Measurement of Fluoride Generated From Fluoropolymer Wire Insulations

Coatings and Contamination Workshop, July 2011

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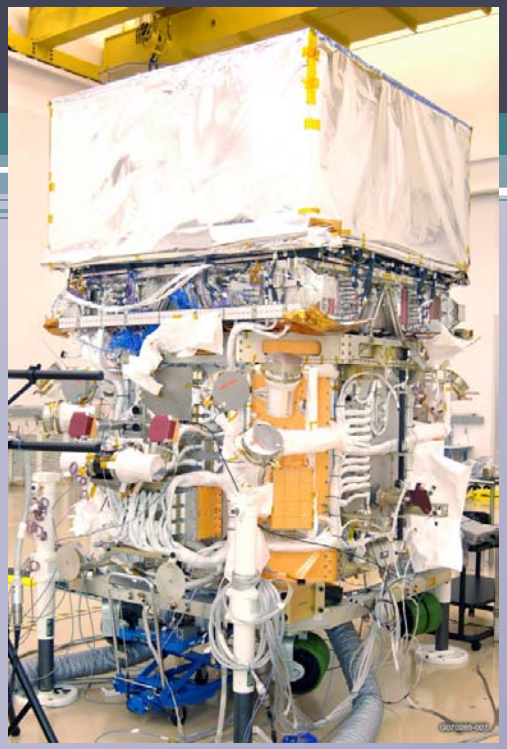
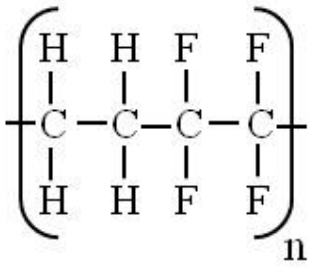


Outline

- Corrosion problem with ETFE insulated wires
- Development of test methods
- Threshold for fluoride content
- Conclusions and recommendations

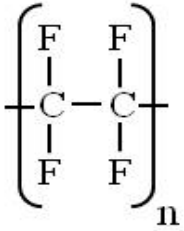
Ethylene tetrafluoroethylene (ETFE)

- Ethylene tetrafluoroethylene (ETFE) is a fluoropolymer that is commonly used in wire insulations for flight hardware.



Ethylene tetrafluoroethylene (ETFE)

- ETFE has better resistance to radiation and higher mechanical strength properties than other fluoropolymers such as PTFE.



Polytetrafluoroethylene (PTFE)

ETFE versus other fluoropolymers

Property	Unit	Teflon® PTFE	Teflon® FEP	Teflon® PFA	Tefzel® ETFE
Tensile Strength	MPa	21-34	23	25	40-46
Elongation	%	300-500	325	300	150-300
Flexural Modulus	MPa	496	586	586	1,172
Impact Strength	J/m	189	No break	No break	No break

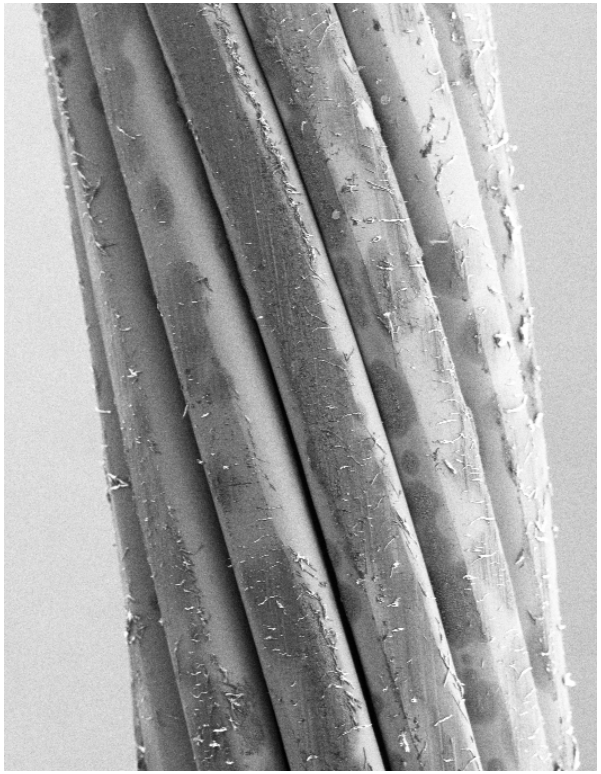
PTFE: Polytetrafluoroethylene
FEP: Fluorinated ethylene propylene
PFA: Perfluoroalkoxy copolymer
ETFE: Ethylene tetrafluoroethylene

ETFE versus PTFE

- ETFE does not have the cold flow issues that are present in incorrectly sintered PTFE insulations.
- PTFE wires need to be checked for correct sintering.
  - Under sintering leads to two different crystal structures
  - Over sintering leads to cracking
- Problems with ETFE?

Definition of problem

- ETFE insulated wires have been prone to corrosion issues.
- As early as 1998, some projects noticed corrosion of pre-wired connectors.
- These connectors were attached to wires with ethylene tetrafluoroethylene (ETFE) insulation.
- Corrosion was noticed in wires and connectors that were bagged or in a confined area.



Outcome of prior investigation

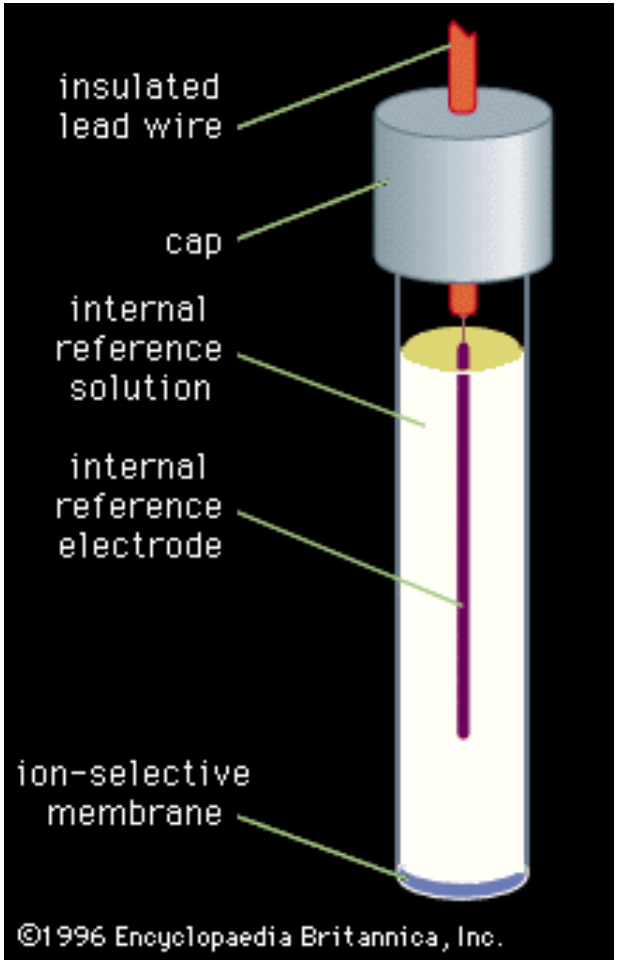
- Carbonyl difluoride which is released during manufacturing, starts the problem.
- COF_2 generation is not contrary to any wire specification requirements.
  - $COF_2 + H_2O \rightarrow CO_2 + 2HF$
- Hydrogen fluoride reacts with copper and forms copper compounds.
- GSFC NASA Advisory (NA-GSFC-2003-03)
  - Store wire connectors and wires in open bags in a humidity controlled environment.
  - Ideally, store in packages that are constantly purged with nitrogen gas.
- GIDEP alert EA-P-98-02 also cautions about risks of ETFE insulations.

Fluoride Measurement Test Method

- AFRL conducted a round robin study to develop a test method for measuring fluoride released from wire insulations.
  - MEB at Goddard participated in this round robin study.
  - This type of test will be useful to manufacturers when they are evaluating wire manufacturing procedures.
  - It will be useful for customers when screening wires.

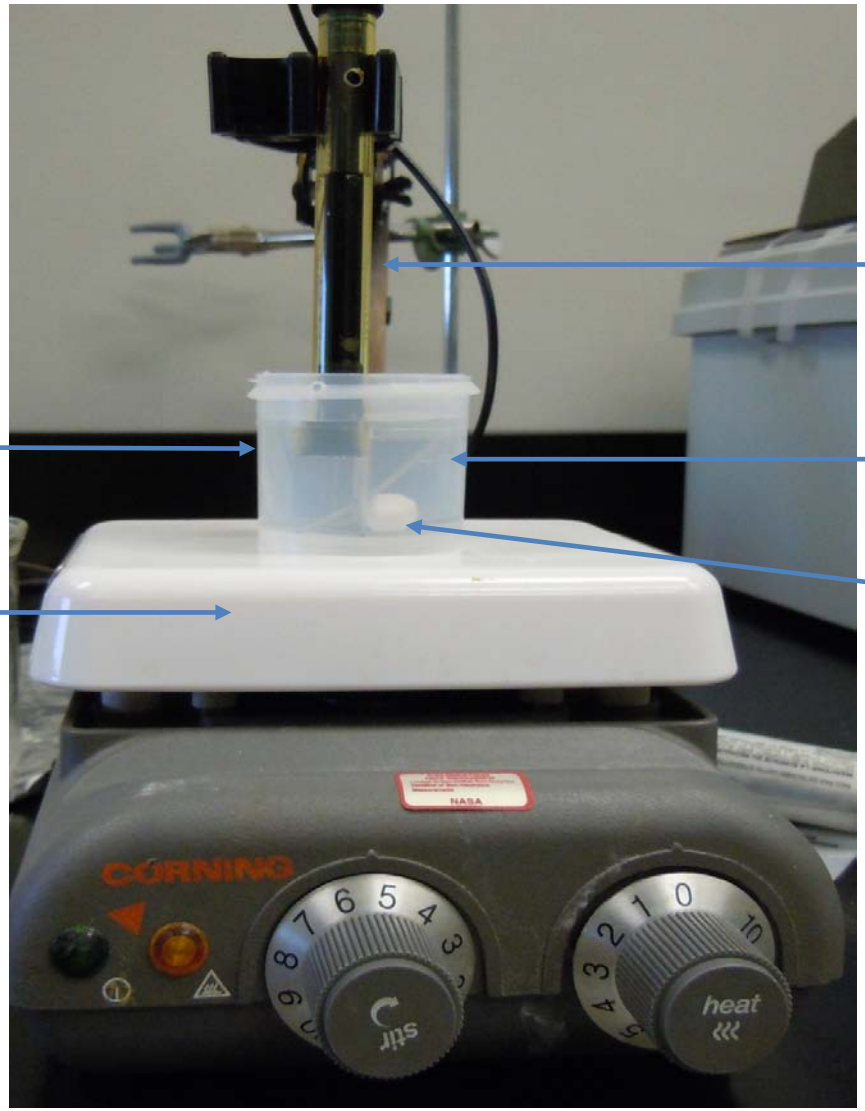
Round robin test method

- 7 day soak of insulation in 70 °C water.
- Measurement of fluoride concentration using a fluoride ion selective electrode (ISE).
- ISE measures potential of the solution.
- Potential is directly proportional to the concentration of fluoride.
- Use solutions with known fluoride concentration to prepare a calibration curve.



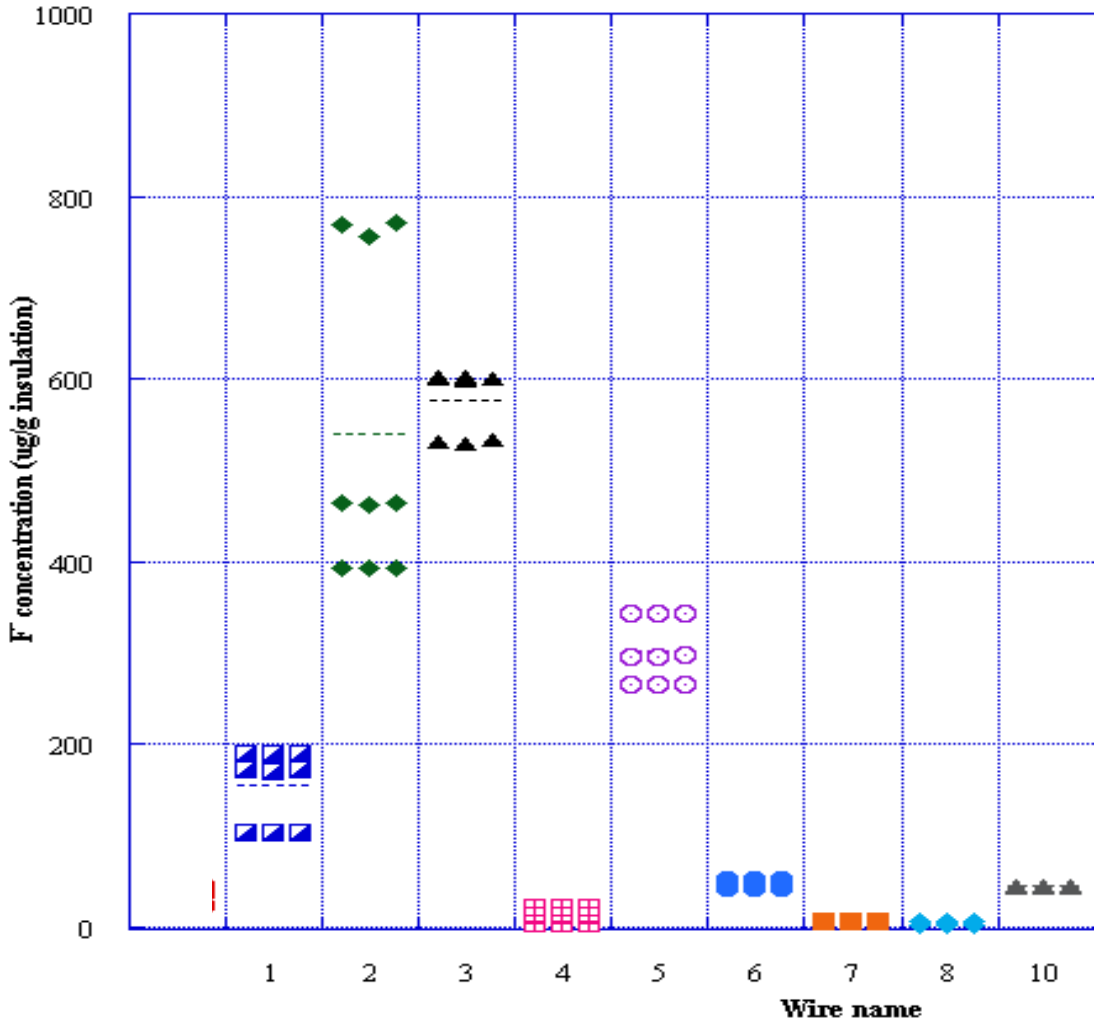
Ion-selective electrode. [Art]. In *Encyclopaedia Britannica*. Retrieved from http://www.britannica.com/EBchecked/media/3147/An-ion-selective-electrode-for-use-in-potentiometric-measurements

Test setup with ion selective electrode



Fluoride extracted after 7 day soak

Results for all wires tested in Round robin study

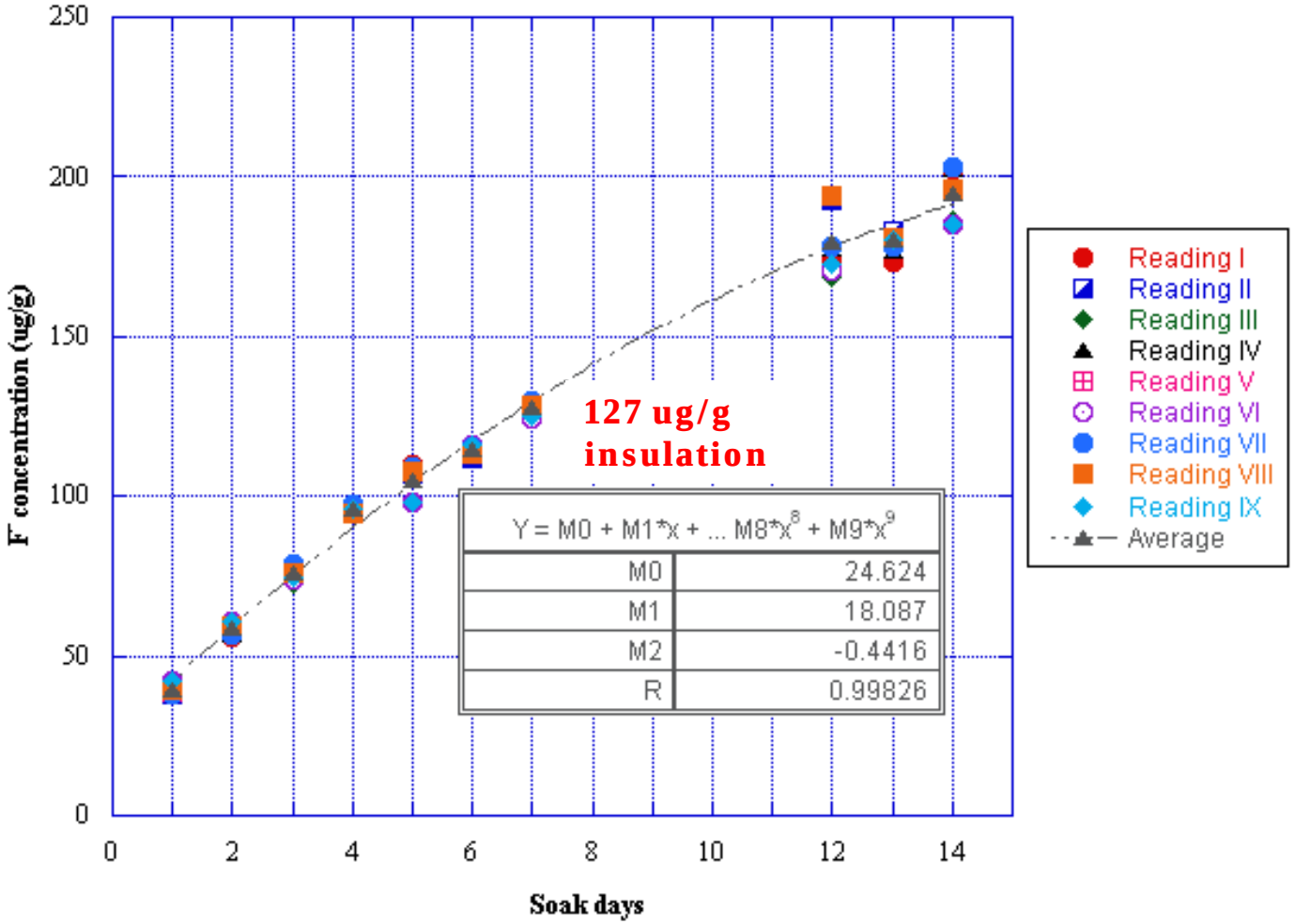


Effect of soak time on extracted fluoride

- 7 day test is often too long.
- Lengthy extraction is unnecessary for standard ETFE wires which often release higher amounts of fluoride.
- As long as fluoride concentration is “high enough”, one day soak may be sufficient.

Effect of soak time on extracted fluoride

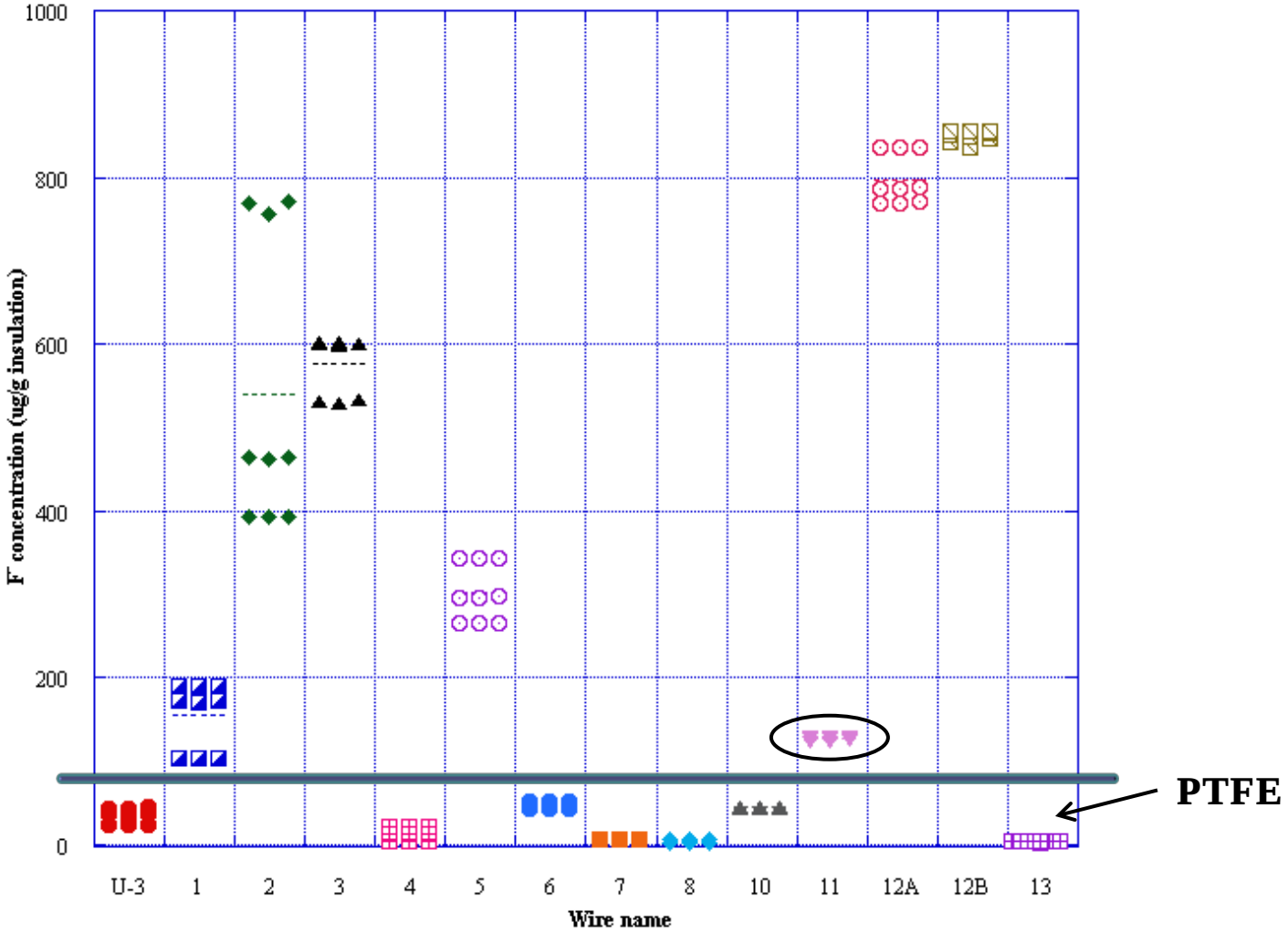
Varying soak time with wire 11



- Measurable fluoride after 1 day of soak for this wire.
- WI for this method is in process.

Fluoride extracted after 7 day soak

Results for all wires tested in this study



- Short soak may be appropriate for wire insulations above the 100 ug/g mark shown above.

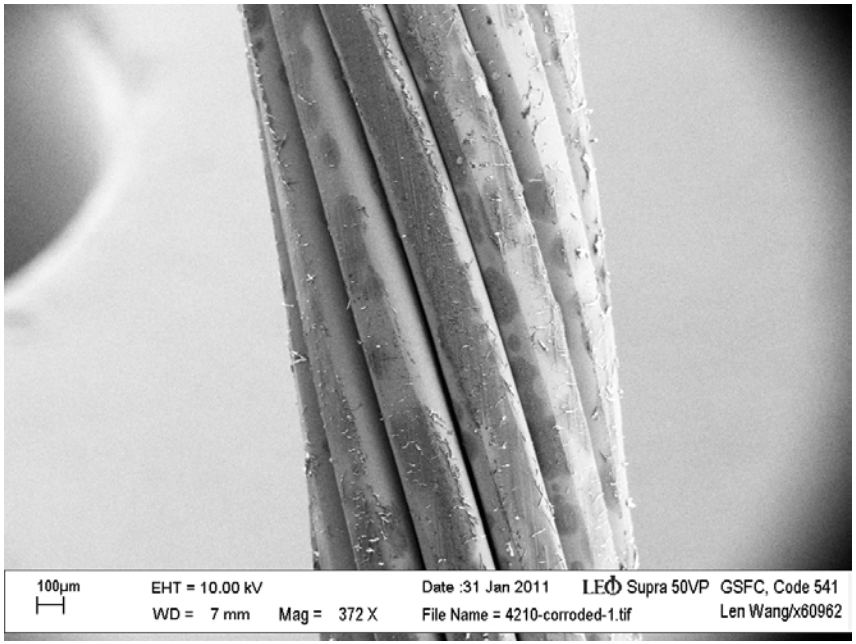
Testing for corrosion

Scanning Electron Microscopy (SEM)

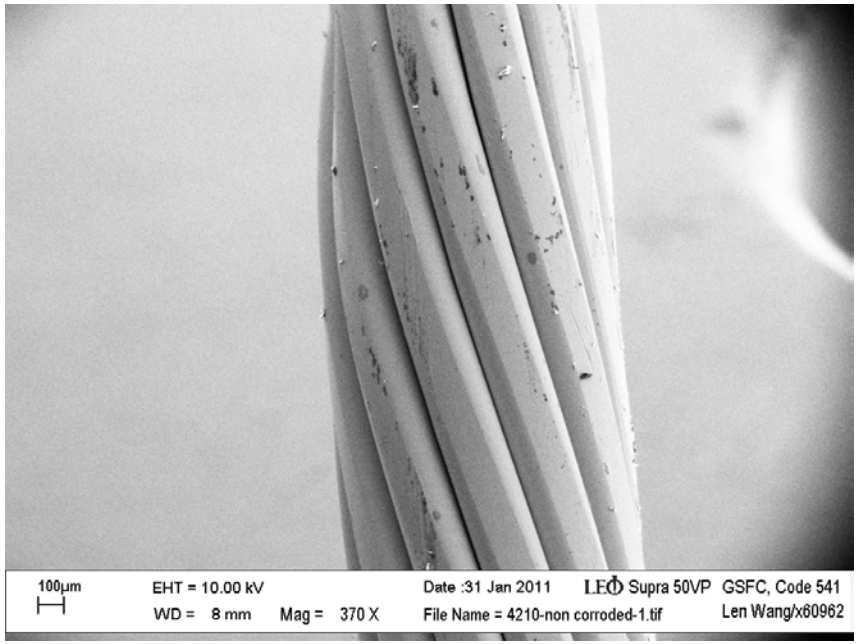
- Visual method of observing corrosion on wire surface.
- Insulation can also be analyzed for corrosion inhibitors.
- Antimony oxide, a fire retardant, also works as a fluoride scavenger.[1]
- $6HF + Sb_2O_3 \rightarrow 2SbF_3 + 3H_2O$
- There is no prescribed amount of Sb_2O_3 that needs to be included in insulations. Since Sb_2O_3 is a white substance, black insulations will often contain less of it.

[1] Morelli, J.J., Fry, C. G., Grayson, M. A., Lind, A. C. and Wolf, C. J. (1991), The Thermal Oxidative Degradation of an Ethylene-Tetra-fluoroethylene-Copolymer-Based Electrical Wire Insulation. Journal of Applied Polymer Science, 43: 601–611.

Inspection with SEM for corrosion



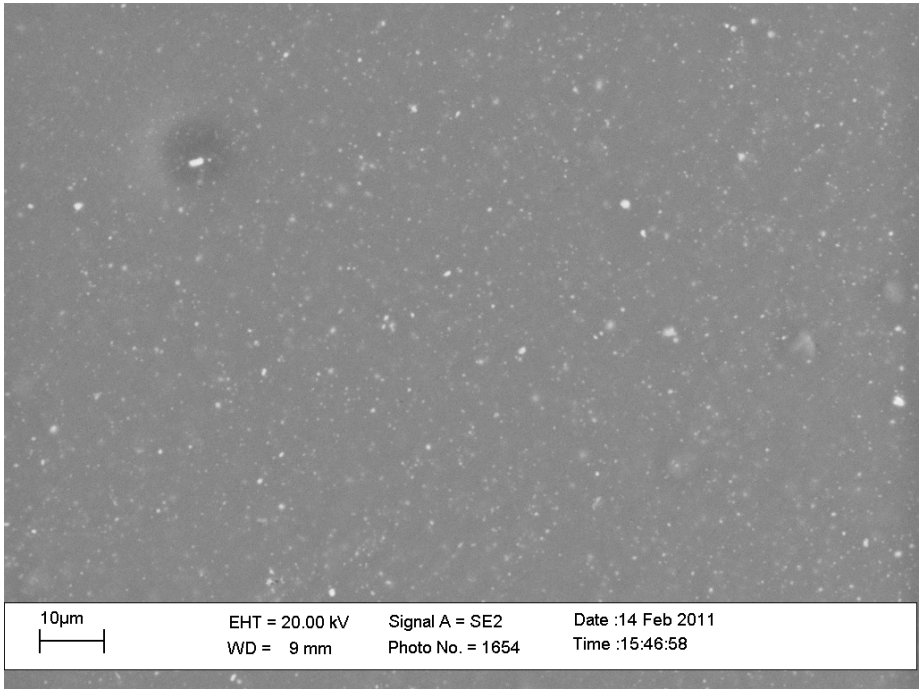
12A



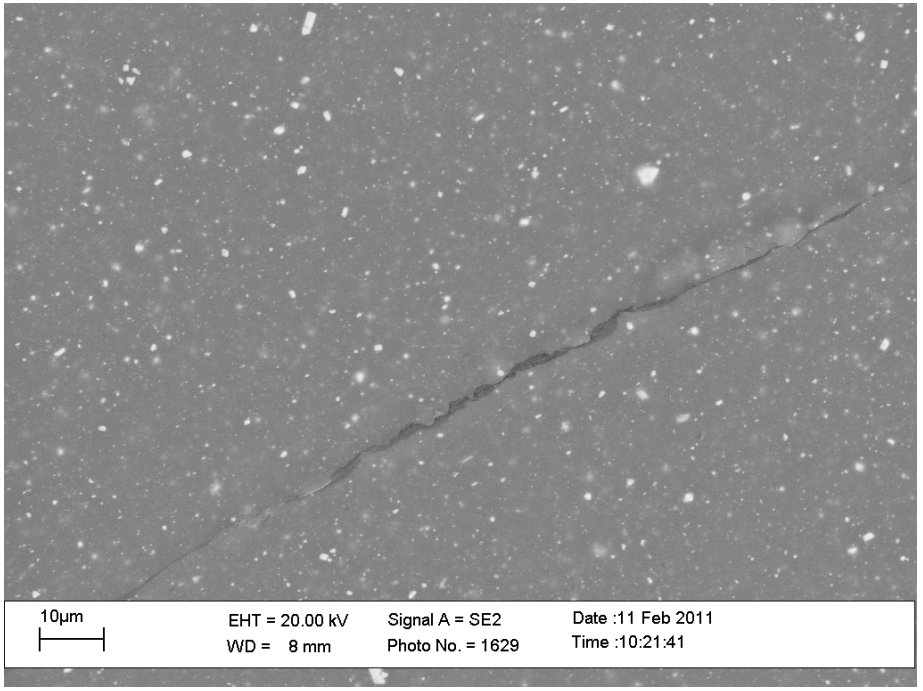
12B

- The wire 12A has corrosion indicated by the dark spots. Wire 12B is free of corrosion.

Antimony oxide



12A

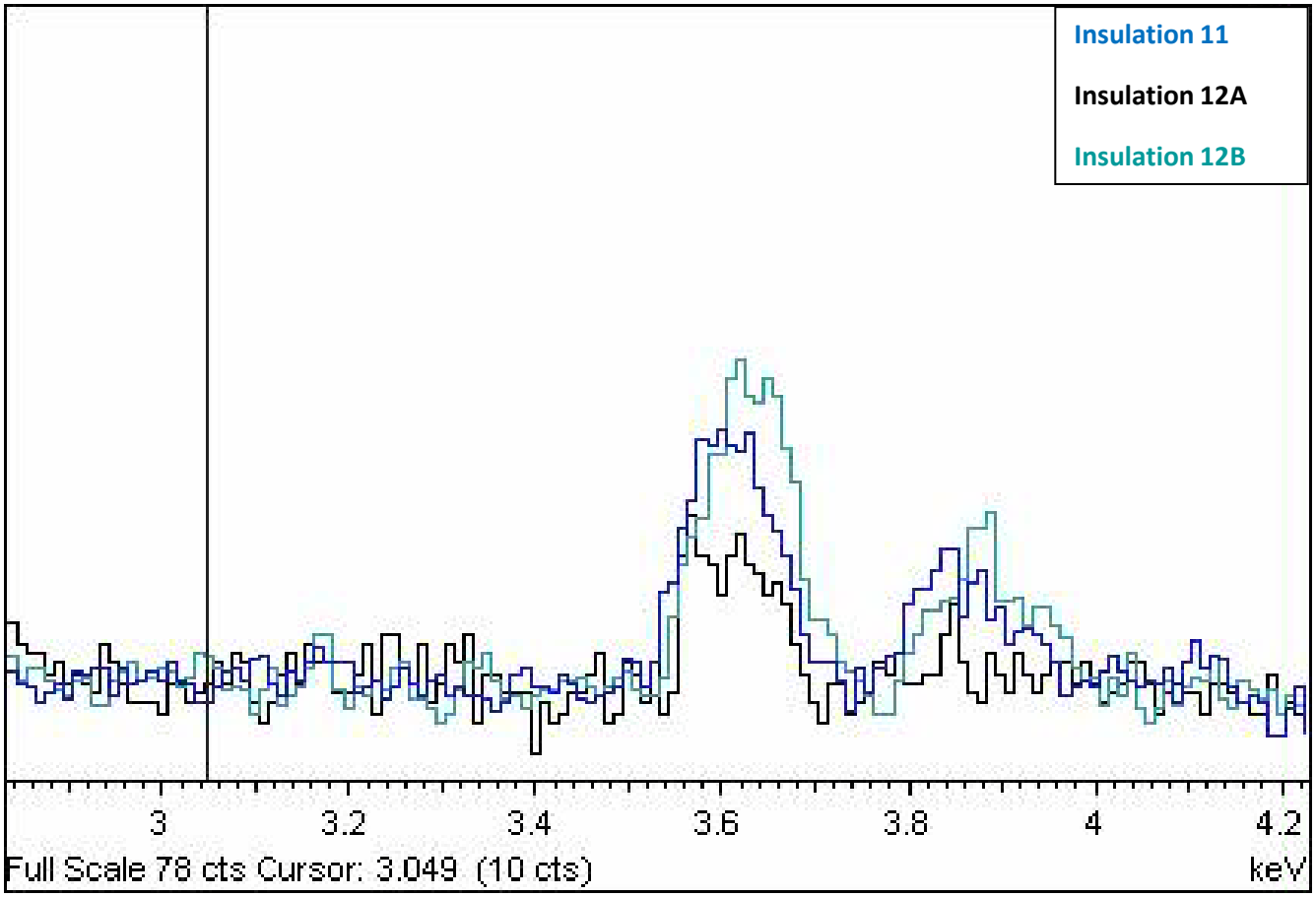


12B

- Antimony oxide, which is often included in insulations as a fire retardant, acts as a fluoride scavenger.
- Here, the insulations of 12A and 12B are compared for Sb_2O_3.
- The shiny particles represent the Sb_2O_3.

Wire	% Area Sb_2O_3
11	6.253
12A	1.964
12B	4.456

Comparison of antimony oxide content using Energy dispersive X-ray spectroscopy (EDS)



- Insulations 11 and 12B, have more antimony oxide than 12A.
- 12A is the wire that was shown to have corrosion using SEM.

Conclusions

- Differences in manufacturing conditions lead to differences in fluoride released.
  - Some ETFE insulations have values that are as low as PTFE insulations.
- High fluoride concentrations, combined with other manufacturing conditions can lead to corrosion.
- SEM/EDS can help identify the presence of antimony oxide and corrosion, but threshold of fluoride should be identified to lower the risk of corrosion.

Recommendations

- Continue following the guidelines proposed in advisory NA-GSFC-2003-03 and when possible store wires in nitrogen purged bags.
- New ETFE insulations that release lower levels of fluoride are now being manufactured (Example Tyco® Low Fluorine Cross-linked cables).
- While selecting ETFE insulated wires, wires with lowest fluoride releasing properties should be selected.
- Ask vendors if they monitor fluoride released from their insulations. Many are not aware that differences in processing conditions can lead to improved product.

Future work

- What would be the effect of heating at a higher temperature for only a few hours?
- More tests to determine role of antimony oxide, and fusing process of insulations.
- Test more wire insulations to find range of fluoride concentrations.
- Identify threshold of acceptable fluoride limit.

Acknowledgements

- AFRL for leading the development of the fluoride ion test method.
- Ms. Molly Powell and Dr. Len Wang from the MEB for assistance with SEM analysis of wires.

Backup slides

Copper mirror corrosion test

- Wires 12A and 12B had the same fluoride levels in the ISE test.

- Will 12A and 12B have the same fluoride levels in other test methods?
- Copper mirror corrosion test described here is an ASTM standard D2671.
- Wire insulation placed into polystyrene test tubes.
- Copper mirror (EMF corp.) is attached to top of the test tube.
- Test tube is capped and placed into a 70 °C water bath for 16 hours.
- After 16 hours, tubes are removed and mirrors are checked for loss of copper coating.

Copper mirror corrosion test

Quantify corrosion based on the area of copper mirror that has corrosion

Quantifying corrosion

Control

11

12A

12B

13

- 12A and 12B are the only ones that show corrosion when tested with the copper mirror.
- They do seem to have the same amount of corrosion, but the quantitative proof is not the same as ISE.

Specimen	% Area Cu loss
11	0
12A	12.76
12B	9.56
13	0

Comparison of test methods

	7 day soak ISE	1 day soak ISE	Copper mirror	SEM/EDS
Test wait time	7 days	1 day	16 hours	N/A
Detectable concentrations (range values for 7 day soak)	Low fluoride levels , even 3 ug/g insulation	Standard range, best above 100 ug/g insulation	Higher range, around 800 ug/g insulation	Any as long as corrosion is present
Cost of test instrument setup	~$ 2000	~$ 2000	~$ 500	~$ 400,000
Quantitative	Yes	Yes	No	No

SEM

EDS gun

Test chamber

Computer attached to SEM