CAUSE AND EFFECTS OF FLUOROCARBON DEGRADATION IN ELECTRONICS AND OPTO-ELECTRONIC SYSTEMS

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Abstract

Trace degradation of fluorocarbon or halocarbon materials must be addressed in their application in sensitive systems. As the dimensions and/or tolerances of components in a system decrease, the sensitivity of the system to trace fluorocarbon or halocarbon degradation products increases. Trace quantities of highly reactive degradation products from fluorocarbons have caused a number of failures of flight hardware. It is of utmost importance that the risk of system failure, resulting from trace amounts of reactive fluorocarbon degradation products be addressed in designs containing fluorocarbon or halocarbon materials. Thermal, electrical, and mechanical energy input into the system can multiply the risk of failure.

KEY WORDS: Fluorocarbons, Degradation, Corrosion

1. Introduction

1.1 General Fluorocarbon Properties

A vast number of considerations must be made in the selection of aerospace materials. These often include outgassing, particle generation, flammability, atomic oxygen resistance, thermal operating limits and mechanical properties. As required by specific engineering applications, fluorocarbon materials offer specific advantages or properties that are not possessed by non-fluorinated materials. The bulk behavior of fluorocarbon materials is often the only property

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considered in their selection. The neglect of trace quantities of reactive products of fluorocarbon degradation reactions can lead to unexpected failure mechanisms within complex or sensitive systems.

1.2 Polytetrafluoroethylene Chemistry

Polytetrafluoroethylene (PTFE) has been valued and used as a highly inert polymer for a wide variety of applications. The depolymerization of PTFE under some conditions (high vacuum, inert gas) has been well studied, and to be one mechanism from cryogenic to high temperatures, unimolecular depolymerization and chain scission[3]. The depolymerization reaction proceeds following reactions (1) and (2). The chain scission follows a free radical mechanism that is followed by either: free radical abstraction, backbiting, elimination, or recombination. The recombination does not necessarily result in the reformation of the original molecule.

PTFE homolytic depolymerization reactions:

$$CF_3\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_n\text{-}CF_2\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_m\text{-}CF_2\text{-}CF_3 \text{ -----> } CF_3\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_n{*} + {*}(\text{-}CF_2\text{-}CF_2\text{-})_m\text{-}CF_2\text{-}CF_3 \quad (1)$$

$$CF_3\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_n{*} + {*}CF_2\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_m\text{-}CF_2\text{-}CF_3 \text{ -----> } CF_2{=}CF_2 + CF_3\text{-}CF_2\text{-}(\text{-}CF_2\text{-}CF_2\text{-})_n{*} + {*}(\text{-}CF_2\text{-}CF_2\text{-})_m\text{-}CF_2\text{-}CF_3 \quad (2)$$

Reactions one and two represent only one reaction pathway. The fragments eliminated in the decomposition of PTFE are not limited to tetrafluoroethylene. There are a variety of fragments formed, including tetrafluoroethylene, hexafluoropropylene, and a variety of perfluoro-oligomers.

The less well-known chemistry of PTFE and other fluorocarbons is the mechanism of the degradation under oxidizing conditions (1). This reaction is of greatest significance in branched perfluorinated polymers. These conditions include the presence of water, oxygen, metal oxides or combinations of the three. This reaction results in the formation of carbonyl difluoride through the hydrolytic addition of water, rearrangement of the resulting alcohol and elimination of the carbonyl difluoride. One carbonyl difluoride reacts violently with water releasing two hydrogen fluoride and one carbon dioxide. These reactions typically have low rates of reaction under conditions of use.

The reactions that form highly reactive products are often ignored due to the insignificance of the small fractional loss of the fluorocarbon to the fluorocarbon's intended performance requirement. In most applications, adequate design margin exists to prevent failures due to the loss of material from the fluorocarbon bulk. The problem that arises is not a result of a loss of bulk properties, but rather a gain of trace properties. The trace quantities of fiercely reactive fluorocarbon degradation products such as carbonyl difluoride can wreak havoc in a wide variety of systems.

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[3] The mechanism of the degradation follows one pathway with one rate limiting step, defining one Arrhenius free energy of activation, that in this case is followed by a series of potential pathways for termination, resulting in a series of potential products.

The degradation of fluorocarbons in the presence of moisture, even at the molecular monolayer level or below, results in the formation of highly reactive species. This is also the case with non-perfluorinated halocarbons including: chlorocarbons, chlorofluorocarbons bromofluorocarbons, etc. In the case of non-perfluorinated species, the number of potential degradation mechanisms increases significantly, and the minimization of one mechanistic degradation rate will result in another one or two being the primary degradation pathway. Additionally, small seemingly insignificant events or interactions can act as initiators for self-accelerating degradation pathways.

1.3 Non-perfluorinated Fluorocarbons

This situation is complicated by the presence of additional materials that can act as reservoirs or additional reactants. Materials such as polyimides and epoxies can act as reservoirs for reactants and products that will shift the equilibria and drive the reactions further, allowing the concentrations to cycle to higher levels and result in greater reactivity. With an active reservoir in the system, thermal cycling will shift the concentrations of the reactive degradation products and subsequently the reactivity of the components of the system resulting in unexpected degradations.

In the case of mixed halocarbons, there are often four additional reaction routes available. These generalized reaction pathways are often referred to as E1, E2, SN1, and SN2 [4]. The reaction pathways E2 and SN2 are bimolecular pathways. The reaction pathways E1 and SN1 are unimolecular. In the case of the unimolecular reactions, the rate limiting steps are the loss of a species from the molecule of interest. Unimolecular reaction rates are largely determined by the stability of the reacting molecule itself. The reaction is less affected by materials present in the system. Unimolecular reactions are typical of reactions of molecules containing bromine, iodine and other highly polarizable groups within a non-polar environment. These reactions are typically not significantly accelerated by other species in the reacting zone. In the bimolecular reactions, the attack of the molecule of interest by a second chemical species is the rate-limiting step. Bimolecular reactions are typically greatly affected by the polarity of their environments and other species in the reacting zone. Typically, these reactions can be significantly affected by changing the chemical composition of their environments. There is a significant likelihood that the degradation of a polymer will occur by any number of pathways.

1.4 Descriptive Chemistry

Simple thermodynamic considerations of the equilibrium distributions of products and reactants are not sufficient to describe the effects of the materials upon the other components. Thermodynamics describes the instantaneous average composition and energies within a system. It must be remembered that even if a system is largely in a state where the reactive degradation products are at extremely small concentrations, within the physical system in a satellite instrument, the instrument cannot necessarily be treated as a single thermodynamic system or state. This is especially the case when the instrument is in operation or in flight. The functional

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[4] The E1, E2, SN1, and SN2 are generalized descriptions of reaction mechanisms used in the field of Physical Organic Chemistry. The mechanism describes a significant amount of detail about the reactions and the products. Greater detail on these types of reactions are organic chemistry text books such as Introduction To Organic Chemistry, Streitweiser and Heathcock, Macmillan Publishing Co., Inc., New York.

operation of an instrument will often result in the energy distribution being neither isothermal nor adiabatic. Thus, creating a situation that violates several assumptions made in general descriptive thermodynamics. Additionally, it can be the case that the system is below the Thermodynamic Limit [5], and thus, statistical thermodynamic description of the system is not valid. This complicates the description of the system.

1.5 Trace Fluorocarbon Degradation

Many of the sources of trace fluorocarbon degradation originate from trace amounts of fluorocarbon degradation and not a general breakdown of the bulk material. These cases tend to be problematic. The bulk material is usually investigated and found to be indistinguishable from its initial state. Often the investigator will verify the integrity of the bulk fluorocarbon system and deem it faultless. This is often due to a lack of data and the assumption that fluorocarbons are stable and that their degradation products are not aggressive.

1.6 Polybromotrifluoroethylene and Polychlorotrifluoroethylene Fluids

These materials are often used as damping fluids in gauges and electromechanical devices. The fluids are often chosen due to the wide operating temperature ranges over which they are liquid. In some systems, the halofluorocarbons are used as controlled density floatation or buoyancy media, such as gyroscopes for satellite guidance, stabilization and control.

These halofluorocarbon materials tend to release free halogens at near ambient conditions by unimolecular elimination reactions in the absence of other reactive species. The unimolecular reactions initiate by the halogen atom, (i.e. Bromine or Chlorine) falling off the halofluorocarbon polymer molecule. This atom is then free to react with other species, and will often react with a like atom forming the molecular halogen (Br_2, Cl_2.) These particular unimolecular reactions accelerate with temperature. In the presence of Lewis acids or free radicals, bimolecular reactions will occur in addition to the unimolecular elimination reactions. In the case of the bimolecular reactions, a second species, such as CuBr, interacts with the halofluorocarbon resulting in a weakening of the carbon halogen bond, resulting in subsequent breakage of the carbon halogen bond. The presence of materials that will scavenge the free halogen will accelerate the degradation of the halofluorocarbon material through depletion of the halogen after its release from the halofluorocarbon. In some cases, the scavenging material will form catalytic or accelerant species that will increase the rate of the halofluorocarbon reactions. Examples of materials that will result in the acceleration of the degradation rates include copper, acids, amines, and unsaturated hydrocarbons.

Free halogens will, despite thermodynamic predictions react with all metals, including the noble metals. Noble metals by definition are those that do not readily dissolve in inorganic acids to unit activity or higher. Bromine will dissolve or react with all metals, including gold. In most systems of interest, the activity of the halogens will not be described by tabulated reaction free energies or EMF tables. This data is usually based upon standard dilute aqueous conditions, and is virtually unrelated to conditions in non-aqueous solution and in multiphase systems. In some systems, gas

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[5] The thermodynamic limit is defined as the limit at which difference of the behavior of the distribution of the members of a particular ensemble and an infinite ensemble vanishes.

phase reactions under vacuum act more closely like the reactions in non-polar solutions than the tabulated aqueous solution phase chemistry.

2. Material Considerations

2.1 Example Case One: Corrosion due to Bromofluorocompounds

In one system utilizing polybromotrifluoroethylene as a buoyancy medium for a gyroscope, there have been with failures of silver copper coin metal electrical leads. The polybromotrifluoroethylene fluid was determined to release molecular bromine through a unimolecular elimination reaction. The bromine then reacts rapidly with the copper and attendant copper oxide in the silver copper leads. The free bromine reaction with the copper proceeds at a rate significantly faster than the reaction does with the silver. Copper in this alloy exists significantly as a small volume copper rich phase between small silver grains. The reaction of the copper with the molecular bromine in this system has been measured. The copper in the leads is nearly completely depleted in all cases studied with in 90 to 120 days on orbit, at 57 °C , despite other operational differences in the gyroscopes.

The rate of the reaction and its effect upon the leads is very complex due to the random nature of the crystal size, processing effects, additional kinetic effects due to other materials in the system, polymeric variability, and electrical variations in the mechanism. The crystal size and packing affects the corrosion depth required and affects the bulk to crystal boundary diffusion of the copper in the lead. Processing due to heat-treating procedures, affects the amount of cuprous oxide (a Lewis acid catalyst), the crystal size, and the potential energy of the lead at a microscopic level. The amount of trace materials can vary dramatically, materials such as soldering rosin, a source of acids and unsaturation that will create additional bimolecular elimination reaction pathways, resulting in the more rapid release of bromine.

Additionally, the bromotrifluoroethylene polymer fluid system by its very nature has a significant variability at a secondary chemical structure level.[6] This affects the reactivity of the fluid based upon the fundamental orientation of bromine atoms within the polymer. There are a number of additives in the bromotrifluoroethylene polymer fluid. The concentration of these additives affects the reactivity of the polymer. Stabilizers added to preserve the polybromotrifluorethylene might actually result in greater degradation of the polymer and the systems that they are in depending upon the mechanism of operation.

Within non-polar non-ionizing solutions, leveling of potential and uniformity of surface activity on a single-phase surface cannot be assumed. Mechanical stress and strain within a system are not negligible in the reactivity of these systems. Corrosion generates areas of weakness within the lead that will result in elevated potential energy regions, due to increased surface curvature, mechanical stress and electrical current density. These regions react faster than the surrounding materials. This results in a positive feedback like, cyclic acceleration of the corrosion process.

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[6] Secondary Chemical structure in polymer chemistry refers to the orientation of the polymer subunits stepping along the chain i.e. whether the bromines from adjacent bromotrifluoroethylene monomers are adjacent, head to head, or whether they are separated by difluoromethylene groups, head to tail.

These leads carry electrical current, as the corrosion progresses, the cross section of the lead decreases and the ohmic heating increases. The elevation of the temperature in this region will further increase the rate of reaction further thinning the lead. The ultimate failure mechanism is often over current fusing of the lead.

In this particular gyroscope application, there is no other option but to use the polybromotrifluoroethylene fluid. The remainder of the system can also not be changed. These system engineering restrictions also require the use of the silver copper leads.

In non-polar environments, bromine exists in molecular form almost exclusively, there is virtually no stabilization of ionic species. The disproportionation of the bromine to bromide and hypobromite is virtually nonexistent due to the lack of stabilization of the ions. Under these conditions, the reaction of bromine with all metals follows first order kinetics with respect to the bromine concentration. The reaction is limited by the rate at which the bromine can arrive at fresh metal surface (ref. 2). The reaction follows the simple steps of coordination with the surface, electron transfer from the metal, and formation of the bromide directly. This is easily distinguishable from the reaction of hydrobromic acid as no hydrogen is formed. There are differences in the rates of reaction of metals with bromine, These differences are largely due to the metal surface availability as the reaction progresses.

The reaction of bromine with copper differs mechanistically from the reaction with silver in the way the reaction products are distributed. In a number of papers, the reaction of bromine with single crystal silver and single crystal copper with bromine were investigated using high speed scanning probe microscopy (ref 3-7.) In the case of the reaction of copper with bromine, the crystalline planes of the copper were sequentially stripped from the surface of the bulk material. The reaction product was not initially seen to deposit on the surface. After sufficient reaction progress growth of islands of cuprous bromide were seen to grow into the scanned area.

The silver reaction with bromine with the silver progresses differently (ref 3,4.) The reaction site being monitored becomes overlaid with a silver bromide layer initially. This layer then forms a barrier to the reaction. The silver reaction then becomes mediated by the diffusion of the silver atoms through the silver bromide coating. As a result, the rate of reaction slows significantly as the reaction progresses. This results in a self-protection of the silver surface.

A further complication of the system is the presence of a large number of additional materials in contact with the polybromotrifluoroethylene floatation solution. Among these are a number of materials that are known to form bromide Lewis acids due to reactions with he bromine. These materials will provide additional reaction pathways for the formation of bromine via SN2 and E2 mechanisms.

As the unimolecular elimination, reaction is primarily controlled by the properties of the polybromotrifluoroethylene, and the gyroscope system requires the physical properties of this material for operation, this aspect of the system cannot be changed, and the presence of bromine must be lived with. Knowing that the reactivity of the free bromine reaction with silver is significantly slower than the reaction with copper, it has been decided to silver plate the leads to significantly decrease the rate of degradation of the leads.

2.2 Example Case Two: Fluorocarbon Copolymers

Fluorocarbon copolymers such as Poly(tetrafluoroethylene, hexafluoropropylene) are perfluorinated polymers prepared from two or more perfluorinated monomer species. The general reactivity of these materials tends to be slightly higher than those of PTFE. Fluorocarbon copolymers are often used in situations where the thermal expansion of PTFE or the mechanical creep of PTFE would result in system problems. Fluorocarbon copolymers can also have properties that better allow melt processing.

A fluorocarbon copolymer was used in the construction of loose-buffered aerospace fiber optic cable. This fiber optic cable is constructed with a step gradient germanium doped silica core, with a quartz sheath, a hermetic carbon coating on the fiber, a tight polyimide fiber buffer, a fluorocarbon copolymer loose buffer, fluorocarbon coated glass braiding and a fluorocarbon copolymer jacket. The fiber is designed for extreme duty applications. The hermetic carbon coating is designed to prevent moisture infiltration that can result in loss of lifetime that can occur because of stress corrosion cracking due to environmental water.

The fiber is jacketed in multiple coaxial extrusion processes. Fluorocarbon copolymer is initially extruded over the polyimide clad fiber core, the fluorocarbon copolymer is then water quench cooled. The braiding is added next and then the outer jacket is extruded over the braiding. The process also involves a large number of spooling and respooling operations within the processing. It was found that it was desirable to employ ionizer guns in the system to minimize electrostatic charge buildup in the system.

Several lengths of fiber optic cable were directly interfaced to the inlet a mass spectrometer. These fiber sections were interrogated under near normal handling conditions. Under these conditions, the cable was determined to generate measurable amounts (approximately 10^{-19} moles of carbonyl difluoride) from about one minutes worth of handling. The handling conditions were approximated by inducing flexion into a coil of about 0.2 meters in diameter. The coil was never deflected more that 50 mm, oscillations were at frequencies of less that 1 Hz. The mass spectrometer measurements also demonstrated that external electrostatic sources would act to create significant amounts of carbonyl difluoride. The detection was carried out upon the 19 amu/z peak in the mass spectrometer (F^+.) The 19 amu/z peak was found to change orders of magnitude with handling. This was differentiable from the H_3O^+ (with the same mass as the F^+ ion) of the residual water based upon the fact that the main species in the mass spectrometer was residual water and the total system pressure did not shift measurably during the measurements. Additionally, during the analysis and subsequent mass spectrometer bakeout the 28, 16 and 12 amu/z peaks rapidly rose indicating the assimilation of the carbonyl difluoride by the mass spectrometer was occurring.

This process in the presence of ubiquitous water will result in the formation of carbonyl difluoride and subsequent hydrogen fluoride trapped within the fluorocarbon copolymer jacketing. Additionally, there will be a significant fraction of water in the one to three percent range dissolved within the polyimide cladding. It is reasonable to assume that the hydrogen fluoride / hydrofluoric acid will also dissolve into the polyimide phase and remain there intact due to the low reactivity of hydrofluoric acid toward organics and the strong hydrogen bond formation characteristics of the polyimide and the hydrofluoric acid.

Under ideal conditions, the carbon cladding on the fiber optic would prevent the hydrofluoric acid and water from attacking the fiber optic. However, during cable fabrication, fiber optic link fabrication, and use the conditions are less than ideal. The fiber is buffered with a tight polyimide buffer. This polyimide is in loose contact with the fluorocarbon copolymer loose buffer. In the process of moving the cable, the polyimide will rub against the fluorocarbon copolymer. This results in the generation of an electrostatic charge being formed. The carbon coating on the fiber can be described as falling between conductive and semi conductive. As a result, the electrostatic charge will build on the fiber over a reasonably short period of time. In effect, the fiber system is an electrostatic generator. The charge will build during manipulation until a discharge occurs.

The discharge occurs through the fluorocarbon copolymer buffer, air gap, and polyimide buffer to the surface of the carbon cladding. It should be remembered that the temperature of a spark discharge will often be in the excess of 10,000 K this is in excess of the evaporation temperature of virtually all known materials. The fluorocarbon copolymer will buffer the discharge temperature through heat absorption and the formation of carbonyl difluoride. The spark in the moist air generates its plasma. The spark passing through the polyimide vaporizes the polyimide. The spark is then dissipated in the carbon cladding through the vaporization of the carbon and in some cases its immediately underlying substrate. This provides a direct path for the residual hydrofluoric acid (from the hydrolysis of the carbonyl difluoride and water trapped in the cable) to attack the germanium doped quartz fiber.

The HF entered through the holes in the cladding resulting in the formation of silicon tetrafluoride gas and germanium tetrafluoride gas. These gases diffused at least partially out of the hole. As the hydrofluoric acid is depleted, the residual water then reacted with the tetrafluorides resulting in hydrolysis. The silicon was deposited as silica gel in the form of small ~10-micron beads and the germanium was deposited as accicular germanium oxide crystals. This releases the HF allowing it to form hydrofluoric acid and continue the process. As the fiber is a multilayer gradient fiber, the various layers of the fiber are under varying levels of stress due to thermo-chemical and thermo-mechanical property differences. This results in a ribbed morphology in the attacked areas. The process will continue until either the HF is lost through diffusion out of the cable or trapped in a stable fluoride form in the cable, or all of the water in the cable is consumed in the formation of silica gel. It should be noted that mild heating will convert the silica gel into silica and release the water. In any case, the reaction continued until the transmission integrity of the fiber was compromised.

It is worthwhile noting that it was determined that the electrostatic static dissipation ion guns added to dissipate the electrostatic charge during the processing were found to act as a source of discharge and aggravate the problem. The processing machinery was determined to contain a variety of materials for roller surfaces that acted with the cable as a van De Graf Generator during cable processing. Stress corrosion cracking of the quartz cladding of the fiber core was determined to be a second potential failure mode within the cable. The presence of extremely small fractures in the quartz cladding of the fiber itself were found to result in failures of the fiber due to breaks. It is interesting to note that the initiation of the hydrofluoric acid reaction tended to abate the stress corrosion cracking of the fiber slightly, resulting in reduction of the failure probability due to strain on the fiber. The manual manipulation of the carbon-clad fiber was sufficient to generate detectable amounts of HF. It should be noted that the sister cable of this system that does not have the carbon hermetic coating is not susceptible to the electrostatic effects seen in this cable. When the carbon clad fiber cable is exposed to a spark source such as a Tesla coil, the fiber draws the spark from the coil. The unclad fiber cable will not draw the spark, and in fact bypasses the cable rather than allowing it to pass through. The clad fiber with minute holes additionally acts to concentrate the attack of the HF present from the processing into point defects. The unclad fiber may improve in mechanical stability with the presence of trace HF due to the smoothing out of the microfractures in the fiber surface, minimizing the potential for stress corrosion cracking.

2.3 Example Case Three: Chlorofluorocarbons Cleaning Solvents

Chlorofluorocarbons (CFC's) have a long history in the aerospace industry. Some of this history has been checkered by the initial assumption that the materials are entirely stable and available as pristine materials. The volatile materials have long been used for cleaning purposes. These were typically used once then discarded. With the Montreal Accord and the elimination of the importation and production of CFC's, usage practices have changed significantly. This includes the recycling of the materials within closed washer systems.

The use of CFC's within high-pressure high velocity washer systems has generated a number of potential problems. The recycling of the CFC's in the washer systems routinely utilizes absorber cartridges to remove the contaminants from the fluid. Unfortunately, due to the indeterminate nature of the cleanliness of parts and equipment cleaned in the pressure washers, and the lack of adequate testing equipment, the cleanliness of the parts coming out of the washer may be worse than when they entered the washer. Additionally, due to the very low conductivity of the CFC's, the pumping, transport and spraying processes can lead to triboelectric generation of electrostatic discharges within the washer. These discharges will result in the formation of reactive degradation products in the washer system.

In most cases, there is little difficulty with reactivity of the degradation products on hardware. This is due to the extremely limited time of contact with the fluid, and the subsequent processing that eliminates the degradation products before they have a chance to react with the parts.

In any number of cases, typically with wiring harnesses, there are problems. The degradation of the residual CFC's has been seen to discolor and pit electroless nickel plating on connector housings, strip and surface corrode silver plated copper wires, strip and corrode gold plated beryllium-copper connector pins. Wiring harnesses are typically built well ahead of the final hardware integration, testing and bakeout. As a result, the harnesses, especially those covered with metal braiding are cleaned in a high-pressure washer to minimize the contamination of the other hardware, and tightly bagged to maintain their level of cleanliness. If these harnesses are not dried in an oven or baked out in a vacuum chamber prior to bagging, the residual CFC's in the harness, typically trapped between the individual wires or between the insulation and the conductor will be in contact with the harness for a time of months to years. In this time frame, the first and second order elimination reactions have adequate time to generate significant amounts of corrosive materials to attack and significantly affect the harnesses. The process of blowing the harnesses dry with compressed air or nitrogen further aggravates the situation due to the formation of condensation or at least increased absorption of moisture from the air. In the presence of oxygen and moisture, multiple reactions occur resulting in dehalogenation, dehydrohalogenation and hydrolysis of the chlorofluorocarbons. In effect, the harnesses are sealed in the bags with trace chlorine gas, phosgene, hydrochloric and hydrofluoric acid vapor and left to react.

A number of wiring harnesses have been investigated and been seen to be degraded with a combination of metal chlorides, metal fluorides, and metal oxides. Gold coating has been penetrated and the underlying leads have been corroded leaving the contacts black with cuprous chloride.

All of these problems could be avoided by the judicious heating of the parts in an oven or heated vacuum chamber before storage. The concentration of the corrosive materials in the pressure washers and solvent storage containers is typically mitigated by the corrosion of the pressure washers and the storage drums.

2.4 Example Case Four: Fluorocarbon ethers

Fluorocarbon ethers such as have been developed for replacement of CFC's in many applications. These include for use as refrigerants and cleaning solvents. These materials possess many of the same properties good and bad as the CFC's. The main exception is in the atmospheric photochemistry.

The use of fluorocarbon ethers has been suggested in satellite loop heat pipes and that they would be electrohydrodynamically pumped for long term transport of heat from one location to another. The capability of electrohydrodynamically pumping the ether has been shown terrestrially. This application was however not a closed loop system. It is improbable that the lifetime of the system operation was investigated. It was only shown that the material could be electrohydrodynamically pumped.

The process of electrohydrodynamic pumping is based upon the differential migration of equilibrium ions within a fluid. In this case, one of the ions is significantly less electrophoretically mobile than the other and as a result, with the imposition of a high electric field, the one ion will drag more bulk material with it than the other ion. The net result is the movement of the bulk solution. This technique has been used with water and non-fluorinated solvents in generating uniform field flows in capillary systems for separation of chemical species and transporting materials in microelectromechanical systems.

The case in point was attempting to use a fluorocarbon ether as an electrohydrodynamic fluid. The result was significant initial performance followed by a rapid decline in performance. The system was disassembled and inspected. It was determined that some of the stainless steel electrodes used to supply the electric field for pumping were covered with a brown deposit on the end facing the counter electrode. Surface analysis showed that the coating was a mixture of oxides and fluorides.

Further investigation lead to the following conclusions. The concept that the electrohydrodynamic pumping is driven by any forces other than differential ion mobility is incorrect. Within a liquid phase, purely dielectric interaction will only result in the orientation of molecules within the electric field, no net movement of the dipole or the fluid will occur. Fluorocarbon ethers are not in an ion/ neutral equilibrium so, there is virtually no reversible ionization present in these systems. Fluorocarbon solvents in general are ionophobes and tend to have no ion stabilizing power at all. The ion formation and elimination process in the system was due to field emission of electrons from the negative electrodes followed be fragmentary ionization of the fluorocarbon ether analogous to the process used in mass spectrometry. The fluorides and oxides in the system were due to the deposition and decomposition of the fluorocarbon ether ions, and potentially residual water, on the surface of the negative electrode. The cessation of pumping of the system was due to shielding and smoothing of the electrode surface, resulting in the decreased field emission of the electrons. The high initial efficiency of the system was due to the large difference in the electrophoretic mobility between electrons and large organic ions in a multiple kilovolt field. The lack of stabilization of ions in the fluorocarbon ether will result in the deposition of reactive species on the surface of the electrodes or reaction of the ions with other components in the system. An electrohydrodynamically pumped system using fluorocarbon liquids for long-term application is not a viable option.

2.5 Example Case Five: Perfluoroethylene

A PTFE polymer coating, filled with an inorganic pigment filler, was employed on the interior surfaces of a reciprocating helium cryorefrigerator. The PTFE coating was used to assure that the reciprocating piston would have lubricated surfaces in the case that the piston impacts the cylinder during operation. The system operates via a moving voice coil drive system and a spring suspension. The piston and cylinder have sub-millimeter clearance and the piston must move freely.

After an extended operation cycle, it was determined that the reciprocating piston was seizing. The cryocooler was vented and deintegrated. Inside the cryocooler, the exposed metal surfaces were corroded. Metal oxides and fluorides dominated the corrosion products that were distributed throughout the cryocooler.

A second cryocooler was obtained from the manufacturer in an unfilled condition. The cryocooler was carefully baked out through a turbo pumped residual gas analyzer (RGA) system through a baked out manifold. After the adsorbed water was removed by heating under vacuum, the cryocooler was charged with ultrahigh purity (99.9999%) helium through a cryotrapped coil into the vacuum baked out manifold system without breaking connection to carefully exclude water.

After another extended cycle, the cryocooler was again opened to the manifold system, and the gas was analyzed by RGA. In spite of significant precautions taken to assure the purity of the helium, a significant amount of carbonyl difluoride and carbon monoxide were present in the gas.

De-integration of the cryocooler showed the presence of corrosion products and the presence of scuffing in the piston. In the extremely dry environment within the cryocooler, the oscillation of the piston and the flow of the helium between the PTFE coating and the exposed pigment from the coating result in the triboelectric generation of localized charge, potentially resulting in electrostatic discharge. Additionally, the scuffing process generates localized high temperatures in excess of the temperature required to generate carbonyl difluoride. As typical of coating pigments both surface adsorbed and bound water will be present in the pigments. The result of the operation of the cryocooler is the generation of carbonyl difluoride that then reacts with the trace water, generating HF that subsequently reacts with the exposed metal surfaces.

3. Experimental

3.1 Material/ Performance Evaluation This paper is a summary of problems seen due to the trace level degradation of fluorocarbon materials. As a result, there has been a wide variety of experimental techniques used in the evaluation of the samples.

3.2 Bromofluorocarbon Degradation Analyses Much of the early analysis of this problem was carried out using Scanning Electron Microscopy of the deposited silver and copper halides. Later Auger electron spectroscopy was used in an attempt to determine the extent of the corrosion, and the mechanism of the reaction. Gas Chromatography/Mass Spectrometry (GC/MS) and Fourier Transform Infrared spectroscopy of the low molecular weight fluoropolymer was also used to interrogate the fraction of the polymer that had lost bromine. Ion Chromatography was used to determine the amount of free bromide in the polymer through an aqueous extraction. Later Ion Chromatography was use in a differential technique. The sample was split into two aliquots, one was extracted with water directly, and the second was extracted with sodium thiosulfate to reduce the free bromine to bromide. The un-reduced sample was analyzed immediately to minimize the conversion of the free bromine to bromide. This showed that the free bromine was the main inorganic bromine species. Other techniques from light microscopy to analysis of telemetry data have been used to evaluate the system.

3.3 Fluorocarbon Copolymer Degradation Analyses The fluorocarbon degradation reactions were carried out using a turbo pumped RGA. The bulk of the data collection was carried out using single ion monitoring of the 19 amu/z peak for F^+ . The vapor pressure in the RGA was controlled by the outgassing of water from the polyimide and the surface of the HFC buffer. This provided a convenient method for monitoring changes in the H_3O^+ peak at 19 amu/z as the total system pressure would have to rise in rough proportion to the 19amu/z peak. This was not seen during the analyses.

Additional testing including SEM for the visualization and elemental identification of the small deposits in the fiber. Electron Spectroscopy for Chemical Analysis (ESCA) was used for the evaluation of surfaces. A number of mechanical tests were carried out to determine the effects of the degradation upon the mechanical properties of the fiber. The number and types of tests carried out are too numerous to delineated here.

3.4 Chlorofluorocarbon Cleaning Solvents The degradation of the chlorofluorocarbon solvents were characterized by the reaction products present on the surface of the metals by SEM and energy dispersive spectroscopy.

3.5 Fluorocarbon Ethers The deposits on the electrode were analyzed by ESCA. The fluorocarbon ether samples were analyzed by GC/MS. No degradation products were detected in the GC/MS analysis of the fluorocarbon ether solvents.

3.6 Polytetrafluoroethylene The deposits and particulates were analyzed by ESCA. The gas phase samples were analyzed by RGA.

4. Conclusions

4.1 Case One Conclusion Knowing that the reactivity of the free bromine reaction with silver is significantly slower than the reaction with copper, it has been decided to silver plate the leads to significantly decrease the rate of degradation of the leads.

4.2 Case Two Conclusion The addition of a carbon cladding, designed to decrease environmental and handling effects on fiber life, having residual electrical conductivity created a conductive path and an electrostatic discharge susceptibility to a quartz based fiber optic, generating a fluorocarbon degradation failure mode not present in the uncoated sister cable.

4.3 Case Three Conclusion All of the problems of chlorofluorocarbon solvent decomposition can be avoided by the judicious heating of the parts in an oven or heated vacuum chamber before storage. The concentration of the corrosive materials in the pressure washers and solvent storage containers is typically mitigated by the corrosion of the pressure washers and the storage drums.

4.4 Case Four Conclusion An electrohydrodynamically pumped system using fluorocarbon liquids for long-term application is not a viable option. The pumping is strictly a result of the ionizing fragmentation of the fluid.

4.5 Case Five Conclusion Tribological and Triboelectric forces both generate sufficient energy to decompose Polytetrafluoroethylene, even under cryogenic conditions. It should be remembered that temperature refers to the bulk, or the average of the ensemble. The "thermal" degradation of a material can occur in extremely limited regions of the material where energy is applied.

4.6 General Conclusions

In applications involving fluorocarbon and halocarbon materials, it is critical that the chemistry of the system, including the trace fluorocarbon and halocarbon degradation products will affect the system. In many cases, protection of the system from the trace reaction products may be counter intuitive.

Due to the extremely low concentrations and small amounts of the degradation products, the direct detection of the degradation products will often be impossible. Additionally, the quantity of degradation products may be below the level at which the population statistic thermodynamics will be representative. It should also be remembered that the definition of the system may be difficult due to the requirement that the system be closed for most thermodynamic descriptions.

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6. References

1. B.B. Baker, D.J. Kasprzak, “Thermal Degradation of Commercial Fluoropolymers in Air,” Polymer Degradation and Stability, (42) 181-188, 1993.
2. H.J. Arnikar, E. A. Daniels, “Kinetic Study of Corrosion of Copper and Aluminum in Bromine and Iodine Solutions in Carbon Tetrachloride,” Transactions of SAEST, Vol 6., 147-148, 1971.
3. C. Benndorf, B. Kruger, “Adsorption and Reaction of Bromine With Ag(110),” Surface Science, 151, 217-288, 1985.
4. P. J. Goddard, K. Schwaha, R.M. Lambert, “Adsorption –Desorption Properties and Surface Structural Chemistry of Bromine on Clean and Sodium-Dosed Ag(111),” Surface Science, 71, 351-363, 1978.
5. C. Y. Nakakura, E.I. Altman, “Visualization of Etching Mechanisms of a Vicinal Cu Surface Using Scanning Tunneling Microscopy,” J. Vac. Sci. Technol. A 16(3), 1566-1570, 1998.
6. C. Y. Nakakura, G. Zheng, E.I. Altman, “Atomic-Scale Mechanisms of the Halogenation of Cu(100),” Surface Science 401, 173-184, 1998.
7. C. Y. Nakakura, E.I. Altman, “Scanning Tunneling Microscopy study of Halide Nucleation, Growth and Relaxation on Singular and Vicinal Cu Surfaces,” Surface Science, 424, 244-261, 1999.