AEROSPACE RECOMMENDED PRACTICE

ARP6167

Issued 2013-11

Etching of Fluoropolymer Insulations

RATIONALE

Provide definition and recommended practice for the etching of fluoropolymer electrical wire insulations.

1. SCOPE

This SAE Aerospace Recommended Practice (ARP) describes the etching of fluoropolymer electrical wire insulations to ensure that all facets of the process from the chemistry to the processing, to the storage and handling are well defined.

1.1 Purpose

The purpose of the SAE Aerospace Recommended Practice (ARP) is to provide a standard practice guide for etching of Fluoropolymer electrical wire insulations. The ARP is subject to change to keep pace with experience and technical advances.

2. APPLICABLE DOCUMENTS

The following publications form a part of this document to the extent specified herein. The latest issue of SAE publications shall apply. The applicable issue of other publications shall be the issue in effect on the date of the purchase order. In the event of conflict between the text of this document and references cited herein, the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

2.1 SAE Publications

Available from SAE International, 400 Commonwealth Drive, Warrendale, PA 15096-0001, Tel: 877-606-7323 (inside USA and Canada) or 724-776-4970 (outside USA), www.sae.org.

AIR5717	Mitigating Wire Insulation Damage During Processing and Handling
ARP6400	Recommended Practice for Processing and Handling Wire and Cable with Silver Plated Conductors and Shields

TO PLACE A DOCUMENT ORDER: **Tel: 877-606-7323 (inside USA and Canada)**
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SAE values your input. To provide feedback on this Technical Report, please visit http://www.sae.org/technical/standards/ARP6167

2.2 ASTM Publications

Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, Tel: 610-832-9585, www.astm.org.

ASTM D5946-09	Standard Test Method for Treated Films Using Water Contact Angle Measurements
ASTM D2578	Dyne Pens

3. GENERAL

The purpose of chemical etching fluoropolymer wire insulations is to enhance the bonding of materials to their surface. The chemistry of etching is achieved by the abstraction of a fluorine atom from a monomer unit and the formation of a free radical. Beginning with PTFE (C2F4) the etching process removes the fluorine from the surface. This etched layer is very thin, only angstroms deep. The etching process then develops double carbon to carbon bonds (C=C), Carbonyl, Carboxyl, Hydroxyl groups and epoxides.

3.1 Etching Quality

The quality of etching as measured by the formation of a boundary layer onto which one can adhere other materials depends on:

a. The etching agent.

b. The etching conditions, i.e., the temperature, reagent concentration, and contact time.

c. The polymer being etched. This process will work with PTFE, FEP, CTFE, ETFE, PVDF, and PFA. It will not work well with irradiated (XLETFE) ETFE insulation.

3.2 Chemistry of Etchants

a. Ethylene Glycol Dimethyl Ether or MONOGLYME is the simplest of the three etchants and has the greatest affinity for sodium and is the easiest solvent with which to form the sodium naphthalene complex. The resulting etchant is very sodium rich but also very viscous, sometimes needing to be thinned for particular applications. The closed cup flash point of this solvent is low (30F). It is recommended to store these etchants under refrigeration in order to limit deterioration.

b. Diethylene Glycol Dimethyl Ether or DIGLYME while it dissolves less sodium napthalene in complex than MONOGLYME, has a much higher flash point (134F) and makes an etchant with the viscosity of about water. It is very stable at room temperatures and above and does not exhibit the same spontaneous decomposition as MONOGLYME does at temperatures near and above its flash point.

c. Tetraethylene Glycol Dimethyl Ether or TETRAGLYME is the most complex of the three solvents. It has a very high flash point (230F). An etchant made with this solvent yields marginal bond strengths since the complexity of the solvent inhibits release of the active ingredient - sodium - to the etching process.

3.2.1 Chemical Etching Detailed

Different polymers are built of different monomers. For example, PTFE is built by combining many monomer units with the structure $CF_2=CF_2$ into a single long chain. Each monomer unit is connected to two others, one at each end, except for the two end units, which are called terminal units. If one connects n monomer units to each other one obtains the polymer: $[-CF_2-CF_2-]_n$. In typical polymers, n is very large and may be in the range of 5000 to 100 000. If n is small, i.e., 10 to 2000, the material may behave like a paste and it is often referred to as pre-polymer. Other polymers are built from other monomers, e.g., PVdF is built by combining the monomer Vinyledene di-fluoride, VDF, $CH_2=CF_2$ to form the polymer PVdF, $[-CH_2-CF_2-]_n$.

When two or more monomers are used together to make the polymer, a co-polymer is produced which properties depend on the ratio of the different monomers used to make it. If only a very small amount of a second monomer is added to the main monomer, a modified polymer is formed. For example, if small amount, (say 0.01 to 0.5 mole %) of the monomer $CF_2=CF(CF_3)$ is co-polymerized with $CF_2=CF_2$, one obtains a modified polymer with much greater plasticity than PTFE. Such modified polymers are a lot easier to work with, e.g., extrude or calendar. When the monomer $CH_2=CF_2$ is co-polymerized with perfluoro (methyl vinyl ether), $CF_2=CFO(CF_3)$ the elastomers Viton GLT and Kalrez are formed.

The polymeric chains occupy the volume of the solid are characterized by how the polymer atoms are arranged relative to each other or by how the polymer chains are arranged relative to each other. If the atoms are arranged in a repetitive way, e.g., each carbon atom occupies a corner of a cube and many such cubes are arranged near each other, then that zone of the solid volume is called crystalline. If the atoms are not arranged in any specific form relative to each other, then that zone of the solid volume is called amorphous.

3.3 Amorphous Zones

In general, every polymer will contain crystalline and amorphous zones and their relative abundance will depend on the following main factors:

a. The symmetry of the monomer unit. More symmetric monomers will produce more crystalline solids.

b. The maximal temperature that the material was exposed to most recently and provided that it exceeded certain critical temperature. The greater the temperature the material was heated to, less hysteresis will be left in it and the new cooling conditions will have a greater influence on its crystalline morphology (i.e., the material will have less “memory” of its previous history).

c. The rate at which the polymer was cooled down. Cooling the material faster will result in a greater fraction of amorphous material vs. crystalline material.

   The pressure on the polymer during the cooling. The effect of pressure is more complex and will depend on the temperature at which it is applied and on its direction. To an extent, greater crystallinity will be produced under greater pressures.

d. The uniformity of cooling of different adjacent zones of the polymer. Non-uniform heating or cooling of the polymer will result in material with stress zones with high amorphicity and a greater tendency for cracking or breaking at these zones. (Such breaks are called “Stress fractures.”)

The amorphous zones of the polymer are etched much faster than the crystalline zones. Therefore, changing the amorphicity of the polymer will change how it will etch and the depth of etching at the same etching conditions. Since the amorphicity depends on the rate of cooling once the material is heated above certain temperature, the rate of cooling will affect the way it will be etched.

The amorphous zones of the polymer are much more open to permeation than the crystalline zones. Therefore, changing the amorphicity of the polymer will change the rate of gas permeation through it.

In general, one desires the material to have a medium amount of amorphicity to be etched well. Too much amorphicity will produce a weak boundary layers and too little amorphicity will require longer etching time and will result in a poor etch.

3.4 Chemistry of Etching

The solid polymer consists of many millions of very long chains of monomers, long molecules which are entangled with each other. The situation may be analogous to a vat containing many long snakes which are entangled with each other. Suppose now that we give the molecules a chance to move relative to each other and pull them in one direction. Instead of having a randomly, oriented long chains, we shall obtain oriented chains or oriented polymer with some layering. An example of a process which partially orients polymer molecules is calendaring. In this process, the polymer is heated and pulled at the same time. Orienting the molecules often increase the material crystalinity. The process of attaching adjacent polymer chains to each other to form a three dimensional solid from the loosely laying chains is called cross-linking. This process produces a solid with much greater dimensional stability but it reduces its processability.

The following should be noted:

a. The mechanical properties of layered or oriented material will have different values in different directions.

b. Heating oriented material can result in shrinking of the material.

c. The shrinking can be to different extents in each direction.

d. Etching of layered material can produce a very weak oriented boundary layer which is not attached to the bulk of the polymer and which may peel off easily. Such a layer will produce very weak bonds and is highly undesirable.

The chemistry of etching is rather complex. For simplicity sake, this ARP uses the etching of PTFE as an example. Etching of ALL fluoropolymers commences by the abstraction of a fluorine atom from a monomer unit and the formation of a free radical depicted by the following formula where C' denotes a free radical associated with the carbon atom.

$$[\text{-CF}_2\text{-CF}_2\text{-}]_n + \text{NANP-} \rightarrow \text{-C'F-CF}_2\text{-}[\text{-CF}_2\text{-CF}_2\text{-}]_{n-1} + \text{NaF} + \text{Naphthalene}$$

This chain with the free radical on it can react in several ways as follows:

a. It can lose another fluorine atom and form a double bond between two adjacent carbons on the same polymer molecule. (Such a bond is called an OLEFINIC bond.)

b. It can react with oxygen to form first a peroxy radical and subsequently an epoxide, a carbonyl or a hydroxy group. These groups form very strong bonds.

c. It can rearrange and result in the braking of the chain and subsequently in the formation of a carboxy group. These group forms very strong bonds.

d. It can react with water or hydroxy radicals.

e. It can react with a free radical from an adjacent chain and cross-link the two chains. This process is undesirable and does not enhance adhesion.

f. It can form ACETYLENIC bonds which occur when the carbon atoms associated with OLEFINIC bonds releases additional fluorines and form TRIPLE bonds between adjacent carbons.

3.4.1 Color of OLEFINIC and ACETYLENIC Bonds

The formation of OLEFINIC and ACETYLENIC bonds is the result of the elimination of fluorine from the surface. When more OLEFINIC and ACETYLENIC bonds are formed on carbons removed from each other by one atom (called conjugated bonds), the color of the material will become darker. OLEFINIC and ACETYLENIC bonds are precursors to the oxygen-containing functionalities. ALL these groups enhance adhesion but to different extents. Elimination of fluorine which results in cross linking of chains does not form color or functionalities which bond easily. For the most part, the color of the surface is a good indication of the quality of etching, however, it is not always the case. The color is viewed on a much deeper layer than the adhesion layer. Perfluorinated monomers, i.e., monomers which contain only carbon and fluorine atoms (like Tetrafluoroethelene (TFE) or Hexafluoropropylene (HFP)), etch to form a lot darker layers than polymers made out of monomers which contain also hydrogen or oxygen. The reason is that perfluorinated polymers can form a lot more conjugated double and triple bonds than other polymers. Etched pefluorinated polymers will form a layer which is much easier to adhere to and which forms a lot more stable joints than polymers which monomer contains also hydrogen, say PVdF or Tefzel.

3.5 Storage of Etchant

The etchant chemistry (solution) has a shelf life in in a sealed container. Exposure to air significantly reduces shelf life. Instructions for storage, use and recycling of the etchant must be followed to safely use and maintained the effectiveness of the etchant (see 3.7).