ECTFE (HALAR®) AS A NEW MATERIAL FOR PRIMARY SAMPLE CONTAINMENT OF ASTROMATERIALS.

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Introduction: Fluoropolymers, such as Teflon® (PTFE, PFA, FEP) and Viton® (FKM), have been used for over 40 years in curating astromaterials at NASA JSC. In general, fluoropolymers have low outgassing and particle shedding properties that reduce cross-contamination to curated samples. Ethylene – Chlorotrifluoroethylene (ECTFE), commonly called Halar® (trademark of Solvay Solexis), is a partially fluorinated semi-crystalline copolymer in the same class of fluoropolymers with superior abrasion resistance and extremely low permeability to liquids, gases, and vapors than any other fluoropolymer (fig. 1). ECTFE coatings are becoming more popular in the nuclear, semiconductor, and biomedical industry for lining isolation containment gloveboxes and critical piping as well as other clean room applications. A study was conducted at NASA JSC to evaluate the potential use of Halar on future sample return missions as a material for primary sample containment.

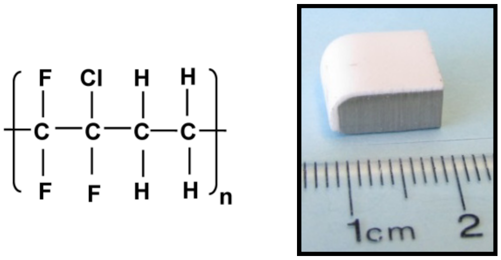

Figure 1: Halar molecular structure and an image of a cut Halar coated stainless steel sample coupon used for testing.

Halar Study: A 15x15x0.5 cm 304 stainless steel plate was spray coated with Edlon, Inc. SC-2001 (white) Halar (ECTFE) to a thickness of 1.0 mm and used for testing and analysis (fig. 1). The Halar sample was precision cleaned at JSC with trichloroethylene (Quickleen II), Oakite Liqui-Det detergent, Dawn detergent, isopropyl alcohol (IPA), ultra-pure water (UPW) ultrasonicated, UPW final rinse, and gaseous N_2 dried. Surface cleanliness was examined by liquid particle counts and before/after optical microscopic inspection. Afterwards, ten 1.0 cm squares were cut to investigate surface roughness and chemical purity using scanning electron microscopy (SEM), gas chromatography–mass spectrometry (GC-MS), and Fourier transform infrared (FT-IR) spectroscopy.

Particle Count Results: Liquid particle counts of UPW during final rinse were taken with a HIAC 3000A liquid syringe sampler with 8000A particle counter. Figure 2 shows the results with Halar having very low particle shedding properties.

Particle Diameter (μm)	HALAR (ECTFE) Particles Per 10 ml Average	UPW Baseline Particles Per 10 ml Average
1	7.5 ± 4.7	5.0 ± 2.1
3	4.8 ± 1.0	3.5 ± 1.1
5	4.0 ± 0.8	2.5 ± 0.4
10	3.5 ± 1.3	2.0 ± 0.7
25	3.0 ± 0.8	1.0 ± 0.7
50	2.75 ± 1.0	1.0 ± 0.7
100	2.75 ± 1.0	1.0 ± 0.7
150	2.75 ± 1.0	1.0 ± 0.7

Figure 2: Average measured particle counts of Halar.

Microscopic Inspection Results: Microscopic surface inspection was conducted with a Leica DM6000 automated optical microscope and a JEOL 7600F Field Emission SEM equipped with a Fisher Scientific UltraDry silicon drift x-ray detector (SDD) and a low-angle backscattered electron (LABE) detector. The surface of a 1.0 cm^2 sample was scanned at 60X to 50,000X magnification to observe surface morphology and features at the micro and nano scales.

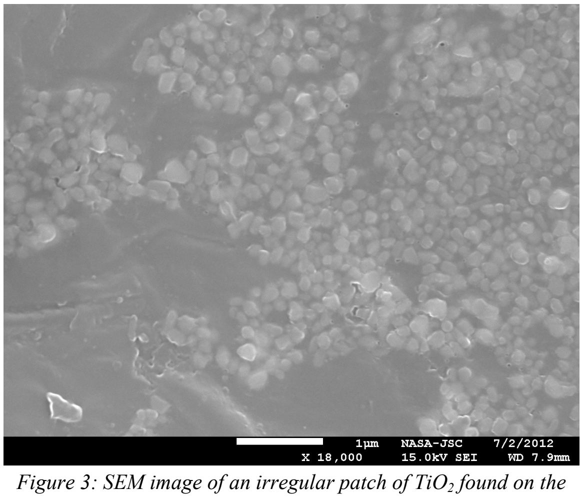

Figure 3: SEM image of an irregular patch of TiO_2 found on the Halar surface.

ECTFE was observed to be extremely smooth compared to other fluoropolymer surfaces. However, heterogeneous textures were observed on the SC-

2001 Halar sample at low magnification. Figure 3 shows a SEM image of an observed surface irregularity. The LABE detector identified 100 nm size anomalies of pure titanium dioxide (TiO_2). The TiO_2 is most likely a coloring pigment white 6 added to the ECTFE – transforming the naturally opaque color to white. It is suspected that the added TiO_2 did not mix properly during the spray application.

FT-IR Results: A Thermo Electron FT-IR Spectrometer 6700 with continuum microscope in reflection mode was used to analyze the Halar.

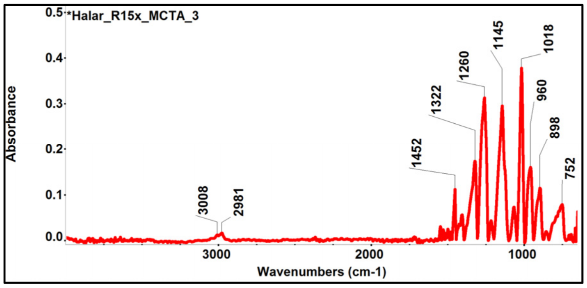

Figure 4: FT-IR absorbance spectra of ECTFE in reflectance mode.

Figure 4 shows peaks at 1018, 1145, 1260, and 1322 cm^{-1} wavenumbers. This is interpreted to be C – F stretching which typically ranges from 1000 to 1400 cm^{-1}. The peak at 752 cm^{-1} is most likely C – Cl stretching. A comparison of the fluorine and chlorine peak intensity is also close to their molar ratio in ECTFE ($[CH_2 - CH_2]_m - [CFCl - CF_2]_n$). The C – H bending observed at 1452 cm^{-1} was identified as methylene (CH_2) and the C – H bending at 898 and 960 cm^{-1} is usually indicative of ethylene (C_2H_4). Aromatic C – H stretch is found at 3008 cm^{-1} and a C – H stretch is observed at 2981 cm^{-1}, which is interpreted as methylene (CH_2). All of the peaks found in the absorbance FT-IR spectra are characteristic of pure ECTFE and consistent with previous documented FT-IR spectra [1].

GC-MS Results: A Varian 3800 with a 1200 quadrupole GC-MS was used for another test of chemical purity. A Halar fragment was pyrolyzed to 500°C for 10 min. Figure 5 shows the GC-MS results for the major ion peaks.

m/z Peaks	Ions
28	Ethylene – $C_2H_4^+$
36, 37 & 38	Hydrogen chloride – HCl^+
85	Chlorodifluoromethyl – $CClF_2^+$
95	Trifluoropropenyl – $C_3H_2F_3^+$
145	Chlorotrifluorobutenyl – $C_4H_5F_3Cl^+$

Figure 5: Major ion peaks from GC-MS analytical results.

The results were again close to the molar ratio in ECTFE ($[CH_2 - CH_2]_m - [CFCl - CF_2]_n$). The peak at m/z = 145 was a chlorotrifluorobutenyl radical, the characteristic dimer of ECTFE. Additional smaller ion peaks were consistent with ECTFE. Hydrogen chloride (HCl^+) was also found in significant quantities and is probably due to the high temperature exposure of Halar.

Discussion: The Halar (ECTFE) coating proved to have a seamless smooth surface where TiO_2 was not found. Future use of Halar spray application should not use color additives that contribute to surface roughness. The material also exhibited low particle shedding properties and was chemically pure. In addition, purported properties of ECTFE include [2]:

- Melting point: 240°C
- Service Temperature: < -76 to 150°C
- Hardness: Rockwell R90; Shore D 75
- Abrasion Resistance at 1000 revs: 0.005 Taber
- Impact strength notch Izod at 25°C: no break J/m
- Water absorption: < 0.01%

The permeability of ECTFE to O_2, CO_2, Cl_2, and HCl are 10 to 100 times lower than PTFE and FEP [3]: Gas Permeability coefficient ($cm^3 \cdot mm/m^2 \cdot atm \cdot day$ at 25°C): H_2 = 109; N_2 = 1.3; O_2 = 10.2. Water vapor Permeability = 0.15 g-mil/100 in^2 per day at 38°C with 90% RH [3]. Off-gassing results have also been reported at < 0.1 $\mu g/cm^2$ [4].

Summary: Future sample return missions may require the use of multiple materials for sample handling systems and storage containers to preserve the scientific integrity of each sample. As future instrumentation becomes more sensitive and scientific investigations inherently cover the entire periodic table, new materials will need to be developed to reduce cross-contamination. Halar (ECTFE) would be a prime candidate for primary sample containment material where the required service temperature can be maintained.

Reference: [1] Forrest, M. J. et al. (2007). The Rapra collection of infrared spectra of rubbers, plastics and thermoplastic elastomers. iSmithers Rapra Publishing. [2] Solvay (2013) Halar Technical Data Sheet. [3] Massey, L.K. (2003) Permeability properties of plastics and elastomers. Plastics Design Library, Norwich , NY. [4] Tewardson, A. (2003) *J. of Fire Sciences*, 21(5), 397-413.