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Tamper-Indicating Enclosures with Visually Obvious Tamper Response

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Abstract:

Sandia National Laboratories is developing a way to visualize molecular changes that indicate penetration of a tamper-indicating enclosure (TIE). Such "bleeding" materials (analogous to visually obvious, colorful bruised skin that doesn't heal) allows inspectors to use simple visual observation to readily recognize that penetration into a material used as a TIE has been attempted, without providing adversaries the ability to repair damage. Such a material can enhance the current capability for TIEs, used to support treaty verification regimes. Current approaches rely on time-consuming and subjective visual assessment by an inspector, external equipment, such as eddy current or camera devices, or active approaches that may be limited due to application environment. The complexity of securing whole volumes includes: (1) enclosures that are non-standard in size/shape; (2) enclosures that may be inspectorate- or facility-owned; (3) tamper attempts that are detectable but difficult or timely for an inspector to locate; (4) the requirement for solutions that are robust regarding reliability and environment (including facility handling); and (5) the need for solutions that prevent adversaries from repairing penetrations. The approach is based on a transition metal ion solution within a microsphere changing color irreversibly when the microsphere is ruptured. Investigators examine 3D printing of the microspheres as well as the spray coating formulation. The anticipated benefits of this work are passive, flexible, scalable, cost-effective TIEs with obvious and robust responses to tamper attempts. This results in more efficient and effective monitoring, as inspectors will require little or no additional equipment and will be able to detect tamper without extensive time-consuming visual examination. Applications can include custom TIEs (cabinets or equipment enclosures), spray-coating onto facility-owned items, spray-coating of walls or structures, spray-coatings of circuit boards, and 3D-printed seal bodies. The paper describes research to-date on the sensor compounds and microspheres.

Keywords: tamper-indicating enclosures; international nuclear safeguards

1. 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 aluminium enclosures that the IAEA deploys with the RMSA fiber loop seal, the NGSS surveillance system, 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 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 analysed by eddy current and potential inability to bring external equipment into a facility. Further, some approaches rely more on post-mortem analysis rather than in-situ verification.

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)

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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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 approach is research and development of cargo-loaded 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[1]. Work comprises the following general tasks: (1) sensor and microsphere development and optimization (i.e., intensity of response, surface area of response, and microsphere composition, size, wall thickness, rupture point), (2) integration of transition metal-loaded microspheres into 3D-printed, spray-coated, or moulded geometries, and (3) testing and evaluation of prototypes, including environmental and industrial considerations. 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 or equipment enclosures), spray-coating onto facility-owned items, spray-coating of walls or structures, spray-coatings of circuit boards, and 3D-printed seal bodies.

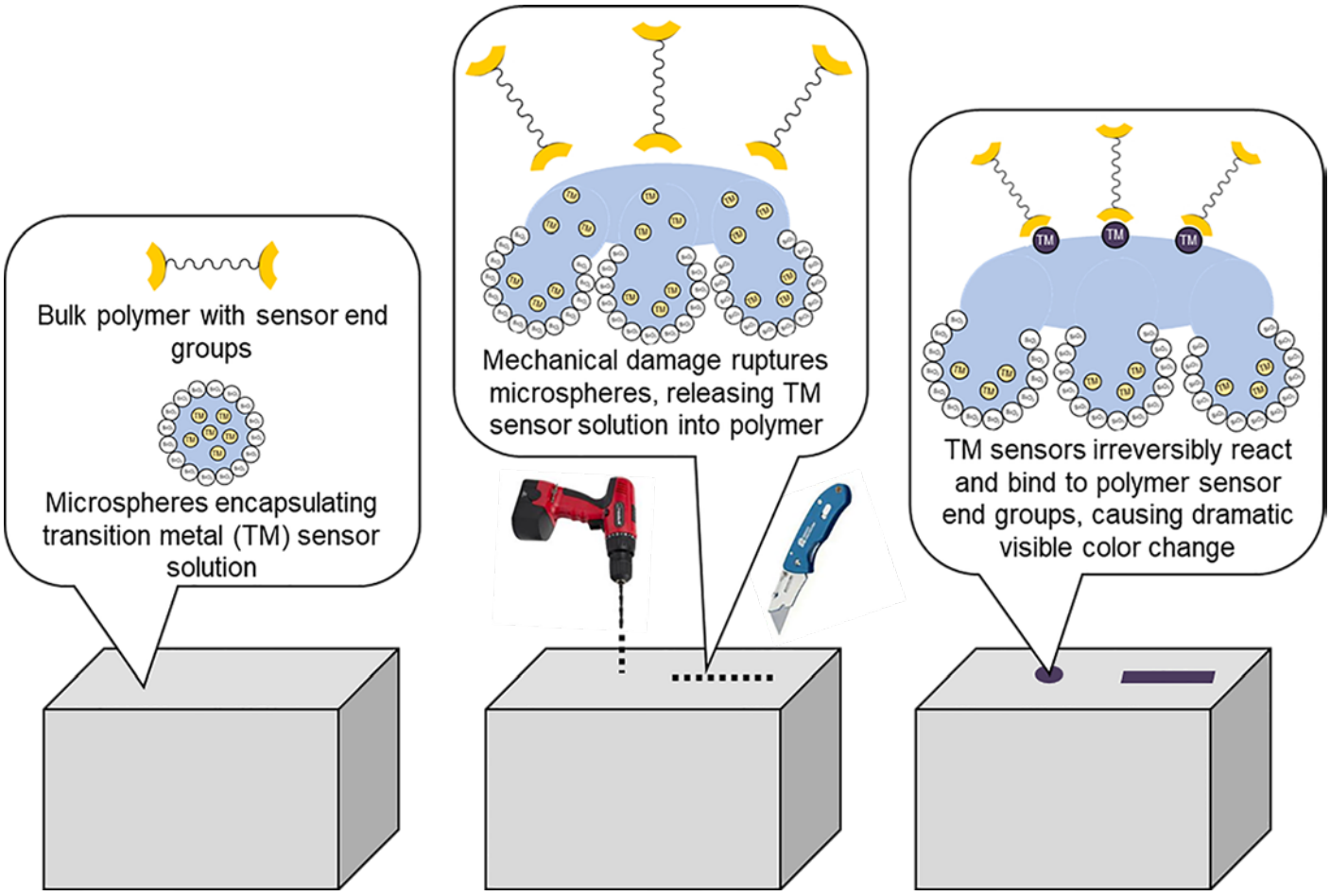

Figure 1: General schematic of R&D concept. A two-phase material consisting of a sensing polymer and transition-metal encapsulated microspheres are 3D-printed or spray-coated on to a unique geometry. Upon tampering, the microspheres rupture and the two sensor components interact to form an irreversible visible color change.

2. R&D of sensor compounds

Transition metal complexes consist of a transition metal center derived from a metal salt (e.g. $FeCl_3$) and an organic molecule. The combination of these components can lead to dramatic and highly visible color changes which may be utilized for sensing application spaces. The initial approach for the goal of this project was to perform a scoping study with various 3d transition metals with one organic sensor (2,6-bis(10-methyl-benzimidazolyl)-4-hydroxypyridine, (HO-Bip)) to establish a qualitative evaluation of color change.[2,3] Figure 2 presents these results along with the chemical structure of the sensor that was utilized.

Once the plausibility of the mechanism was confirmed, our second goal was to make a series of transition metal complexes with a commercially available sensor. The compound 5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (Ephen) was chosen as the sensor because it is cheap, colorless, and can be easily polymerized using various methods. The series of transition metal complexes were prepared via combining dilute solutions of the metal salts ($CrCl_3$, $Mn(OAc)_3$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $CuCl_2$, $NiCl_2$, and $ZnCl_2$) with a dilute solution of Ephen in a 1:1 molar ratio. This ratio was chosen because it represents the minimum binding of the sensor to the metal salt. Two common solvents were investigated, methanol and dimethyl sulfoxide (DMSO). These solvents were chosen as these are expected to have good penetration into epoxy-based polymeric materials while also allowing efficient solubility of the metal salts.

Figure 3 shows the results of mixing $FeCl_2$, $FeCl_3$, $CoCl_2$, and $CuCl_2$ with the sensor, Ephen. The other metal salts, $CrCl_3$, $Mn(OAc)_3$, $NiCl_2$, and $ZnCl_2$, did not yield an easily visible color change in either solvent. All solutions from Figure 3 have concentrations of 10 mM except the

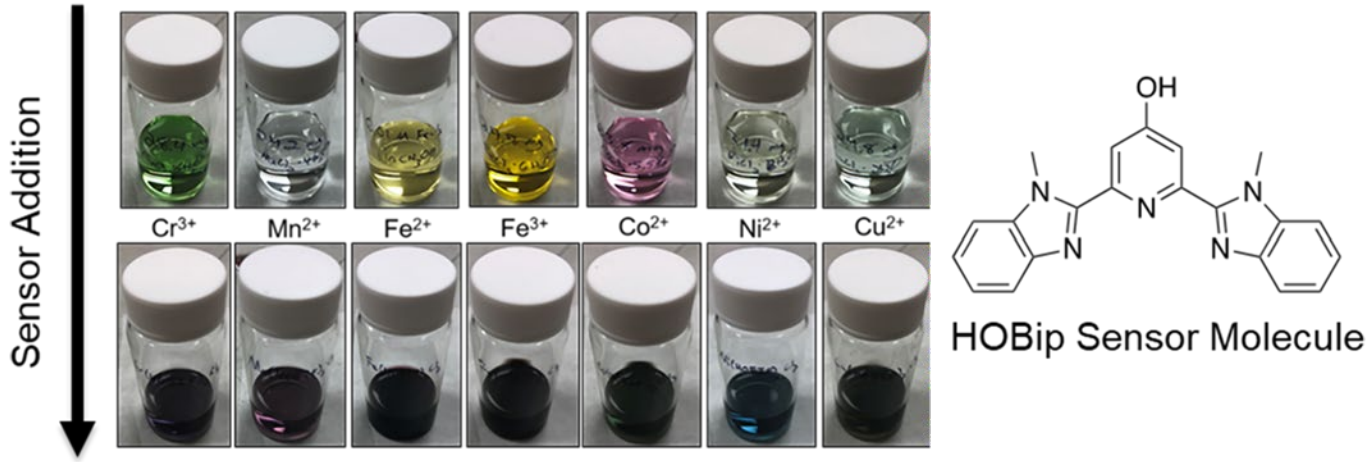

Figure 2: Qualitative scoping study results on 3d transition metal color changes with addition of organic sensor in methanol. All metal solutions get significantly darker, and many have a dramatic color change.

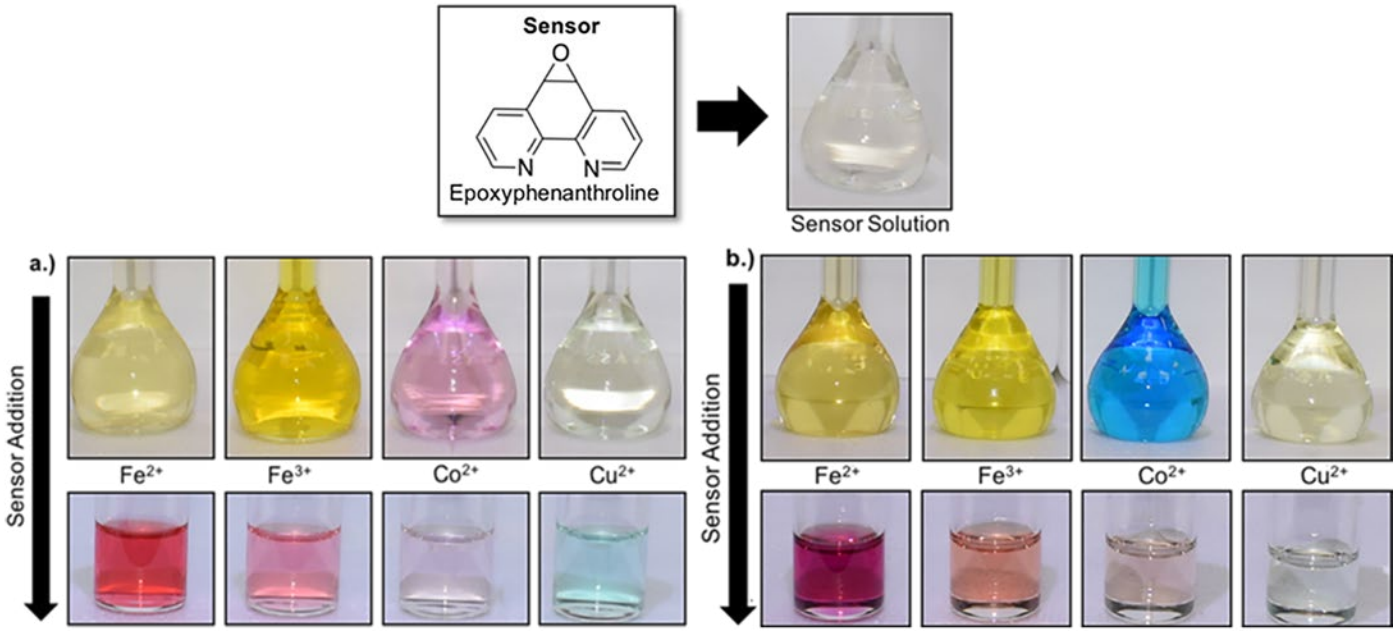

Figure 3: Colorless sensor solution in both methanol and DMSO (top); (a) addition of sensor solution to various metal salt solutions in a 1:1 molar ratio in methanol; (b) addition of sensor solution to various metal salt solutions in a 1:1 molar ratio in DMSO.

Fe^{3+} ($FeCl_3$), which had to be diluted to 2 mM. The transition metal complexes formed when mixing the Ephen sensor with the Fe^{2+}, Fe^{3+}, and Co^{2+} solutions, all of which produced dramatic and visibly obvious color changes.

A more quantitative look at the color changes is shown in Figure 4. The solutions above were analyzed by UV-Visible absorbance spectroscopy and the results were plotted as a function of wavelength. The two most intense transitions occur with the Fe^{2+} and Co^{2+} ions. In the case of Fe^{2+} where the solution initially absorbs around 375 nm (visibly yellow), addition of the sensor dramatically shifts the absorbance to around 510 nm (visibly red). The Co^{2+} DMSO solution on the other hand begins as an intense, broad peak between 550 nm and 750 nm (visibly blue) and addition of the sensor produces a broad, weak absorbance around 500 nm. The other solutions do not produce such intense transitions.

The most visibly obvious color changes occurred in the solutions of Fe^{2+} and Fe^{3+} in both methanol and DMSO. The Co^{2+} transition was also visibly obvious but only occurred in DMSO. The next goal is to physically incorporate these sensor molecules into a polymer backbone (Figure 5) and to investigate the stability of these complexes over time in air, over 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 much quickly over time. The molecular structure of the thermoset materials will also aid in mitigating radiation damage.

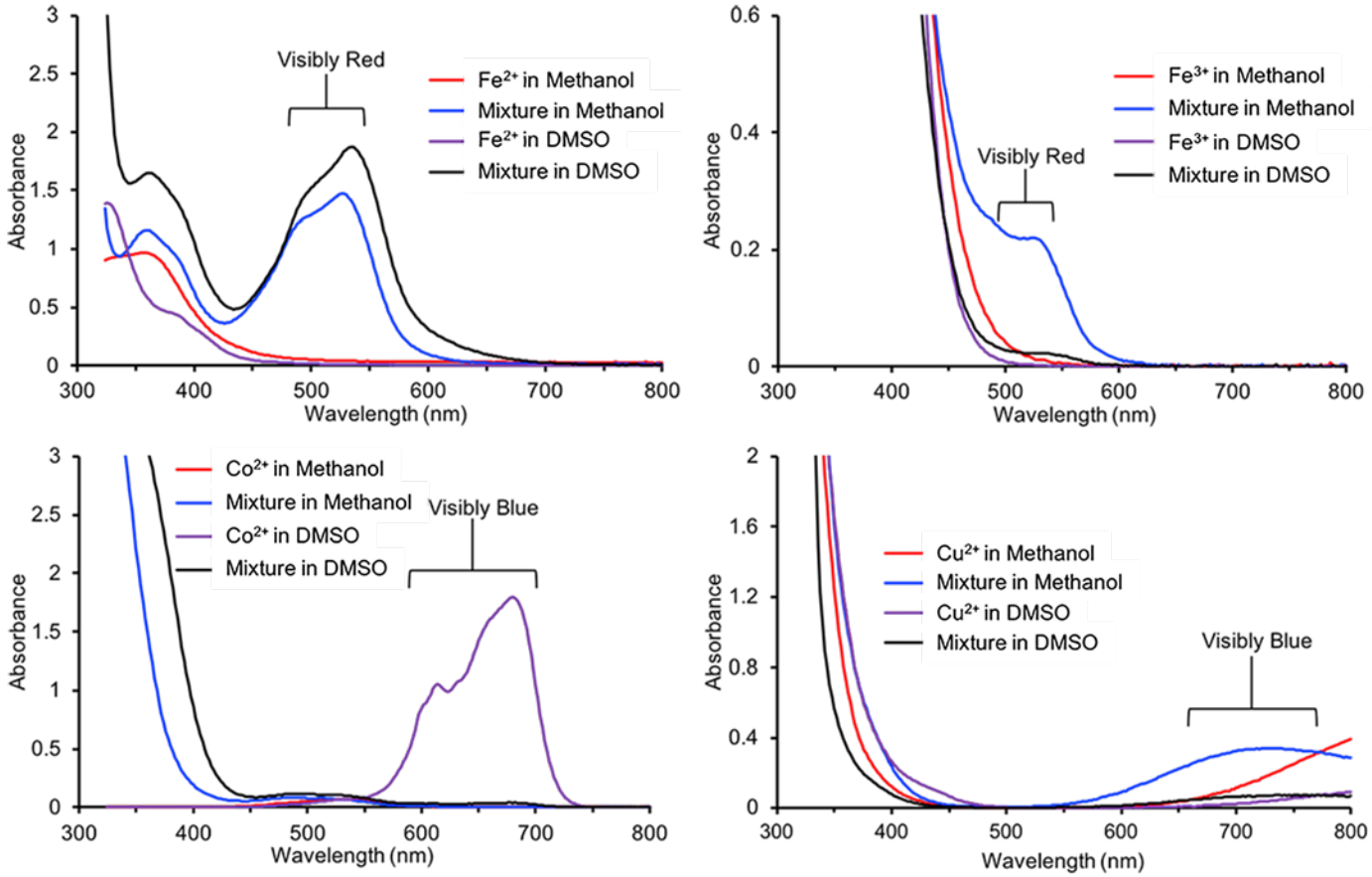

Figure 4: UV-Visible absorbance spectroscopy of Fe^{2+} (top left), Fe^{3+} (top right), Co^{2+} (bottom left), and Cu^{2+} (bottom right) before and after addition of the sensor. The visible colors of the most intense peaks are labeled.

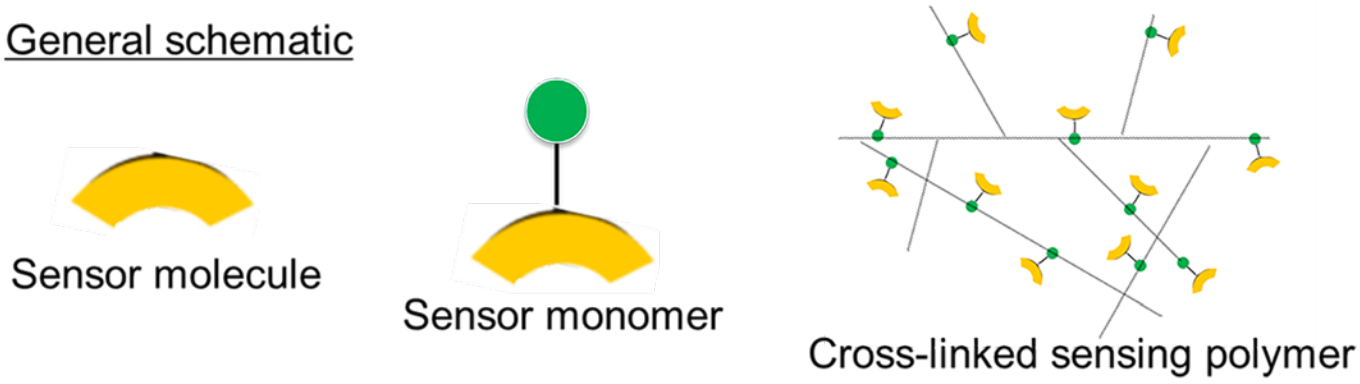

Figure 5: General schematic of incorporation of organic sensor into polymeric material. Both UV-curable and heat-curable materials will be prepared and evaluated.

3. Development of microspheres

A variety of wet chemistry microsphere synthetic methods have been developed in the literature in which capsule formation is carried out in liquid medium, starting from a solution, a liquid-in-liquid emulsion, or a solid-in-liquid suspension.[4] Template materials are often employed to direct the size and shape of the products during synthesis. One templating strategy involves the use of "soft" templates that are sensitive to synthesis parameters such as temperature, pH, solvent polarity, etc. and have been demonstrated to form hollow nano- and microstructures composed of SiO_2, carbons, polymers, metals, metal oxides, etc.

Our efforts focus on the use of emulsion templates. Emulsions are defined as two immiscible liquids (usually hydrophobic and hydrophilic pairs) where small droplets of one liquid are finely distributed within another continuous liquid phase. Emulsions can be oil-in-water (o/w) or water-in-oil (w/o), and surfactant compounds are often required to assemble at the interface of the two liquids to decrease the interfacial tension and increase thermodynamic stability. Precursor species for the microsphere shell self-assemble (often with the aid of co-surfactants) at the interface of the droplets and the continuous phase and the shell can subsequently be formed through, for example, polymerization. This method can produce spheres in the nano- to micron-size regime. Cargo species of interest can be incorporated in one step into the microspheres through solubilization within the emulsion droplets.[4,7]

The requirements for the microsphere wall material are primarily structural in nature, serving to mechanically contain the cargo compound. The structural properties of the microsphere must be commensurate with the strains expected for the particular application, i.e. they must be sufficiently robust to withstand 'normal' environmental conditions yet able to rupture under tampering conditions. These properties are associated with the intrinsic tensile properties of the wall material itself, as well as the wall thickness and microsphere radius. Based on these criteria, three types of candidate materials were down-selected for investigation and optimization: polymeric, siliceous, and polymer-silica core-shell composites.

Three different polymeric materials were studied: Urea-Formamide (UF), Melamine-Urea-Formamide (MUF), and Poly(methyl methacrylate) (PMMA).[5] The first two materials are copolymers prepared by o/w emulsion polymerization procedures, whereas the third entry comprises a homopolymer microsphere prepared via an evaporation/phase-separation procedure. Microspheres ranging in diameter from 10 – 250 µm were synthesized and filled with the different mobile phase materials such as mineral oil and hexadecane.

Of the three materials studies, UF microspheres performed the best due to several properties: robust synthetic method that afforded the capsules in high yield, a relatively narrow size distribution, uniform particle surface properties, synthetically adjustable sizes across a wide range, and compatibility with all of the tested mobile phase materials. The above combination of desirable attributes was not exhibited by either the MUF copolymer or PMMA microspheres, in spite of other advantages such as higher thermal stability and lower diffusivity in the case of MUF.

The development of a variety of microspheres with different structural properties would provide a flexible selection of materials to coincide with the mechanical characteristics/detection sensitivity of the corresponding tamper-indicating device design. Siliceous systems were subsequently studied to impart increased mechanical strength into the microsphere walls.

Silica microcapsules were prepared by the acid-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) in a w/o emulsion.[6] Stirring speed and method during the reaction had a large effect on the microsphere size and purity, as shown in Figure 7 below. Overhead stirring at 1000 rpm with

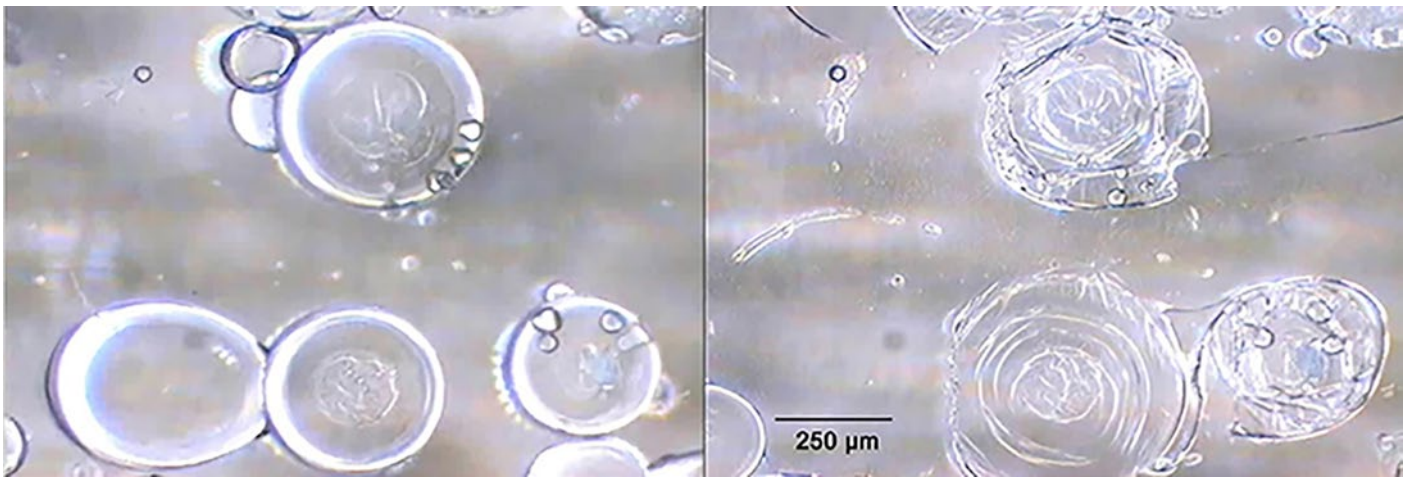

Figure 6: Video microscope screen capture images depicting intact (left) and ruptured (right) mineral oil-filled UF microspheres. The mechanical stimulus was exerted by a micro-manipulator tip pressing on the top plate of a microscope cover slip.

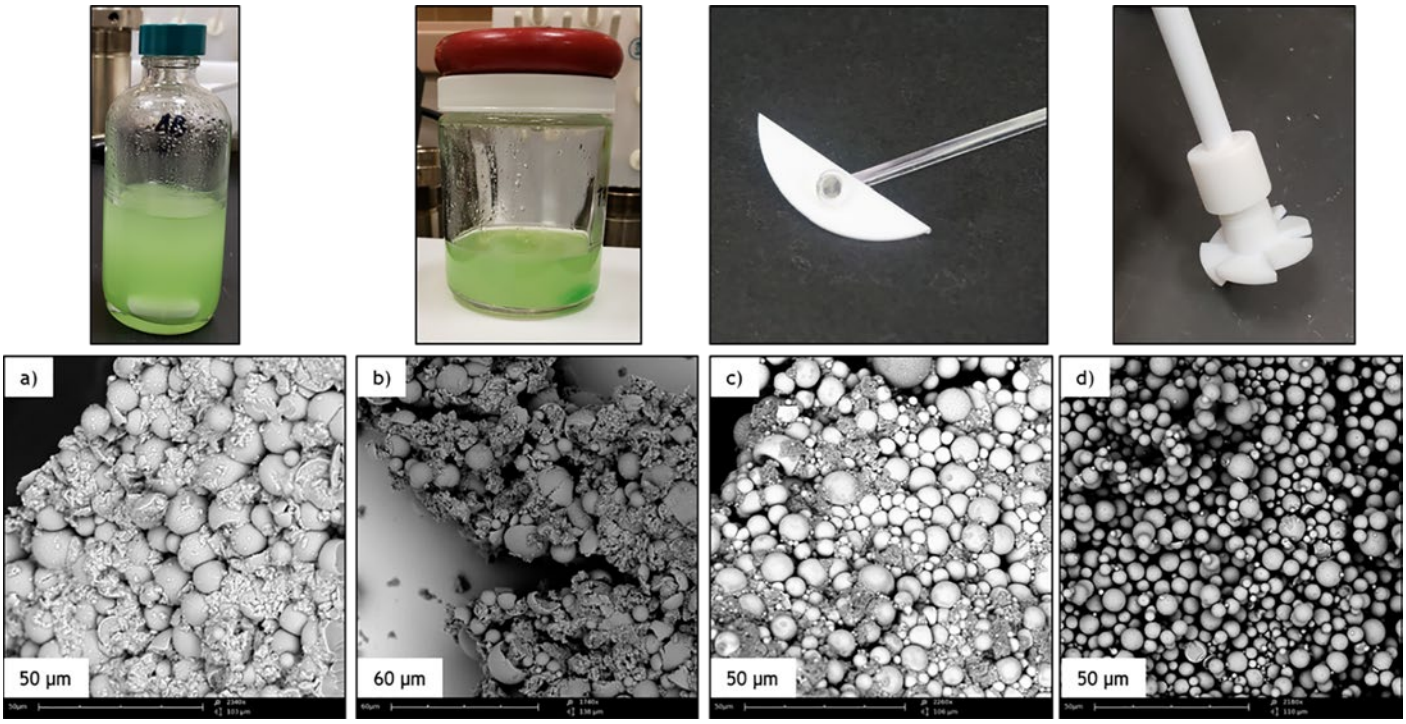

Figure 7: Scanning Electron Micrographs (SEMs) of silica microsphere products a) with magnetic stirring in a narrow glass bottle b) magnetic stirring in a wide glass jar c) overhead stirring in a glass round bottomed flask with a paddle impeller and d) overhead stirring in a plastic bottle with a propeller impeller.

a propeller impeller provided the best shear conditions to produce clean silica microspheres with a roughly trimodal size distribution of 0.5 - 1, 2 - 5, and 10 µm. Cu^{2+} and Fe^{3+} transition metal ions were successfully encapsulated as cargo in the aqueous mobile phase.

Crushing and grinding of these dried microspheres between two glass slides showed very little to no breakage, pointing towards the high mechanical strength of the silica microspheres compared to polymeric. It is well known, however, that silica microspheres contain micro- and mesoporosity,[6] which is undesirable for long term containment of cargo molecules. Our next efforts will focus on combining the low permeability of the polymers with the mechanical strength of the silica to form a core-shell polymer-silica composite microsphere material.

4. Summary and Next Steps

SNL continues to develop a material that results in an obvious, visual response (irreversible color change) upon tamper. The material will be 3D-printed for customizable inspection equipment, or spray-coated for application to facility-owned equipment. The material adds to the TIE toolbox, which is currently limited in options. R&D will continue on transition metals and microspheres, culminating in

the integration of the transition metals and microspheres into 3D-printed and spray-coated prototypes. The prototypes will undergo environmental testing upon fabrication. Future testing for durability and vulnerability will also be conducted.

5. Acknowledgements

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