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Visually Obvious Tamper-Indicating Enclosure based on O_2-Sensitivity

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Abstract

Tamper-indicating enclosures (TIEs) are used in treaty verification regimes to ensure that monitored items such as containers of nuclear material or inspectorate equipment enclosures are not accessed without detection. While tamper-indicating devices (TIDs) are used to detect unauthorized opening of separable parts (for example, a lid or door), TIEs are volumetric in nature and are deployed over an entire item. Current TIE approaches are generally based on (1) passive materials in which an inspector qualitatively inspects the surface for anomalies, (2) active approaches such as conductive materials or fiber meshes that provide a tamper alert, and (3) external equipment used to examine a material for anomalies such as eddy current. Sandia is currently performing R&D on approaches that provide a visually obvious response to tamper such that the tamper attempt is readily seen by an inspector without the need for external equipment. Two approaches are under investigation – one based on microcapsules that can be sprayed or painted onto existing surfaces, and one that can be used to develop custom equipment (the subject of this paper).

Introduction

Tamper-indicating enclosures (TIEs)[1] are used in treaty verification regimes to detect access to an item of interest. Items of interest can include, but are not limited to, (1) inspectorate-owned equipment enclosures in which detecting access is desired to ensure trust in information stored or processed within the enclosure and (2) facility-owned enclosures containing nuclear materials that have been measured by inspectors and require maintaining continuity of knowledge in the absence of the inspector. Current deployed TIEs typically fall within three categories. The first are materials that an inspector will primarily visually inspect for signs of unauthorized access, such as the ubiquitous anodized aluminum enclosures that the International Atomic Energy Agency (IAEA) deploys with the Remotely Monitored Sealing Array (RMSA) fiber loop seal, the Next Generation Surveillance System (NGSS), legacy surveillance systems, and other monitoring equipment. The second category are active electronic methods/materials that continuously monitor the volume for signs of unauthorized access, such as the conductive foil within the Electronic Optical Sealing System (EOSS) fiber loop seal and the fiber mesh embedded in the enclosure of the NGSS. The third category are externally deployed indicators of penetration or access to materials, such as eddy current or imaging devices. Note that both the second and third category also require visual inspection. The limitations to these three categories are the subjective and time-consuming process of visually inspecting surfaces, the inability to deploy an active approach in some situations because of batteries or because of environmental conditions or facility requirements, and the limited materials able to be analyzed by eddy current and potential inability to bring external equipment, such as a camera, into a facility. Further, some approaches rely more on post-mortem analysis rather than in-situ verification.

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[1] Note that TIEs are essentially volumetric seals. As such, they must have an integrity and identity element. The integrity element (tamper-indicating) is the thrust of this work. The identity element will be addressed separately.

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The existing toolkit for TIEs is limited regarding the complex issues involved, and many technologies are old which may leave them more vulnerable. Simple visual approaches capable of high detection sensitivity have not received adequate research and development, although applications already exist that could benefit from such a capability. Sandia National Laboratories (SNL) recognizes these limitations and is developing "bleeding" materials (analog of visually obvious colorful bruised skin that doesn't heal) that provide inspectors the ability to readily recognize using simple visual observation that penetration into the material has been attempted without providing adversaries the ability to repair damage. Such material can significantly enhance the current capability for TIEs, used to support treaty verification regimes.

SNL's previous approach was research and development (R&D) of transition metals inside microspheres embedded in 3D-printed structures or spray-coated onto existing surfaces, that when penetrated or tampered, cause an irreversible color change that is visually obvious. Due to initial difficulties with microsphere formation based on a transition metal approach, SNL divided the work into two separate paths. The first is an O_2-sensitive approach that is used to develop custom equipment (the subject of this paper), while the second more closely follows the earlier work by using cargo-loaded microspheres. The anticipated benefits of this work are passive, flexible, scalable, cost-effective TIEs with obvious and robust responses to tamper attempts. These responses result in more efficient and effective monitoring as inspectors will require little or no additional equipment and will be able to detect tampering without extensive time-consuming visual examination. Applications can include custom TIEs (cabinets, equipment enclosures, seal bodies), or (with development of the microcapsule approach) spray-coating/painting onto facility-owned items, walls or structures, or circuit boards.

Custom Approach Using O_2 Exposure

Previous R&D [1] on a custom approach focused on encapsulated transition metals. Due to the challenges associated with the transition metal-based approach, a mitigation approach was investigated. The mechanism utilizes an O_2 sensitive compound, 3-(3,4-dihydroxyphenyl)-L-alanine (L-DOPA), to initiate the visible and drastic color change [2]. In an inert environment such as a glovebox, bubbles of a L-DOPA aqueous solution are inserted into partially cured polydimethylsiloxane (PDMS), a very oxygen-permeable silicone. Once fully cured, the PDMS piece is encapsulated inside epoxy (828/T-403), shielding the silicone from the aerobic environment. Upon a tamper event, the silicone is exposed to the air and oxygen permeates through the entire layer causing the irreversible L-DOPA-to-melanin polymerization to occur (Figure 1 & Figure 2). This initiates the bubble color to convert from a faint yellow to a dark brown over a 24-hour period (Figure 3).

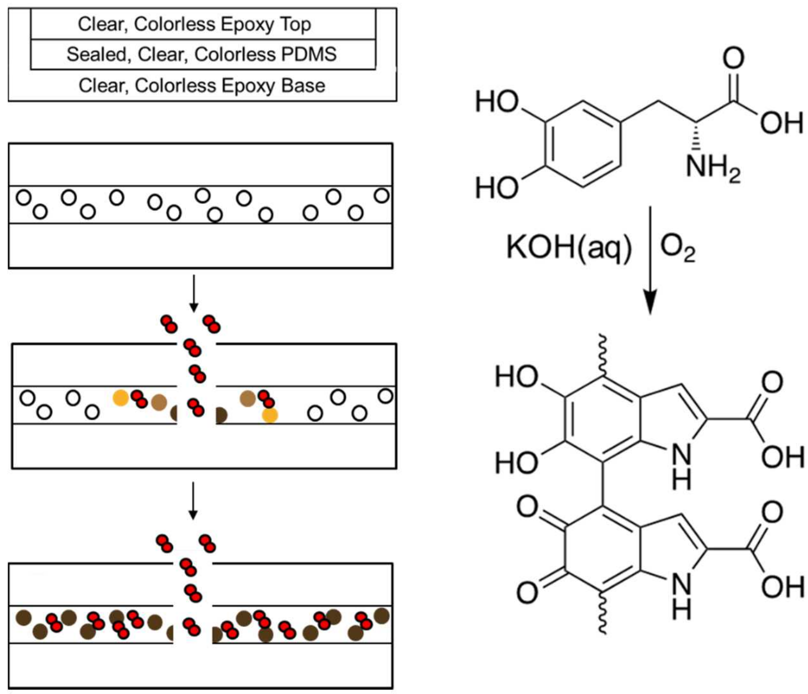

Figure 1: Setup and mechanism of O_2 sensitivity in L-DOPA-based TIE. A tamper event exposes the PDMS layer to air, which then permeates slowly through the entire layer. The L-DOPA in the aqueous bubbles irreversibly polymerize to poly(L-DOPA-melanin), which is a dark brown color.

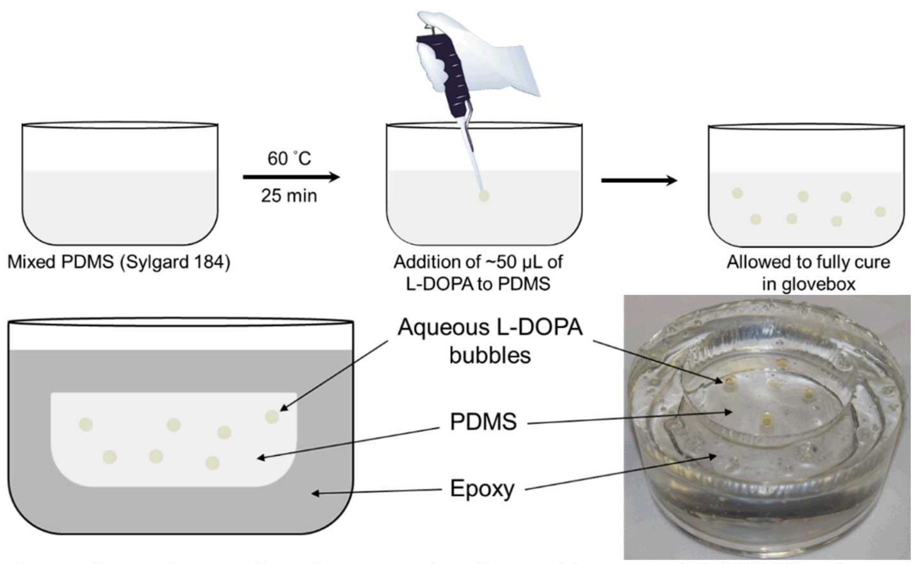

Figure 2: Initial experimental procedure for preparing O_2-sensitive material. PDMS and epoxy components were degassed in a glovebox antechamber overnight and over a weekend, respectively. All processing occurred in an N_2 environment inside a glovebox.

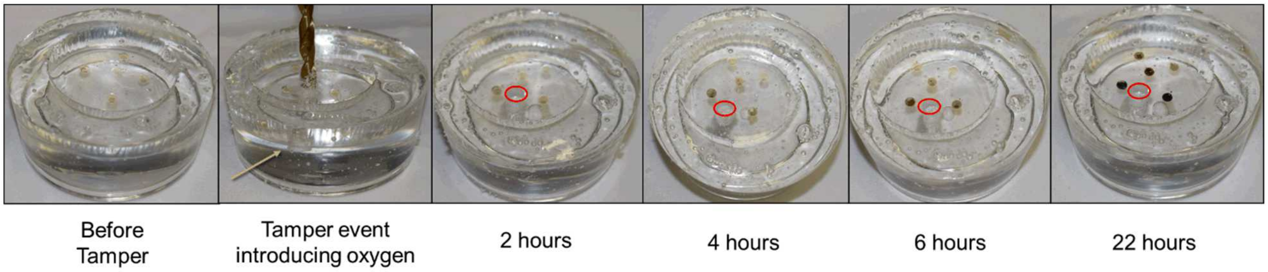

Figure 3: Time lapse photos of tamper indication over a 22-hour period. Orange arrow indicates bottom of drill hole into epoxy and red circles indicate tamper site.

This tamper-indicating mechanism has some noteworthy advantages. These include 1) no synthesis of materials required, 2) all materials are commercial-of-the-shelf products, 3) no organic solvents present, 4) a robust system is created due to epoxy encapsulation, and 5) one single tamper site can compromise (turn brown) the entire TIE over time, which makes an inspector's job much easier and quicker.

This work has recently been expanded on a variety of fronts on both processing and relevant materials. For processing, L-DOPA solution were absorbed on to water beads (Figure 1Figure 4), which are polymeric spheres composed cross-linked sodium poly(acrylate), the same super-absorbent material used in baby diapers. These water beads can either be colorless or multicolored, which not only provide a substrate for L-DOPA solution absorption but also a unique identification factor as well. Furthermore, they are very inexpensive, and allow much easier mixing with the silicone instead of water bubble injections.

Figure 4. Image of colored water beads (left) and integration of L-DOPA-soaked water beads into the "N" of an NA-22 exemplar (right). The beads are encapsulated by the silicone, and the NA-22 text and surrounding is encapsulated with the epoxy. Bubbles present from processing provide inherent unique identification.

Further integration studies have also been performed using cross-linked sodium poly(acrylate) powder to absorb the L-DOPA solution. It was determined via simple experimental studies that the optimal L-DOPA solution absorption to the polymer was 300 weight% and next step experiments determined how much of the L-DOPA polymer is needed in the silicone to make a homogenous and nicely filled mixture (Figure 5). It was determined that a simple 40 weight% polymer in silicone provides a smooth sample with a drastically noticeable color change upon exposure to an aerobic environment.

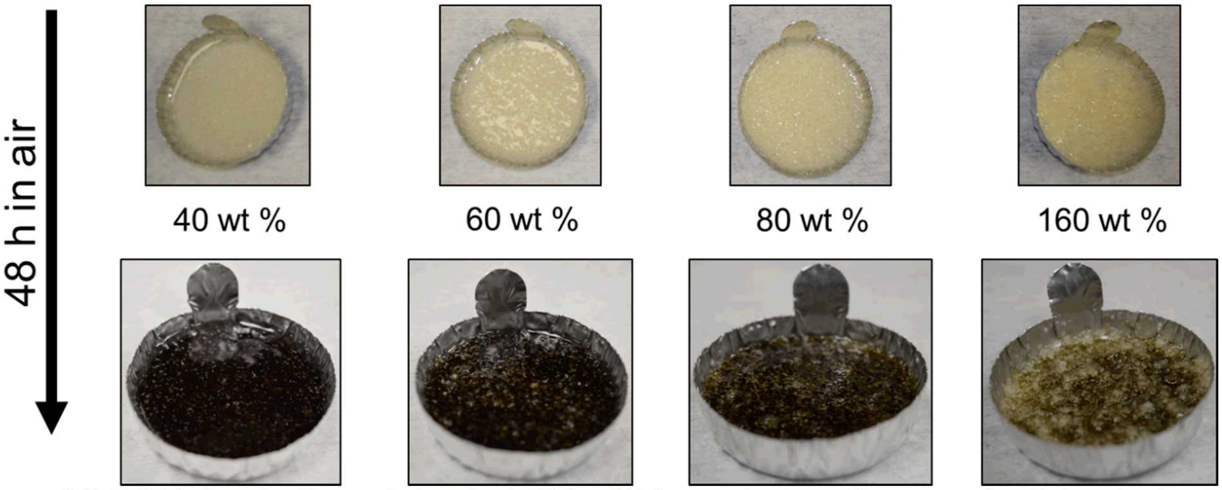

Figure 5. L-DOPA doped sodium poly(acrylate) (300 wt%) integration into silicone samples. Before (top) and after (bottom) exposure to air for 48 hours.

To expand on the work above in both a scientific and use-case perspective, manipulating the sensing solvent was next attempted. 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 either glycerol (T_b = 290 °C, T_f = 18 °C), propylene glycol (T_b = 187 °C, T_f = -60 °C), or ethylene glycol (T_b = 197 °C, T_f = -13 °C). Concentrations of other components, such as L-DOPA and KOH, had to be modified due to the organic nature of the protic solvents. O_2 response results are shown in Figure 6.

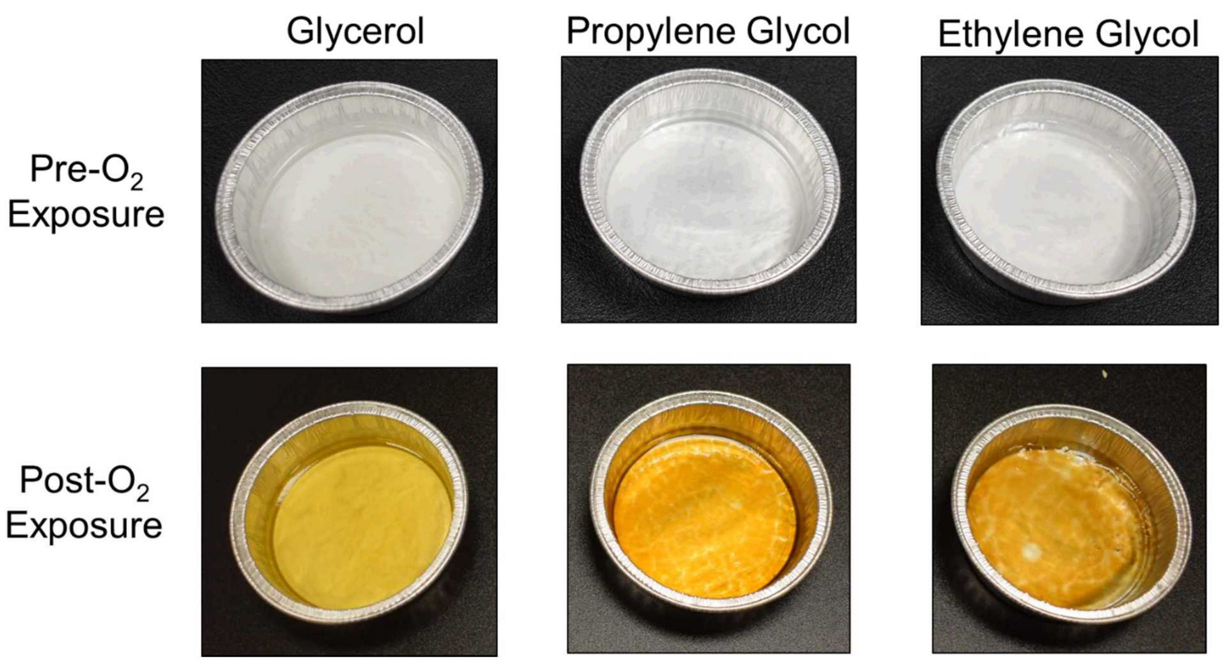

Figure 6. Silicone samples containing solutions of L-DOPA, KOH, and a protic organic solvent.

Mixing of the silicone with the L-DOPA organic solutions had some slight observational differences compared to the water-based samples. Because the miscibility of silicone and water is the lowest of the solvent types, the water is mixed heterogeneously and leads to the most transparent sample. The organic solvents, however, are slightly more miscible due to their organic constituents. This leads to some translucency or opacity when mixed with the silicone. This property actually aids in the visualization of the color change since a white background is provided. Furthermore, there is some slight phase separation seen in the ethylene glycol and propylene glycol samples which inherently provides some unique features for anti-counterfeiting purposes.

Once pure organic solvents were proven with the same O_2 mechanism established with water, the final solvent experiments had relevant combinations of water and organics to yield a balance of solubilities and thermal properties. All of the organic solvent samples bring the high range of the temperature scale up, but not nearly as much on the low range. This is where mixtures of water and organic solvent can be beneficial as the low range can be manipulated significantly. A 66:43 (by weight) glycerol/water mixture, 60:40 propylene glycol/water mixture, and 80:20 ethylene glycol/water mixture have freezing/boiling points at -46 °C/112 °C, -48 °C/107 °C, and -46 °C/127 °C, respectively. The water presence allows concentrations of L-DOPA and KOH to go up, if needed, and also lowers the freezing point of the mixture compared to some of the organic solvents; alternatively, the organic solvent increases the boiling point of the mixture. Silicone samples of the mixtures showed equivalent color changes. With that success, glycerol was chosen as an exemplar to make environmental samples where the silicone is fully encapsulated in epoxy (Figure 7). 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.

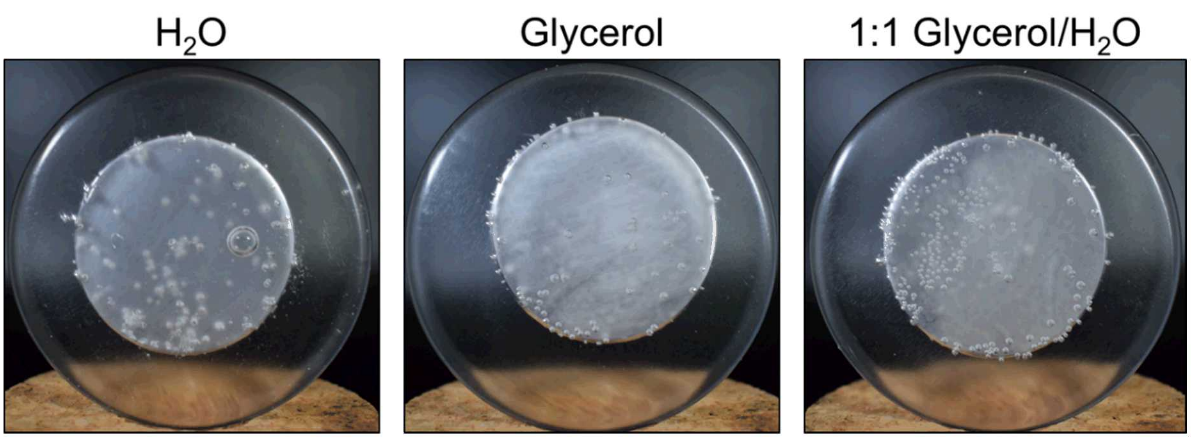

Figure 7. Coupon samples of the three types of solvent systems used. Silicone sample is encapsulated in epoxy, providing an environmental barrier from O_2.

Next Steps

Future work in these polymer sensing systems include 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. More specifically, thermoset (cross-linked) materials are being prepared instead of thermoplastic materials, which can melt/degrade quickly over time. The molecular structure of the thermoset materials will also aid in mitigating radiation damage. Finally, the water beads mentioned earlier in the text have been ground up and will be used as a filler instead of the intact water beads (Figure 8). This will allow the unique identifier features to remain but at the same time will allow the silicone material to be used in much thinner areas with tight dimensions.

Figure 8. Crushed up water beads used to absorb L-DOPA water solution for sensing.

Conclusions

The existing toolkit for TIEs is limited regarding the complex issues involved, and many technologies are old which may leave them more vulnerable. Further, currently deployed TIEs are limited by the subjective and time-consuming process of visually inspecting surfaces with no obvious anomalies, the inability to deploy an active approach in some situations because of batteries or because of environmental conditions or facility requirements, and the limited materials able to be analyzed by eddy current and potential inability to bring external equipment, such as a camera, into a facility. Simple visual approaches capable of high detection sensitivity and inability of an adversary to repair tamper attempts have not received adequate research and development until now. This project focuses on improvements to TIEs by researching and developing prototypes of materials that irreversibly change color upon tamper (penetration into material). Such material improves effectiveness (obvious visual observation of tamper) and efficiency (rapidly seeing locations of tamper-attempts) of inspections, with no additional equipment needed.

Acknowledgements

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