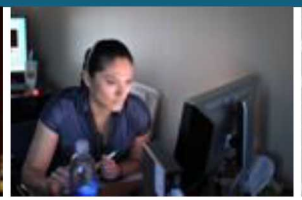
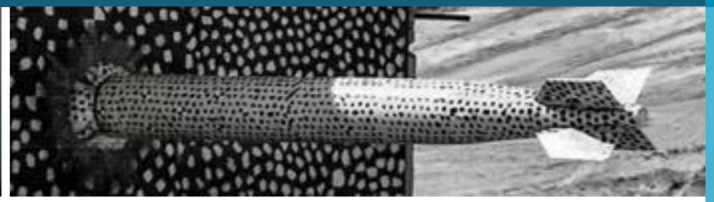
Presented virtually at the 61st Annual INMM Meeting
July 2020

SAND2020-6390C

Sandia National Laboratories

Visually Obvious Tamper-Indicating Enclosures based on O_2-Sensitivity





Presented by:

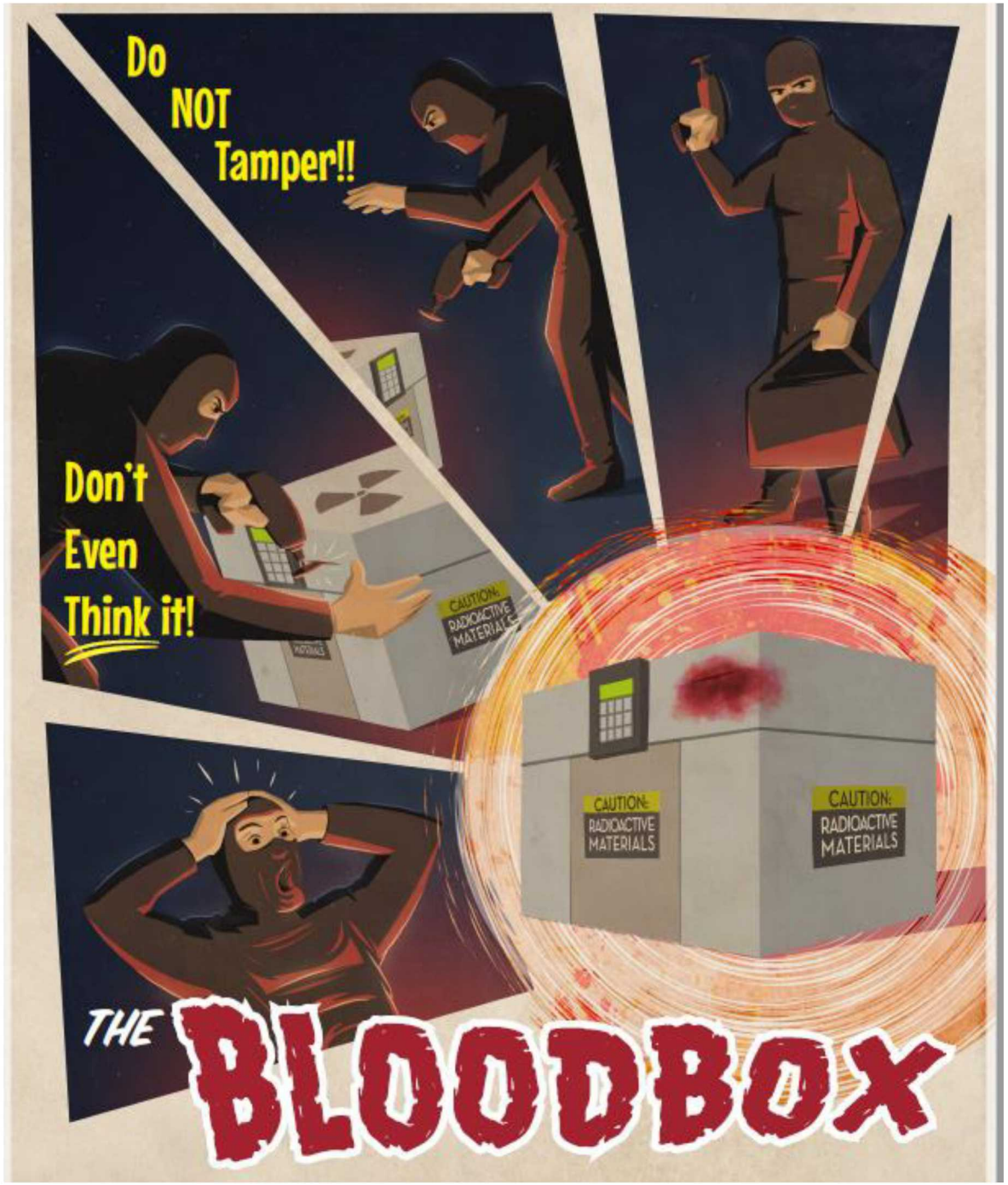
Heidi A. Smartt, PhD

SAND2020-

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Acknowledgements

- The authors would like to acknowledge and thank the U.S. National Nuclear Security Administration (NNSA) Office of Defense Nuclear Nonproliferation R&D Safeguards portfolio for funding and supporting this research.
- Thank you to team members Cody Corbin and Jason Livesay.


Do NOT Tamper!!
Don't Even Think it!
CAUTION: RADIOACTIVE MATERIALS
CAUTION: RADIOACTIVE MATERIALS
CAUTION: RADIOACTIVE MATERIALS
THE BLOODBOX

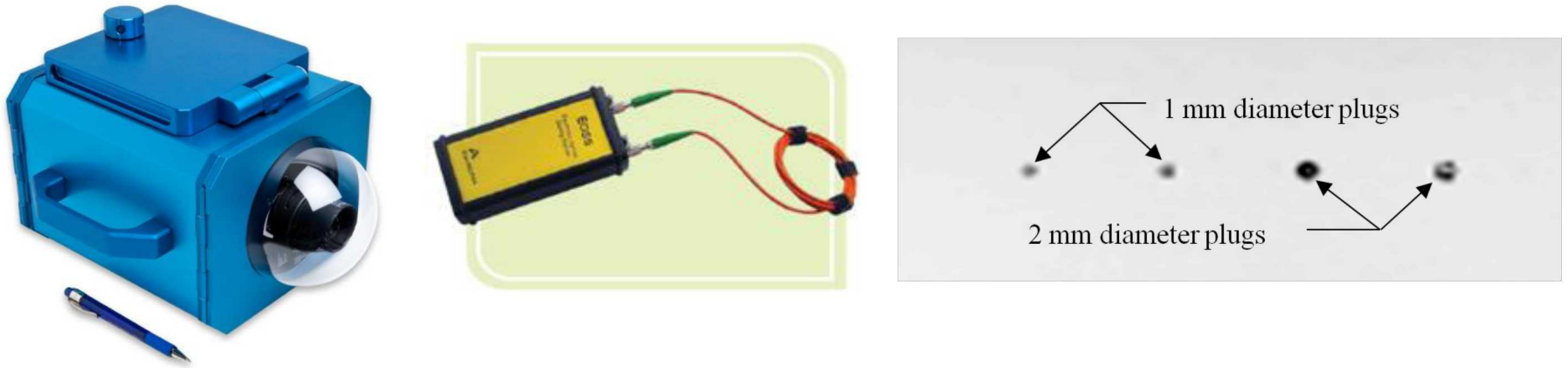
Project Overview and Goals

- Improve tamper-indicating enclosures (TIEs) by making response to tamper obvious through simple visual inspection, facilitating rapid and objective inspections
- Material should:
  - Dramatically change color irreversibly upon tamper
  - Not allow adversary to repair or hide tamper-attempts
  - Be robust to environment and facility handling
  - Be 3D printed or poured into an enclosure mold and cured (for custom equipment)
  - Be applied by paint or spray coating (for application to existing surfaces)
  - Be low cost and deployable across wide range of applications

Concept of approach

Background

Current TIEs typically require time consuming and subjective inspections, active monitoring technology, or external verification mechanisms. There are no current approaches that upon tamper, result in obvious responses with only visual inspection needed.

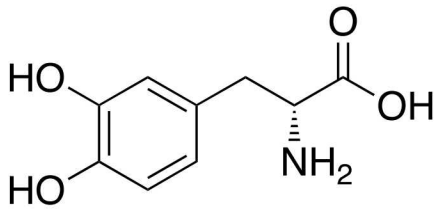


(Left) NGSS surveillance system uses both anodized aluminum, which is verified subjectively on both the outer and inner surfaces via visual inspection and touch, as well as active self-monitoring using conductive materials. (Middle) The EOSS fiber loop seal uses active self-monitoring using conductive foils. Active methods require power and are not applicable in some scenarios. (Right) Metal containers can be verified using eddy current – an external electronic instrument capable of finding disturbances in the metal, including drilled and plugged holes.

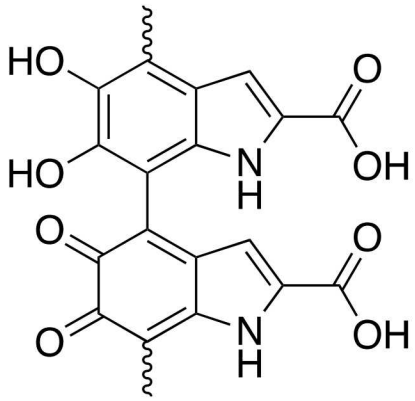
Technical Approach

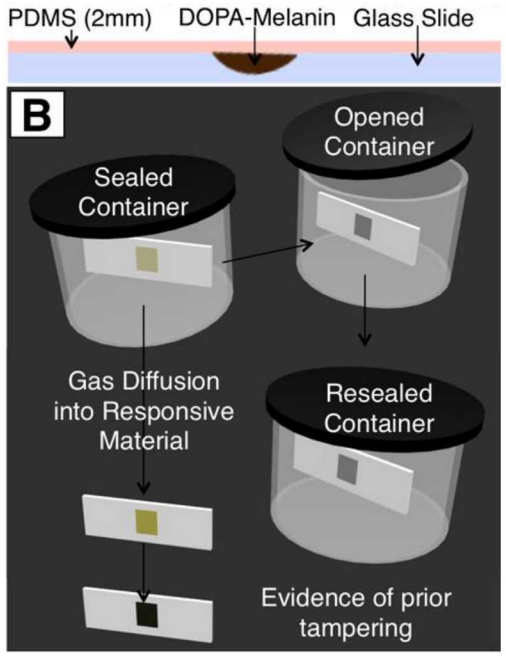
- Design and develop prototype materials for (1) custom enclosures, and (2) application to existing surfaces.
- Extensive material R&D has occurred since ~2015 (SNL LDRD, NA-22 funding)
  - Original idea was that same material would be used for custom and existing enclosures but have separate fabrication/application methods
- Status of current R&D:
  - Custom enclosure approach is based on O_2 sensitivity
  - Approach for application to existing surfaces based on sensor-loaded microcapsules that cause irreversible color change upon rupture
- O_2 sensitivity research is focused on optimizing thickness of O_2-impermeable layer and fabrication methods.
- Microcapsules research is focused on materials and formation methods, and optimizing in terms of wall thickness, size, permeability, and force required for rupture.

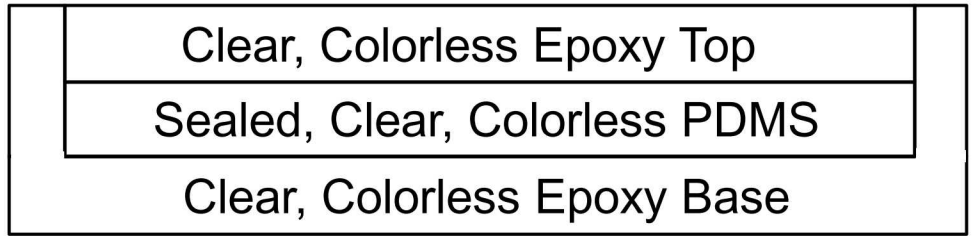
O_2-Sensitive Tamper Indicating Material

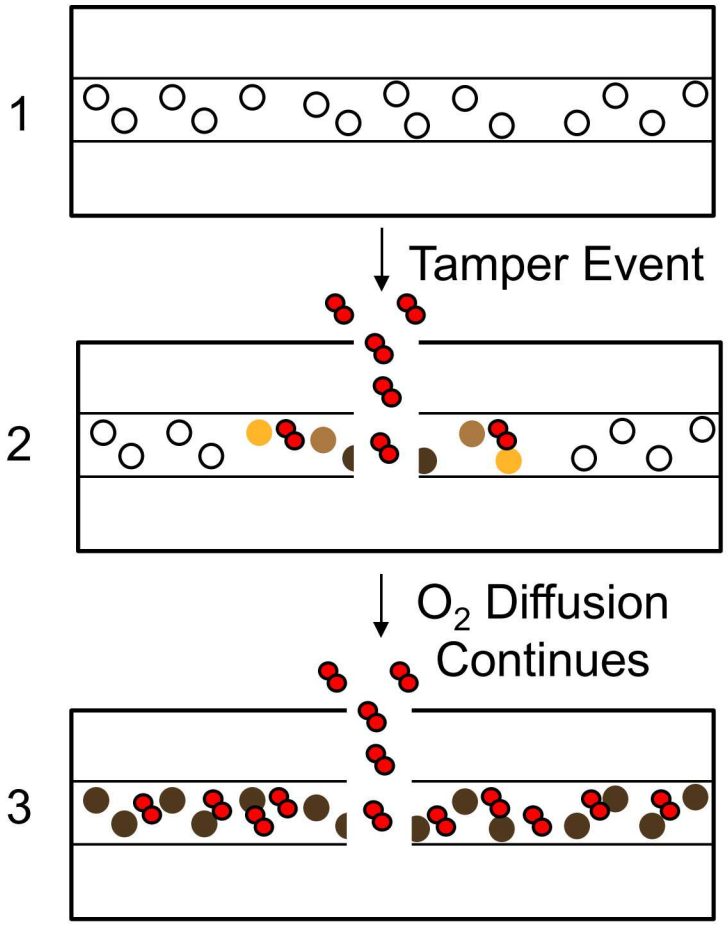


in KOH(aq)









PDMS Layer
- Permeable to oxygen
- Contains bubbles of aqueous L-DOPA/KOH
- Inherently contains unique identifiers

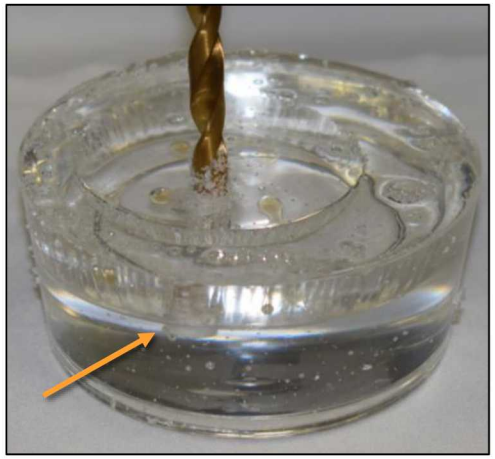
Epoxy Layers
- Minimally permeable to oxygen
- Seals PDMS layer & O_2 sensitive L-DOPA
- Tampering allows oxygen to flow into and diffuse through PDMS
- Inherently contains unique identifiers

ACS Appl. Mater. *Interfaces,* **2016**, 8, 4314−4317

L-DOPA Tamper Event

= tamper hole

Before Tamper



Tamper event introducing oxygen

2 hours

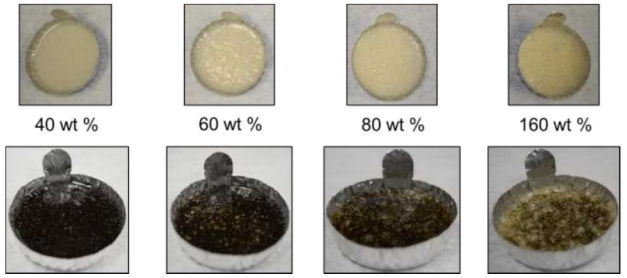
4 hours

6 hours

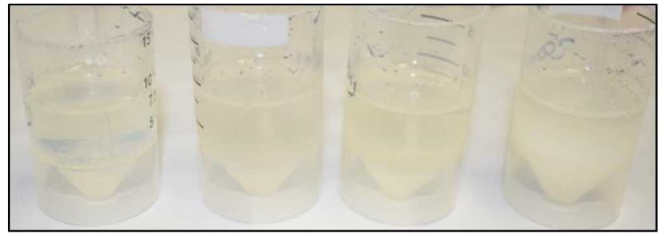
22 hours

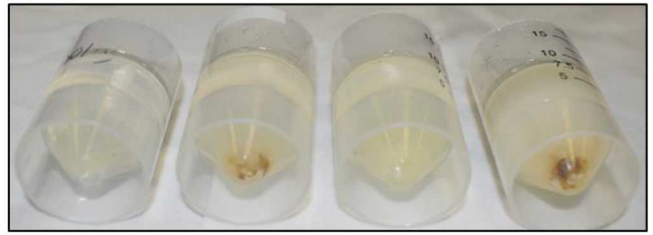
Process Improvements

Polymer Substrate - Silicone



Polymer Substrate - Epoxy





High-boiling Polyprotic Organics

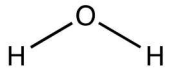
Water has temperature limitations that may not prove useful in all environments. Can we expand the temperature range of the sensing?

Using high-boiling polyprotic solvents rather than water was expected to allow both L-DOPA and KOH solubility while expanding the temperature range at which these materials can be utilized.

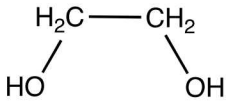
- To test this, water was replaced with;
  - Glycerol (T_b = 290 °C, T_f = 18 °C)
  - Propylene glycol (T_b = 187 °C, T_f = -60 °C)
  - Ethylene glycol (T_b = 197 °C, T_f = -13 °C)

T_b = Boiling point

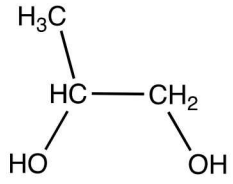
T_f = Freezing point



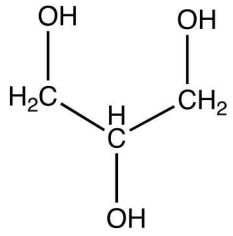
H_2O



Ethylene Glycol



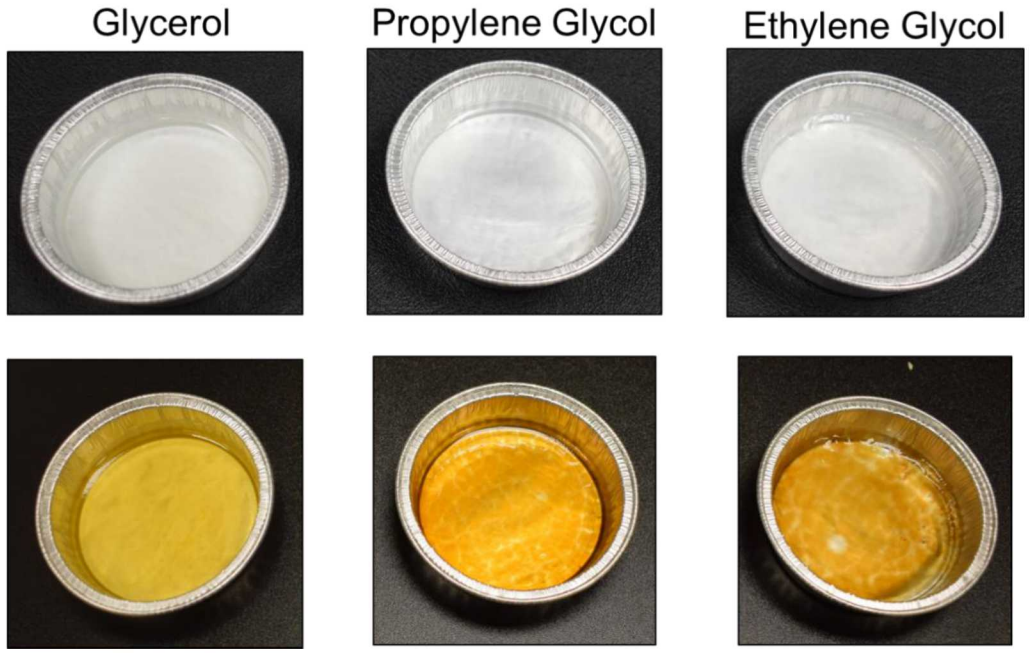
Propylene Glycol



Glycerol

Pre-O_2 Exposure

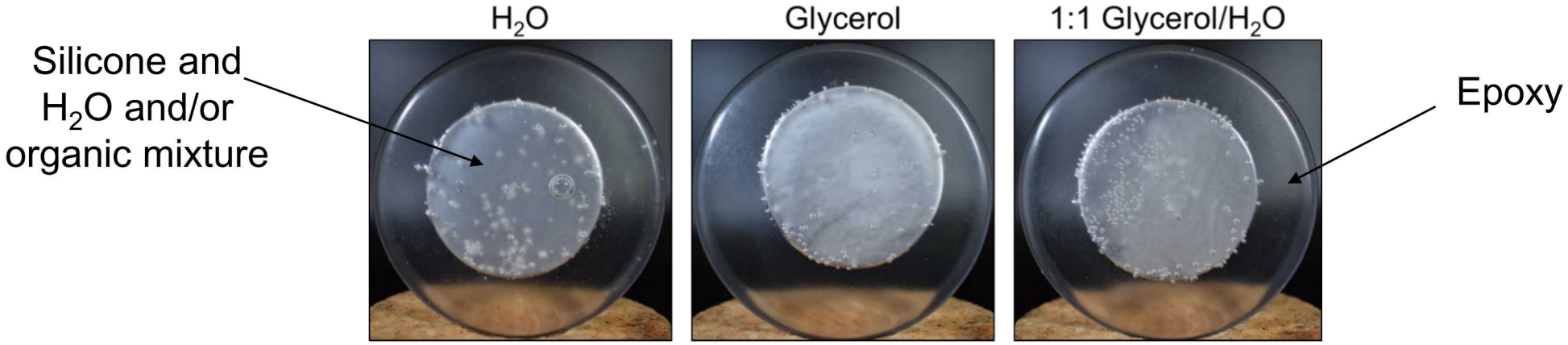
Post-O_2 Exposure



Balancing Solubility and Thermal Properties

Once pure organic solvents were proven with the same O_2 mechanism established with H_2O, the final solvent experiments had relevant combinations of H_2O and polyprotic organics to yield a balance of solubility and thermal properties.

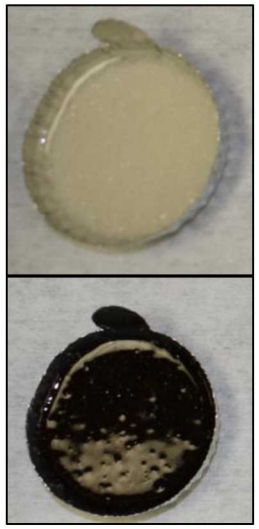
Bubbles formed during processing lead to inherent areas that would be difficult to replicate for an adversary.



These coupons will be thermal cycled in a humidity chamber to determine 1) any chemical effects on the epoxy and 2) if increased O_2 diffusion due to in elevated temperatures leads to a false positive color change.

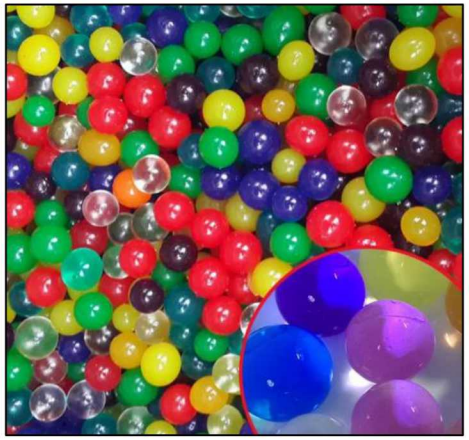
L-DOPA Sensing Summary

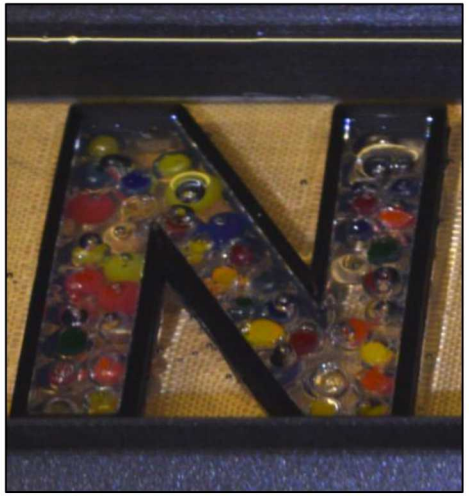
Sylgard & encapsulated in epoxy



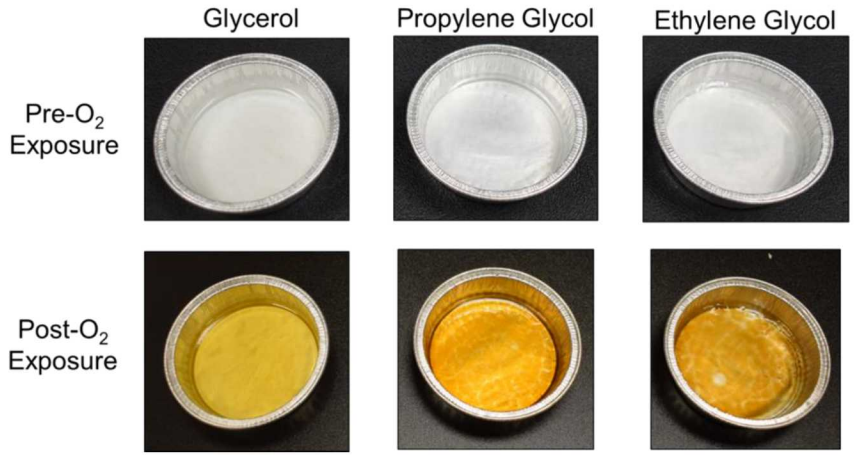
NaPolyA & encapsulated in silicone

NaPolyA & encapsulated in epoxy





L-DOPA solution absorbed by beads & placed in Sylgard/Epoxy



Future work on L-DOPA Materials

- Investigation of the stability of these materials over time in air, over time in heat, and in the presence of corrosive materials.
- Radiation testing will also be a major characterization required for the safeguards application space, and the R&D in progress has been designed to utilize robust materials.
  - Thermoset (cross-linked) materials are being used because of this, along with the difficulty of repair expected for an adversary.
- The water beads mentioned earlier in the previous slide have been ground up and will be used as a filler instead of the intact water beads.
  - Allows unique identifier property to remain with the added benefit of the silicone material used in much thinner areas with tight dimensions.