil becomes less stable to oxidation. It was concluded that the aromatics in the oil act, at least in part, as an inhibitor to the oxidation.

An inhibitor that extends the inhibition period until it is consumed is known as an anti-oxidant. When it is exhausted, the oil may be replenished with more after the oil is suitably

refined again. The compound DBPC, 2, 6-di-tert-butyl-para-cresol, and occasionally some of its analogues, have been used effectively for this purpose. Its presence has been shown to double the life of a transformer.<sup>15</sup> There are a number anti-oxidants, of the amine compound type, that are more effective for mineral oils than DBPC. But they cannot be used in electrical applications because they cause large increases in the dissipation factor.

There are different opinions about the reactions of an anti-oxidant that inhibit oxidation. One<sup>16</sup> maintains that it reacts with the hydroperoxide to yield relatively inert products. Another claims that the antioxidant suppresses the propagation sequence by reacting preferentially with the chain carrying free radicals.<sup>17</sup> These active radicals are converted to stable molecules, while the anti-oxidant radical, which ensues, is relatively inert.

Deactivation of a metal catalyst to inhibit oxidation has been achieved by use of certain chelating agents. Metal ions form complexes with these compounds in which they lose their ionic character, and hence their ability to propagate free radical chains. Also, a metal surface may be passivated by adsorbing the chelating agent. This would prevent reaction of the metal oxide, copper oxide for example, with hydroperoxide to form a complex that generates free radicals. Since a metal deactivator reacts with a limited supply of catalyst, which is not replenished during the oxidation, its effect should be relatively permanent. In contrast, the effect of an anti-oxidant is not permanent as shown above. Melchiorre and Mills<sup>11</sup> found better inhibition of oxidation by a metal deactivator than by an anti-oxidant. However, presently, di-tert-butyl para-cresol is used much more extensively than metal deactivators.

It would seem logical to add both kinds of inhibitor to an oil, one that reacts with hydroperoxide and one that deactivates a metal catalyst, to get a relatively high degree of thermal stability. However, this may result in too high a dissipation factor since these additives are fairly polar and only a small amount can be tolerated in the oil. Also, decreasing their concentrations to satisfy the dissipation factor requirement may result in both being altogether ineffective.

The following is a recipe of a sufficiently stable transformer oil, for operation at about 100°C that is based on experience and the thermal stability considerations noted above.

|                                              |              |
|----------------------------------------------|--------------|
| Aromatics                                    | - 30%        |
| Naphthenics                                  | - 5%         |
| Aliphatics                                   | - 65%        |
| Sulfur (?) and nitrogen containing compounds | <10 PPM each |
| Additive                                     | - .15%       |

Inhibitors are generally not added to the oil for power transformers, where special care is taken to avoid causes of oxidation. Oxygen is carefully excluded, and the oil is maintained as dry as possible.

### Silicone Fluids

There are a number of silicone fluids which are rated for relatively high temperature applications, generally for 150°C and sometimes even above 200°C, as dielectrics. They are of the methyl and phenyl silicones, which are polymers with these general formulas.



where the R's are methyl or phenyl groups. The C-H (primary), Si-C, and Si-O bonds in these structures are relatively stable thermally and resistant to oxidation, compared to the C-H (secondary and tertiary) and C-C bonds in a mineral oil. The silicone oils also have some very desirable dielectric and physical properties, such as low losses and low viscosity-temperature coefficients. However their high cost has restricted their use to small sized devices.

The following are some of the characteristics of the degradation of silicone fluids that are pertinent to their use in electrical devices. Pyrolysis occurs above 200°C, and causes volatilization and a decrease in molecular weight. Exposure to oxygen is deleterious above 150°C, and results in increases in viscosity and, finally, gelation. Copper was found to inhibit the oxidation of a silicone fluid at 200°C, while other metals, such as lead, steel, tin and zinc, had no significant effect.<sup>18</sup> This is in marked contrast to the oxidation behavior of mineral oils. Acids, which can often be avoided, induce gelation.

A study was made by Scala, Hickman and Loeffler<sup>19,20</sup> of some of the kinetics of oxidation of silicones, which included dimethyl silicone (DC 200, Dow Corning). Some oxidation of this liquid was detected at 150°C; and it gelled at 250°C, when the rate of oxygen absorption was relatively high. A mechanism was proposed for the oxidation of silicones, which is essentially the same as that given above for mineral oils, with a hydroperoxide intermediate in the propagation of a free radical chain. Gelation is probably induced by the acids that are generated, since acids advance polymerization and cross-linking of a silicone.

Use of inhibitors to suppress oxidation effects in silicone fluid dielectrics is severely restricted by the magnitude of the temperatures, above 150°C, at which they have to be effective. It is important that the inhibitor does not introduce a quantity of ions into the dielectric medium that would substantially increase its dissipation factor. While a number of anti-oxidants have been found which contribute little to the dissipation factor at temperatures of 100-125°C in mineral oils, this is less likely to be achieved at 200-250°C for silicone fluids because the dissipation factor increases rapidly with temperature.

The highest temperature rating of a silicone fluid can be obtained by isolating it to avoid oxidation, and then the thermal stability is based on pyrolytic reactions. Schiefer<sup>21</sup> determined apparent initial decomposition temperatures for three silicone dielectric fluids, in nitrogen. These are based on measurements of vapor pressure as a function of increasing temperature, at a rate of 2°C per minute, and are the point where the log vapor pressure versus 1/(absolute temperature) plot changed slope. They were found to be 315°C for dimethyl silicone, 320°C for phenylmethyl-dimethyl silicone and 372°C for phenylmethyl silicone. Their magnitude is related only qualitatively to the degree of thermal stability, as they probably reflect fairly high rates of decomposition due to the high rates of temperature rise used for the vapor pressure measurements. In fact, the maximum operating temperatures of these silicone fluids are not more than 250°C, which is considerably below those values. A mechanism for the pyrolytic decomposition of a silicone fluid was suggested by Lewis.<sup>22,23</sup> It was based on weight loss data for a series of dimethyl silicone liquids (DC 200, Dow Corning). First, the polymer chain was assumed to cleave at a site where an impurity atom was located. One of the fragments would then react to give a product with a cyclic structure. This kind of product has been found to be formed in the pyrolysis of a silicone.

### Askarels

A number of dielectric fluids which are widely used in capacitors and transformers are known as askarels. This is a generic name that pertains to their non-flammability. These dielectric fluids are generally certain chloro diphenyls and chloro benzenes. The most common chloro diphenyls are mixtures of isomers, of trichloro diphenyl (Aroclor 1242), of tetrachloro diphenyl (Aroclor 1248) and pentachloro diphenyl (Aroclor 1254). There are two chloro benzenes in this group, the 1, 2, 4-trichloro and the 1, 2, 3, 4-tetrachloro derivatives. They are used in solution with a chlorinated diphenyl, generally to lower its viscosity. The thermal stability of askarels is relatively high with regard to pyrolysis and oxidation. In fact, their operation capability at high temperatures, above 150°C, is limited by the occurrence of high dissipation factors resulting from dissolved impurities, and not to the onset of thermal instability. Often, however, the thermal rating of a device in which they are present has to be relatively low, or an askarel can not be used, because of deleterious solubility effects, as they act as solvents and swelling agents for many organic resins and components. This has to be considered regarding the stability of dielectric or structural materials that are exposed to an askarel, and the possible introduction of an impurity from the solid to the liquid, where it can be harmful.

Thermal degradation of askarels begins to become significant at about 200°C. Munch<sup>24</sup> determined

<sup>24</sup> Monsanto trade name.

the effects of air, copper, iron, lead-tin solder and aluminum on the change in dissipation factor of Aroclor 1242 due to heating at 200°C for up to 800 hours. Dissipation factor changes are often more sensitive to the presence of deleterious degradation products, than results of chemical reactions used to detect them. He found, here, that none of these variables individually had a substantial effect on the thermal stability of this fluid. The decrease in thermal stability due to air was further enhanced by the presence of copper. An ASTM method<sup>25</sup> is available to determine the stability of an askarel at 200°C and 210°C, with air present. It serves mainly for quality control.

Askarels for electrical applications are required to be free of an impurity which easily generates hydrogen chloride.<sup>5</sup> This effect can lead to instability of an electrical device. Such an impurity may be a compound with substituted chlorine, in an aliphatic hydrocarbon or in an aliphatic branch of an aromatic, or an aromatic with added chlorine. The presence of these deleterious impurities is detected by analyses for hydrolyzable chlorine (with alcoholic sodium hydroxide).<sup>26</sup> These tests are sensitive to parts per million,  $\pm .1$ , hydrolyzable chlorine.

#### Sulfur Hexafluoride

The use of sulfur hexafluoride as a dielectric medium in high voltage equipment, which includes high power circuit breakers, transformers, x-ray apparatus and high frequency devices, has increasingly focused attention on its thermal stability characteristics. The main concern is its reactivity, as well as that of its products of discharge, with the solid components of an electrical device. In the gas phase, however, where there is no effect of a solid, sulfur hexafluoride is quite stable pyrolytically, at least to 500°C.<sup>27,28</sup> Very little information is presently available about the various possible thermal reactions of sulfur hexafluoride with metals, insulators, semiconductors and other components of electrical equipment, to serve as a basis for temperature ratings. In contrast, more has been published about reactions of its products of electrical discharges.

The significant consequences of thermal reactions of sulfur hexafluoride in electrical equipment are loss of this gas and deterioration of the solids. A meaningful study of this would have to consider possible effects of impurities that may be present, such as moisture and air, on the reactions. Some data was obtained by Mears<sup>29</sup> on heating of sulfur hexafluoride with various metals and insulating materials at 150°C and at 223°C for 270 days. The metals were

silicon steel, mild steel, copper and aluminum. This listing is in order of their observed degree of reactivity, with silicon steel being most reactive. It appeared that all the materials tested are quite compatible with sulfur hexafluoride at 150°C, which should not be exceeded.

Activated alumina was tested, in this study, as a scavenger for reactive gaseous products. It did reduce the concentration of corrosive gas that was produced by decomposition of sulfur hexafluoride.

When the use of sulfur hexafluoride in electrical equipment entails considerable discharges, the reactivity of the products of discharge with the other components has to be considered regarding the overall stability. The products that are of concern are those that remain after the discharge, or are also formed then. These are acidic,<sup>30</sup> comprising of fluorine and lower fluorides of sulfur, as well as hydrogen fluoride and oxyfluorides which are due to the presence of moisture, oxygen and organic compounds.<sup>31</sup> Absorbents such as activated alumina have been used, quite effectively to lower their concentrations.<sup>30,31</sup> Schumb, Trump and Priest<sup>29</sup> found that both metals and nonmetals are attacked by the products of a low current dc discharge in sulfur hexafluoride. The metals they tested followed this order of reactivity with these products: brass > copper > steel > stainless steel > aluminum. This order of reactivities should be compared with that for the thermal reactions of metals with sulfur hexafluoride. The difference in relative positions of copper may be of some significance. Some data were obtained recently by Kamazashi<sup>31</sup> and by Takuma<sup>32</sup> on the exposure of several polymer films, which are used as insulators, to the products of corona discharges in sulfur hexafluoride. On the basis of weight loss, the following order of resistance to these products was found: polytetrafluoroethylene > polyethylene > polystyrene > polypropylene > polyethylene terephthalate > vinyl chloride > cellulose triacetate.

Understanding of the reactions of sulfur hexafluoride and of its discharge products has as a back up the chemistry of fluorine and hydrogen fluoride. Reference to the reactions of these materials and methods used to handle them is useful for electrical application of sulfur hexafluoride to help exploit its desirable dielectric properties.

#### CONCLUDING REMARKS

Presently, the various dielectric fluids that are available and the methods used to prepare and maintain them are adequate to satisfy most thermal requirements for electrical equipment. It is the solid insulating member, of organic nature, that often limits the thermal rating and operational life of a device. However, as a shift occurs to more thermally stable and more solvent resistant solid insulators, the promise of increased thermal ratings will eventually call for similar

improvements in the fluid media. This would be achieved by upgrading the thermal stability of present fluid dielectrics and developing new ones.

The use of dielectric fluids at higher temperatures than now, will demand even more attention to their degradation phenomena and effects on dissipation factor. It is reasonable to expect that very careful and new techniques will have to be used to exclude impurities that could induce decomposition or increase the dissipation factor. Mechanisms of degradation and means to inhibit it, and the nature of deleterious impurities may well be quite novel, especially where new liquids and solid dielectrics are used.

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