Measuring and Increasing the Suspension Time of Lanthanide Oxysulfide Particles with Modifiers via Fluorescence For Use in Anti-counterfeiting Applications

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Abstract

BrandWatch Technologies produces micron-sized lanthanide oxysulfide particles called taggants that fluoresce with specific wavelengths of infrared (IR) light. These taggants are used to provide a covert level of security to prevent counterfeiting and diversion in markets such as currency, passport/ID documents, and many others. Due to the specific gravity of the taggants, which is around 4 to 5, they fall out of suspension quickly. Different modifiers were added to a mixture of taggants and DI water to be explored in order to increase the suspension time, but a standard, quantitative test method was also desired. Two separate testing methods were developed for taggant suspension analysis. A qualitative means of measuring suspension time called the Fluorescence Penetration Test (FPT) utilized a timelapse of photographs of a vial with taggants in suspension under an IR laser, and measured the penetration depth of the beam. A quantitative test called the Emission Spectroscopy Test (EST) was developed as a way of determining the concentration of taggant at a specific location along the vial based on the intensity of fluorescence that was emitted. Both methods provide detailed results that are used to help understand the amount of time the taggants remain suspended and the ability of the taggants to be detectable. Modifiers, such as Hydroxyethylcellulose (HEC) and several commercial brand aqueous polymeric dispersants from Croda International, were used to test the effectiveness of FPT and EST, as well as the capability of the modifiers as industry applicable suspension agents. The most promising results come from the 2% HEC sample increasing the suspension time from ~15 minutes to ~8 hours without being too viscous for industrial use.

1. Introduction

Counterfeiters can cause issues such as loss of revenue, competition with cheaper fraudulent products, and loss of customer loyalty. Additionally, counterfeiting is commonly associated with the illegal drug and black market industries, causing the problem to extend much further than just a company's profitability. There is a wide range of industries affected by this problem and therefore a need for commercial and forensic security applications that are capable of identifying products or materials, preventing fraud, and deterring counterfeiters. For forensic analysis, taggants are used to track common chemicals that are used in the making of explosives. This gives agencies more regulatory action for detecting explosives that are used maliciously. Currently the use of barcodes that are printed on packages are highly vulnerable to forgery since they are visible and easy to imitate. Most counterfeiters today copy anti-counterfeiting technologies within 18 months of the technology being released to the public [1]. This places a huge demand on creating technologies that are undetectable or nearly invisible to the public. Through the use of detection systems using microscopic taggants, products on the market can be protected from typical counterfeiting methods. The micron-sized particles, made from a lanthanide series oxysulfide, interact with infrared wavelengths to reflect visible wavelengths of light. The mechanism for this effect is **fluorescence**, and results in an up-conversion from lower energy infrared photons to visible light [2]. Typically with conventional light emission, higher energy photons will drop energy levels in order to fluoresce to a lower energy wavelength (Figure 1).

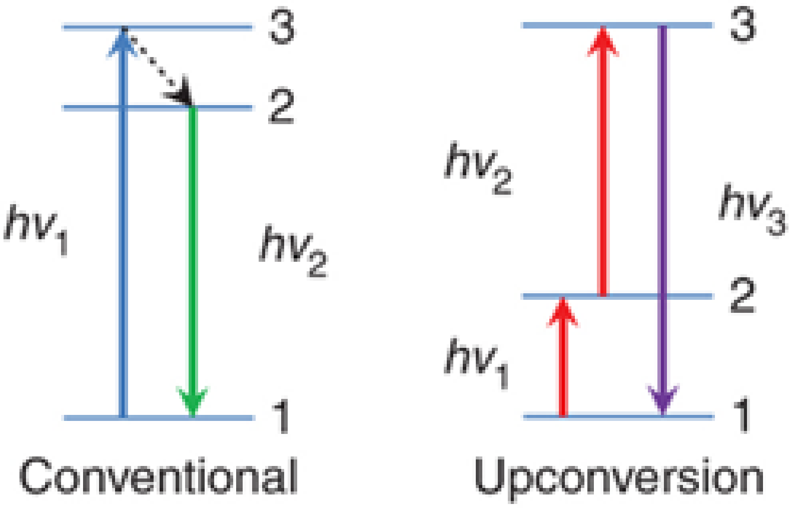

Figure 1: Representation of conventional light emission of a higher energy photons dropping in energy to emit light and upconversion fluorescence with two or lower energy photons converting into a higher energy photon [3].

This conventional fluorescence is referred to as a Stokes shift. However, the upconversion phenomenon exhibited by the taggants occurs when two or more infrared photons are absorbed sequentially to emit a higher energy visible light photon. Because the emitted light is a shorter wavelength than infrared, the difference in wavelengths is referred to as an anti-Stokes shift.

BrandWatch Technologies manufactures their own taggants to be suspended in inks and paints for anti-counterfeiting in currency, packaging, documents, and products. At this present time, BrandWatch has an issue with the suspension time of their taggants in inks. The taggants have a specific gravity of 4 to 5 and easily fall out of suspension to form a layer at the bottom of the container. This layer that falls out of suspension also affects inkjets since it forms a thick ‘cakey’ substance that clogs the jets. When the taggants have fallen out of suspension, it is difficult to resuspend the particles, typically done by shaking or stirring. The lack of ability to resuspend is another problem that will be faced since stopping an entire printing line or production line in order to replace a new inkjet or flexographic ink fountain is not ideal. The challenge that is presented for this project is to increase the suspension time of the taggant to a time of over 24 hours and to develop a means of analyzing the suspension time of the taggants. Improvements could increase the number of applications that BrandWatch can use their taggants with, without having to modify any existing printing technologies.

2. Background

2.1 Lanthanide Oxysulfide as an Anti-counterfeiting Material

Taggants can be used to identify products, prevent fraud, and deter counterfeiting with high reliability and minimal effect. Examples of existing anti-counterfeiting techniques include watermarking and holograms which allow users to determine the authenticity with a simple visual inspection [2]. Both of these techniques utilize the effects that can be seen by an ordinary person from a visual inspection of the material. Lanthanum oxysulfide taggants are also visually inspected for authenticity but in a more discreet and indirect way. Lanthanide oxysulfides have fluorescent properties under the right circumstances in which valence electrons are excited into higher energy states and dropped back down to the original energy state, emitting visible light along the way [4]. BrandWatch Technologies uses a lanthanum oxysulfide taggant which emits green or red wavelengths depending on the dopants that absorb the energy from infrared light. These particles are mixed into inks and dyes to be printed on substrates to form a fluorescent signature for commercial and forensic applications. Covertness is incredibly important for taggants to prevent even further counterfeiting of the taggants themselves [5]. A large area of focus is increasing the taggant suspension time in inks to ease the printing application process of using inks with these powders.

2.1.1 Multilayering of Taggants for Enhanced Security

Multilayering taggants is primarily a process that uses nano-sized taggants, whereas BrandWatch's particles are primarily in the micron range. With nanoparticles, several layers of taggants can be printed onto a designated substrate which increases the level of security by adding in multiple levels of identification [5]. The multilayer approach enhances security because of the phase change nanoparticles it contains. This allows the owners of brands to trace products even after the microstructure of the particles is destroyed from physical damage or bleaching. At this present time, BrandWatch is looking to steer away from nanoparticles in order to prevent the environmental effects nano-sized materials have, and the taggants are not as reliable when produced on the nanoscale due to some particles not containing all of the necessary dopants to fluoresce the characteristic color.

2.1.2 Microparticle Printing using a Piezoelectric Inkjet System

Polymer microparticles were present for the piezoelectric inkjet system, which will be used for comparison to BrandWatch's taggants. In the study, the viscosity and surface tension of the inks were optimized for piezoelectric inkjet printing. The research was primarily looking at the fabrication of the microparticles with the system, but the use of the piezoelectric inkjet printer sparked interest as a means of applying the taggant infused inks. The inkjet was able to create specific patterns and geometries with the microparticles, which could be useful for BrandWatch to improve their anticounterfeiting measures further. Unfortunately, this inkjet requires a special chamber with a radio frequency plasma deposition system which is highly unlikely for BrandWatch's customers to obtain [6]. More common printing methods are considered to effectively find improvements to the suspension and printing challenges with the BrandWatch taggants.

2.2 Possible Taggant Suspension Mechanisms

The primary issue with BrandWatch's taggants are that they are 4 to 5 times denser than water and fall out of suspension quickly. Testing methods and solution additives are both areas of research that could aid in increasing suspension times of the taggants. BrandWatch would prefer to avoid specialized equipment that would be needed since the customer of their taggants would then need to acquire the same equipment. Due to this, the focus will be on solution additives such as suspension agents, surfactants, and rheology modifiers. The following are possible suspension mechanisms that have been published for different material systems and purposes.

2.2.1 Suspension Techniques for Alumina Nanoparticles

Alumina (Al_2O_3) nanoparticles can be suspended in water-based suspensions using an *ultrasonic vibrator*, even though Al_2O_3 is 3-4 times denser than water [7]. These suspensions cannot stay stable for a long time and must be de-agglomerated with an ultrasonic disruptor. This may be of interest to research as an ultrasonic disruptor may help with keeping the taggants suspended in colloidal solutions, but unfortunately this is not a viable option for BrandWatch since some of their clients do not have access to these types of devices.

2.2.2 Nanoparticle Stabilization of Microparticle Suspension via Charge

A stabilization mechanism for microparticle suspension using different volume fractions of slightly positive charged zirconia nanoparticles in a negatively charged colloidal suspension of microparticles is being researched [8]. During the tests, polystyrene latex microparticles were used to test the suspension times with several volume fractions of nanoparticle zirconia. Figure 2 shows the results from the research performed where settling experiments with a 3.04 micrometer latex suspension were tested. Different volume percentages of the charged zirconia were used in comparing suspension times.

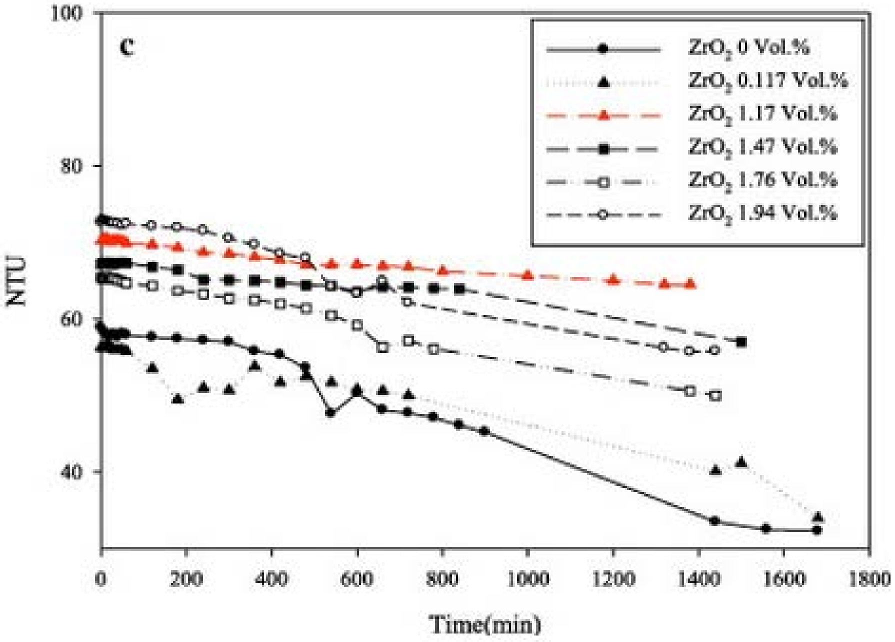

Figure 2: Results from a turbidity test (NTU) as a means of determining the suspension time. The 1.17 Vol.% ZrO2 suspension had the longest continuous suspension.

The tests appear to point towards a volume percent of 1.17 nanoparticle zirconia provided the longest suspension time increase. Values remain fairly continuous with the 1.17 volume percent whereas different volume percentages would fall out of suspension over time at a faster rate [8]. The positively charged zirconia nanoparticles are an area to research with the taggants, however the differences between the polystyrene latex particles and lanthanide oxysulfide particles may cause discrepancies in the results. Investigating the conductivity of particles and its influence on suspension time could be an area of future research with BrandWatch taggants.

2.2.3 Polyelectrolytic Dispersants and Particle Size Variations

A more coarse alumina powder with a bimodal particle distribution has been shown to exhibit a usable viscosity with high density suspensions. This suspension can be loaded up to 70% of solid when a polyelectrolyte dispersant was used as well [9]. A polyelectrolyte is a polymer group that dissociates and becomes charged in water, causing it to repel via double layer forces. These double layer forces develop near charged surfaces in aqueous environments where the first layer corresponds to the charged surface and the second layer refers to the neutralizing charge containing accumulated counterions. The result of these charges leads to differences in ion concentration within the gap which will generate an osmotic pressure and force between them. The powder that was utilized in this article fit within the size range of the taggant that is used for BrandWatch's taggants which is between 1 and 10 microns. It should be noted that the dispersant used acts primarily through an *electrostatic mechanism*. Dispersants are useful to de-agglomerate powders, which is an issue that BrandWatch is having with their taggants.

2.2.4 Titanium Dioxide Nanoparticle Dispersion and Suspension

Another study described titanium dioxide nanoparticles being dispersed and stabilized in water. A *block copolymer dispersant* was compared to a common polyelectrolyte dispersant for this powder for use in a water based acrylic varnish foundation [10]. They are commonly used to impart a surface charge to more neutral particles to enable stable dispersion and suspension. Block copolymers are blocks of different monomers that are attached to each other. A charge can be formed with these molecules to induce repulsion in a similar fashion to polyelectrolytes. It was found that although the polyelectrolyte works, the copolymer could perform better with the correct block lengths in terms of dispersion and powder clustering. Although BrandWatch's powders are not on the nanoscale, it is useful to see that dispersion agents of the same type will work for a variety of particle sizes. Titanium dioxide was a material that was indicated as possibly being useful for the research as it is commonly used in printing applications.

2.2.5 Glass Silicate Powder Suspension in InkJet Printer Systems

A glass silicate dielectric powder was examined for use in inkjet printer systems comparing the effectiveness of polyelectrolyte dispersants with carboxylate or sulfate groups. A potassium polycarboxylate was found to be the most effective in this case, but other dispersants had measurable success as well. With this combination, a useful range of printing parameters were able to be met with further optimization still to be done. The developed suspension could be loaded at 20%, which is above what would be required by BrandWatch. Sedimentation rate was also dependent on how much dispersant was used, with the ideal amount being 2 wt.% powder resulting in 11% sedimentation over 10 hours [11].

2.2.6 Use of dispersants, pH, and sonication to stabilize suspensions

A solution was found to accurately determine particle size distribution of doped cesium oxide powder suspensions. Ultimately, a combined effort of a dispersion agent, an adjustment of *pH to between 3 and 5*, and sonication of the suspension were needed to accurately measure the particle sizes due to strong particle agglomeration [12]. This powder ended up consisting of particles less than .1 micron wide, which is smaller than this taggant. However, Most water-based inks have a pH of 8-9.5. Inks with lower pH levels tend to have increased viscosity and are more likely to agglomerate. The effects of pH is an area of study that could be further examined for the use of increasing suspension time of the taggant particles in combination with dispersing agents.

3. Experimental Procedures

3.1 Materials

3.1.1 Solution Preparation

All samples were prepared under a fume hood and with proper personal protective equipment, such as safety glasses and gloves, to prevent unwanted exposure to potentially hazardous materials. All testing was conducted using the same safety equipment. Vials filled with taggant and suspension agents were transported in a polyethylene bin.

3.1.2 Water Suspensions

The preliminary suspensions were prepared by filling 20 milliliter vials with deionized (DI) water and adding 1 wt.% taggant. Once the taggant had been added, the suspensions were mixed thoroughly. Mixing the suspensions typically involved shaking the vials except for suspensions that would bubble when shaken, i.e. the samples provided by Croda, in which case a stir rod was used to best distribute the taggants. Assumptions were made that both mixing methods create similar convective forces that don't influence the suspension times differently.

3.1.3 Hydroxyethylcellulose (HEC) Suspensions

Six solutions were prepared with different weight percentages of HEC in the Chemistry Department. Each solution weighed a total of 200 grams with varying amounts of deionized water and HEC 250GR, a lower molecular weight version of HEC. The solutions ranged from 0.5-3% HEC by weight, increasing by increments of 0.5%. The water was first put in a can and stirred with a mechanical mixer to create a slurry, then the HEC powder was added while the solution was being mixed. 2-3 drops of Kathon LX, a microbiocide, was then added to protect the mixture against viruses and bacteria. 6-10 drops of 6M NaOH were also added to create the desired increase in viscosity [13]. The entire mixture was then stirred for 20 minutes at 2000 RPM and left overnight to cure. Once the solutions had cured, they were poured into 20 milliliter vials and taggant was added at different weight percentages for testing. Three vials of each HEC solution were prepared with 0.5%, 1%, and 2% taggant added. Only the 1 wt.% taggant suspensions were used for testing in order to keep the results consistent. HEC suspensions were mixed by shaking the vials in which they were contained. The 2-3 wt.% HEC samples needed to be mixed with a stir rod due to their high viscosities and may not have been uniformly mixed in the initial stages due to the taggants clumping. Figure 3 shows a visual comparison between DI water and 3 wt.% HEC roughly 10 minutes after the HEC mixture has been made and mixed.

Figure 3: A comparison of taggants in DI water (left) and 3 wt.% HEC (right) after 10 minutes.

HEC was used as a standard rheology modifier since it was readily available from the chemistry department. There is a minimal difference between HEC and other rheology modifiers because they all operate very similarly to thicken the solution. Due to this effect, HEC remained the only rheology modifier used.

3.1.4 Croda Suspensions

BrandWatch Technologies provided five aqueous polymeric dispersants manufactured by Croda International to be tested. Samples were prepared by filling 20 milliliter vials with deionized water, adding the Croda agent, then adding a certain amount of taggant. For each agent, two samples were prepared. The first batch of samples contained 2% dispersing agent by weight, and the second contained 5% agent by weight. For all samples, 1% taggant was added to the solution after the Croda agent was added, and the solutions were mixed thoroughly with a stir rod.

3.2 Test methods

3.2.1 Fluorescence Penetration Test

The Fluorescence Penetration Test (FPT) consisted of determining suspension time by analyzing the penetration depth of the 980nm near infrared (NIR) laser into the top of a sample in a 20 milliliter vial. The setup as seen in Figure 4 consisted of a laser being centered 1 inch above the top of the suspension filled vial. A GoPro camera was then set up 2.5 inches away from the vial in a dark environment. Pictures were taken over time at 0 seconds, 30 seconds, 1 minute, 3 minutes, 5 minutes, 15 minutes, 30 minutes, 45 minutes, 1 hour, 2 hours, 4 hours, 8 hours, 12 hours, and 24 hours. Pictures were saved under their respective times and suspension agent for organization of the results.

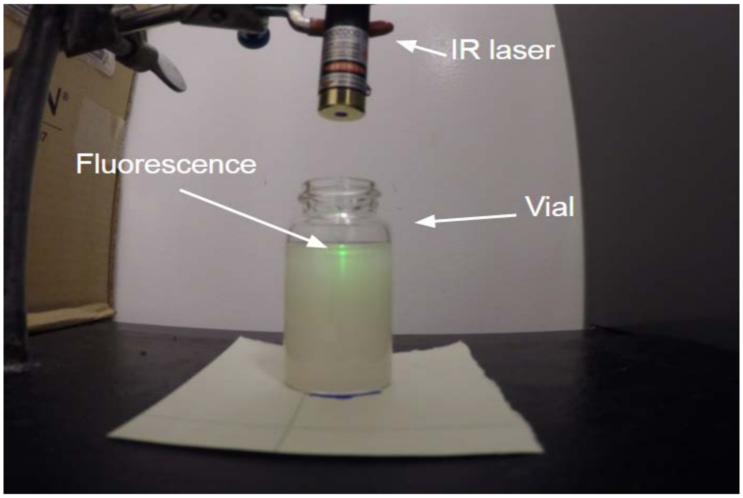

Figure 4: The setup for the FPT taken from the GoPro camera

The results were then quantified with the penetration depth over time. KLONK image measurement software [14] was used to analyze the pictures for beam penetration depth as well as fluorescent glow depth. Figure 5 shows an example of the fluorescence from the NIR laser being measured by its penetration depth and the glow depth. The blue signifies the higher intensity beam penetration measurement whereas the glow depth refers to the distance of fluorescence at any intensity throughout the vial.

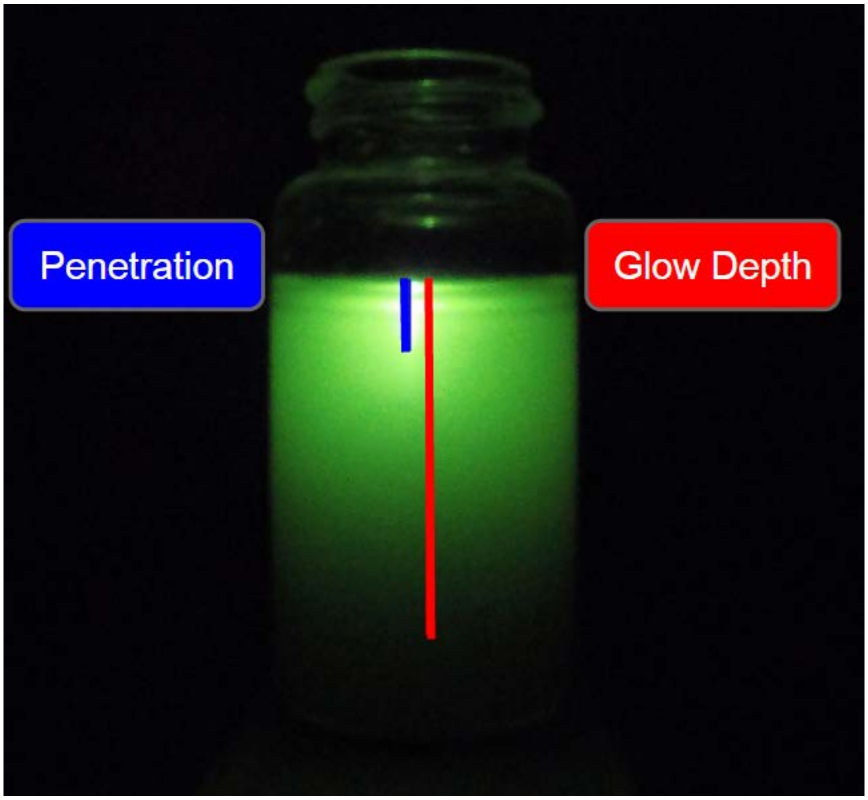

Figure 5: A comparative view of the penetration and the glow depth achieved by the IR laser.

The fluorescent glow depth of the taggants was discarded due to inconsistencies with the measurements. Some images formed concaving glows towards the top of the suspension which made it difficult to determine where to begin the measurement for the depth. Another difficulty that was encountered was the existence of a gap that formed over time at the top of the vials. This gap made sense due to the taggants falling out of suspension and there not being enough taggant towards the top of the suspension to glow (Figure 6). Penetration of the beam was used solely as a means to measure the taggants ability to stay suspended over time.

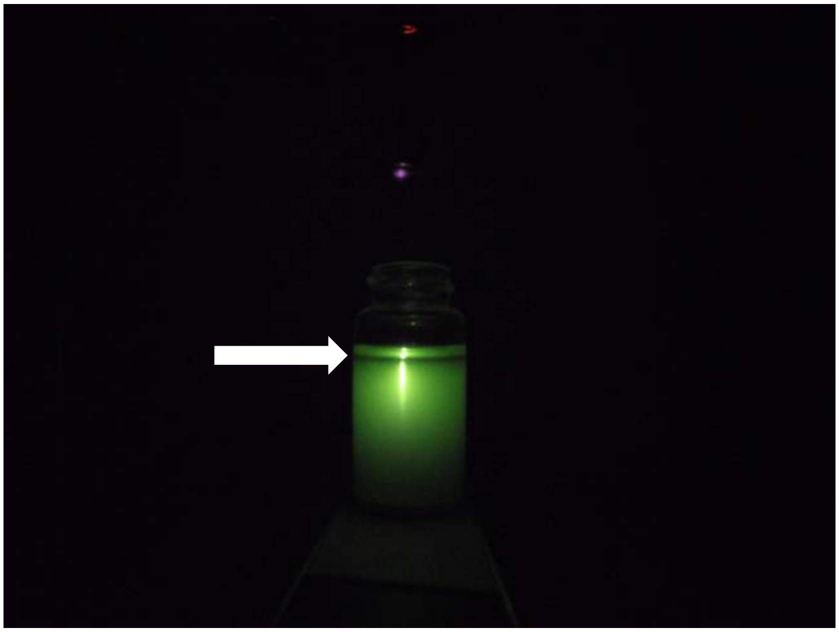

Figure 6: Example of a gap forming in the 1% HEC after 15 minutes

Unfortunately, as this is a qualitative test, the penetration depth did not accurately measure the suspension of all the taggants that remained in suspension. During the beginning of a test it is difficult to determine how far the beam is actually penetrating the sample due to the high concentration of taggants at the surface of the solution. Even when the penetration of the laser reached 100%, some taggants still remain within the suspension since the fluorescing beam was still visible to the naked eye. This meant that some taggants were still in suspension. During the time the beam was not at 100%, it was also difficult to measure the concentration of taggants that were in suspension since the beam was being blocked by a high concentration of taggants. The FPT provided help for understanding the nature of the taggant suspension, but another test was needed to provide a quantitative means of analyzing the suspension time.

3.2.2 Emission Spectroscopy Test

A quantitative measurement technique was created in order to relate the actual concentration of taggants to the intensity of the fluorescence that was emitted. The fluorescence can be tracked horizontally as it falls out of suspension using the 980nm laser pen and a fiber optic cable to pick up the emitted wavelengths and transfer the data to an OceanOptics USB 4000 sensor, from which the corresponding OceanView software can plot the intensities. However, this testing method needs to be consistent for every trial and the interface of the laser, vial, and fiber optic cable must remain in the same position to collect accurate data. An example of this interface can be seen in Figure 7.

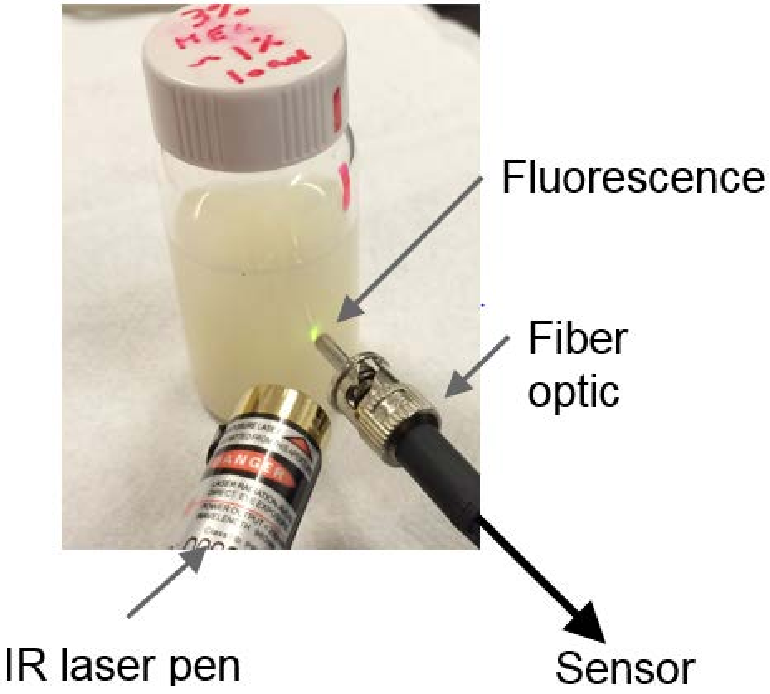

Figure 7: EST interface of IR laser, vial, and fiber optic cable.

A rig was a necessary component of the EST to ensure that data was being collected from exactly the same location on each vial at every time interval. The rig seen in Figure 8 was developed in SolidWorks and 3D printed to keep all components of the test in a consistent location for each trial.

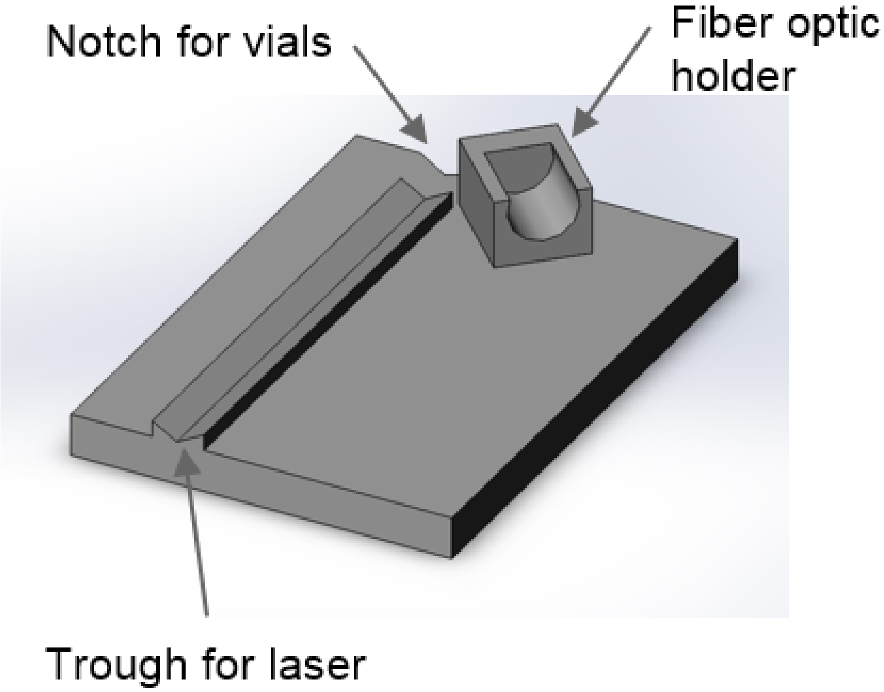

Figure 8: The prototype rig designed for the EST in SolidWorks.

The same 980nm NIR laser from the FPT was used to excite the taggant particles during the EST, however the ambient light did not affect the data. Emitted wavelengths of fluorescence were picked up with a fiber optic cable that connected to an Ocean Optics sensor which transferred the data to a laptop via USB. Figure 9 shows an output of OceanView with the specific wavelengths of fluorescence. The prominent wavelengths include: 528, 548, 554, 660, and 670 nm, all of which are denoted by the general color of light they emit in the figure.

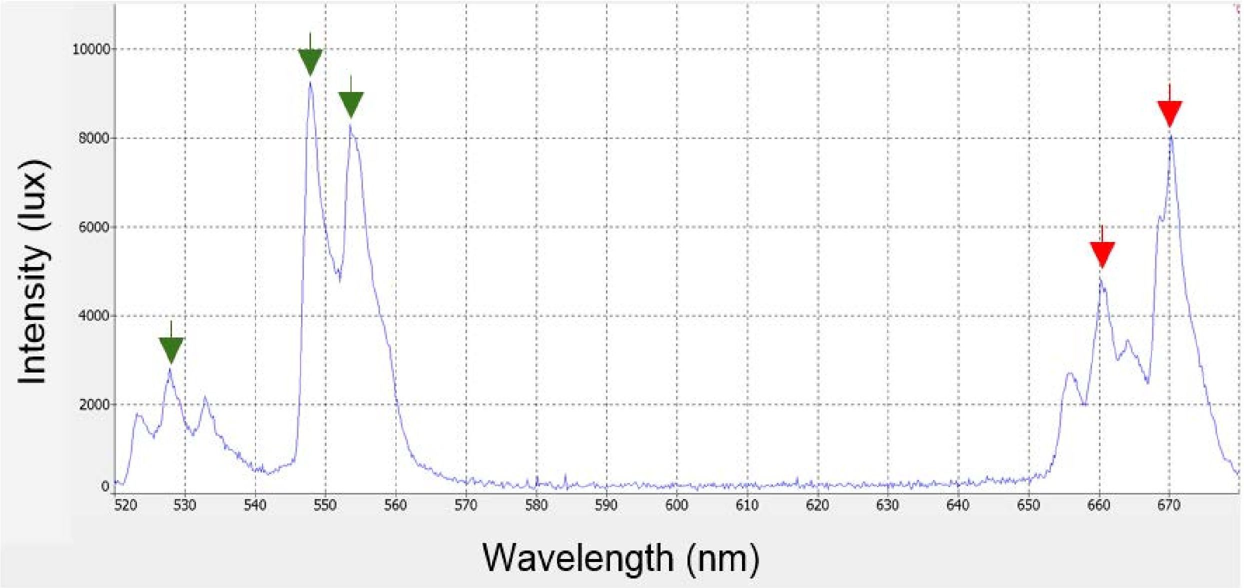

Figure 9: OceanView output with the emitted wavelengths highlighted.

The sensor was fixed in place in order to allow a straight fiber optic connection to the rig to minimize any losses that may occur with a bent cable. Data from this sensor was monitored over time using OceanView software, which provided intensity values for the wavelengths that were emitted. A calibration curve was required before testing in order to relate the fluorescence intensity to the concentration of the taggant in suspension. To make this curve, DI water samples were prepared from 0.1% to 1% taggant by weight in 0.1% increments to determine the intensity outputs of these concentrations at time zero. Measurements were taken at the same time intervals as the FPT. The use of only DI water for the calibration was done after a test of intensity between DI and several HEC samples, since no major difference could be found.

4. Results

4.1 Testing

4.1.1 Preliminary Screening

In total, 12 samples were prepared for testing; 6 HEC solutions from 0.5% to 3% in 0.5% increments, 5 Croda solutions (designated as 2234, 3315, 4913, 4974, and 7000) with different suspension agents, and 1 DI water solution. Each of these solutions was prepared with 1 wt.% taggant to make the suspension to be tested. The initial tests were performed visually by observing how well the taggants remained suspended over a short period of time. Out of the 5 Croda samples, only 1, designated 3315, was selected for future testing because the others showed little to no improvement in particle suspension. The 0.5% HEC suspension was also eliminated for similar reasons. The DI water sample was kept as a baseline for testing to compare with the other samples. After this early assessment, 7 samples consisting of DI water, 5 HEC from 1% to 3%, and one Croda were selected for testing and analysis with the FPT and EST.

4.2 X-Ray Diffraction (XRD) Testing

Before tests were developed x-ray diffraction (XRD) was performed on the taggants to confirm the phase of the material. From the test, a record of yttrium oxysulfide (Y_2O_2S) was found to be matching the results that were retrieved from the taggants. Figure 10 shows the results that were found from XRD testing. The crystal structure was found once the phase of the taggants were confirmed through research of the literature of the yttrium oxysulfide particles.

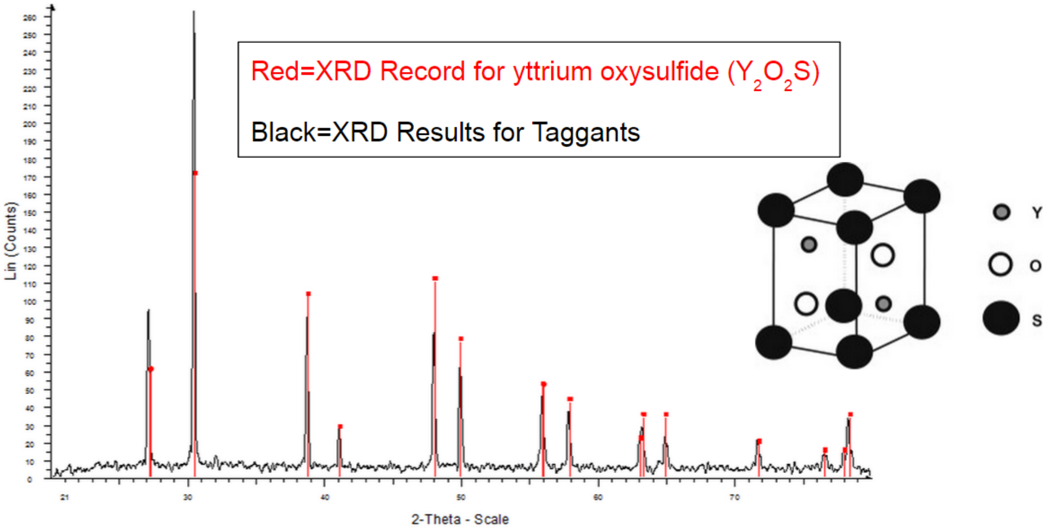

Figure 10: X-ray diffraction test results with the yttrium oxysulfide crystal structure on the right.

4.3 Scanning Electron Microscope (SEM) Testing

Scanning Electron Microscopy (SEM) was also performed after results from the XRD were compiled. The SEM provided a closer view of the taggant powder which was used to confirm the size of the particles (~1-10 microns). Figure 11 shows two images taken from the SEM; Figure 11a is showing the powder, while 11b shows a close-up of one taggant.

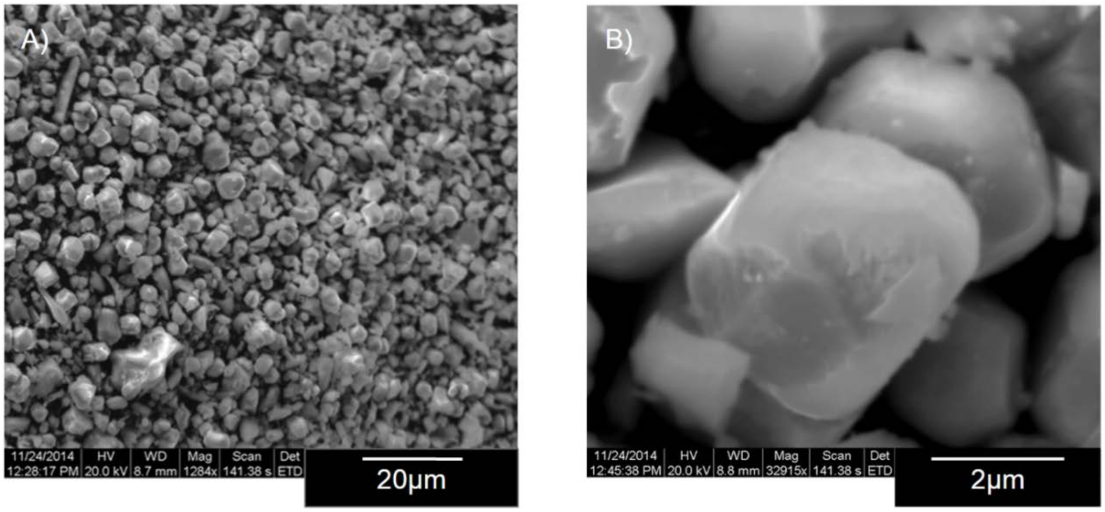

Figure 11: A) Magnification 1,284 showing the variation of size between the particles. B) Magnification 32,915 showing a single taggant for its size and shape.

The taggant particles are not uniform and at some times jagged and rough. This unique geometry helps the powder stick together and adhere to whatever they come into contact with. However, this may help explain why these particles are difficult to resuspend.

4.4 Fluorescence Penetration Test

The FPT was performed on the 7 remaining samples over a 24 hour period. This test allowed the visualization of how the agents affect suspension time through the depth of the NIR laser as seen by the resulting fluorescence. Note that 100% fluorescence penetration does not mean 100% of the taggants have settled to the bottom. This is simply an indicator that most of the taggant powder has fallen out of suspension (Figure 12).

Figure 12: Fluorescent Penetration over time in DI Water measuring the suspension time of taggants.

The laser was able to completely penetrate the DI water and Croda 3315 samples within 15 minutes, but all of the HEC samples displayed significant improvements. As the HEC percentage increased, the fluorescent penetration over time decreased. From Figure 13, different penetrations occur at time 0 which in theory

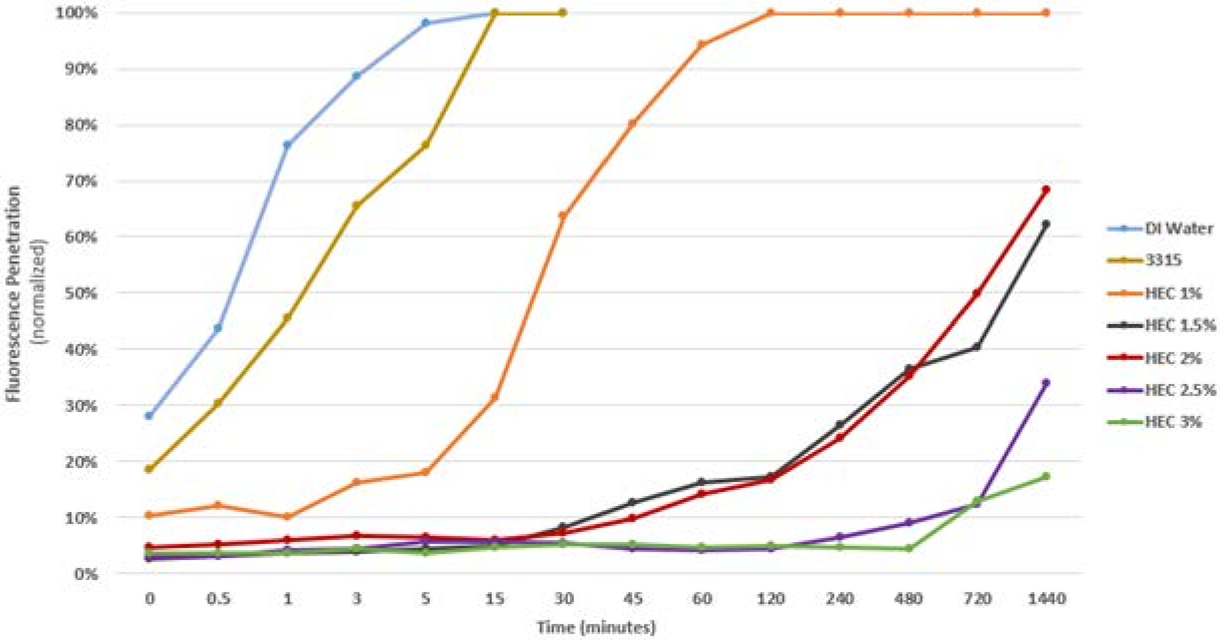

Figure 13: FPT results from the 7 samples over a 24-hour period.

should not happen. This could be occurring from human error since time 0 may not be exactly at 0 seconds and since the taggants fall so swiftly in DI water and the Croda suspension agents used. This also may be reflected by HEC's slightly off-white color which causes the suspension to be more opaque, especially when the taggants are added to the suspension.

The HEC 0.5% suspension was also withheld from the data due to the fact that it was becoming drowned out by IR light. The camera that was used (GoPro Hero 4) was capable of capturing IR light and the vial was filled with IR instead of fluorescing taggants (Figure 14). This made it hard to define the regions of fluorescent penetration and glow depth with KLONK.

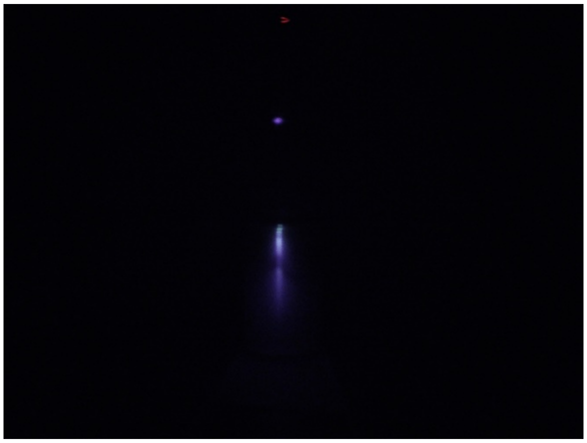

Figure 14: Example photo of the 0.5% HEC suspension being difficult to measure due to the abundance of IR compared to the fluorescence.

These results suggest that the 2.5% and 3% HEC samples will keep taggants suspended the longest. However, due to their incredibly high viscosities, they are unusable for inkjet and flexographic printing so they were not used for further testing. The 1.5% and 2% HEC samples demonstrated significant improvements in suspension time without drastically increasing the viscosity, so they were the primary samples used for the rest of the tests.

4.5 Emission Spectroscopy Test

Before accurate testing could begin with the EST, a calibration curve was made to relate intensity of fluorescence to concentration of taggant. Figure 15 below displays the multiple trials of increasing taggant loads from 0.1% to 1% in 0.1% increments at time zero. The peaks correspond directly to taggant loading, with the 1% sample showing the highest peak and the 0.1% showing the lowest fluorescent intensity.

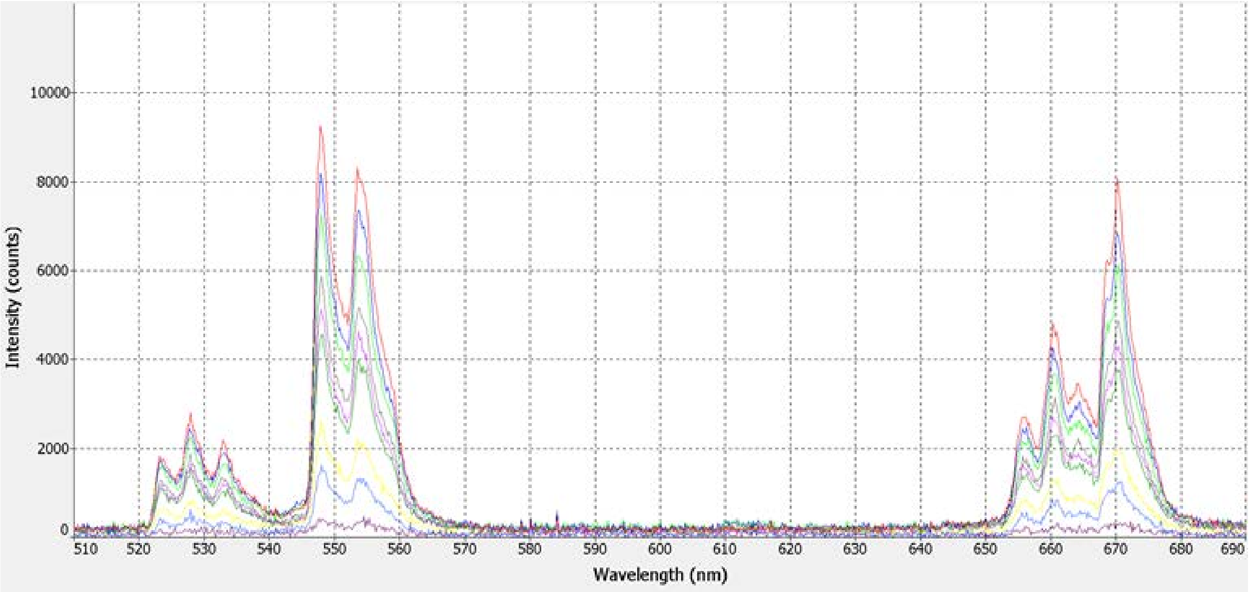

Figure 15: An output from OceanView with the intensities of specific wavelengths of fluorescence being analyzed.

Each different color in the figure shows the intensity output of the trials. The data retrieved and tracked for analysis was focused on the largest peak (548 nm). This was due to the higher intensity readings from even the low concentrations of taggant. From this data a calibration curve, shown in Figure 16, was created to generate fluorescence intensity vs. taggant concentration.

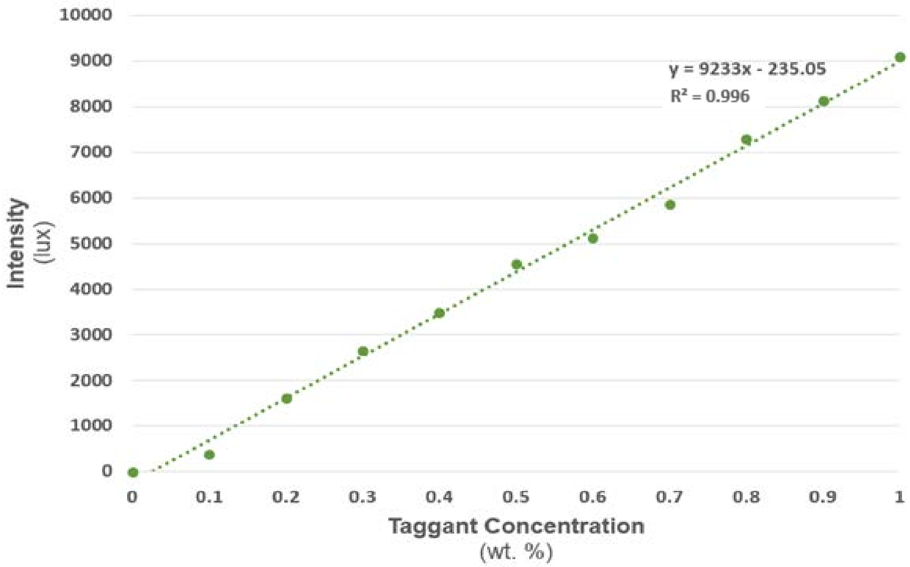

Figure 16: Calibration curve relating the output intensity of fluorescence to the taggant concentration.

The calibration curve was crucial in finding the relationship between the intensity of fluorescence that was given to the concentration of taggant at that spot in the vial. The equation below shows this relationship where I is the intensity of fluorescence and C is the concentration of taggant in wt.%:

$$C = (I+235.05)/9233 \tag{1}$$

Using this equation, the future tests would give an output fluorescent intensity to be converted into the taggant concentration at that location on the vial.

Figure 17 shows the EST results for DI water, 1.5%, and 2% HEC. The DI water was plotted to show the comparison between water and the two HEC suspensions.

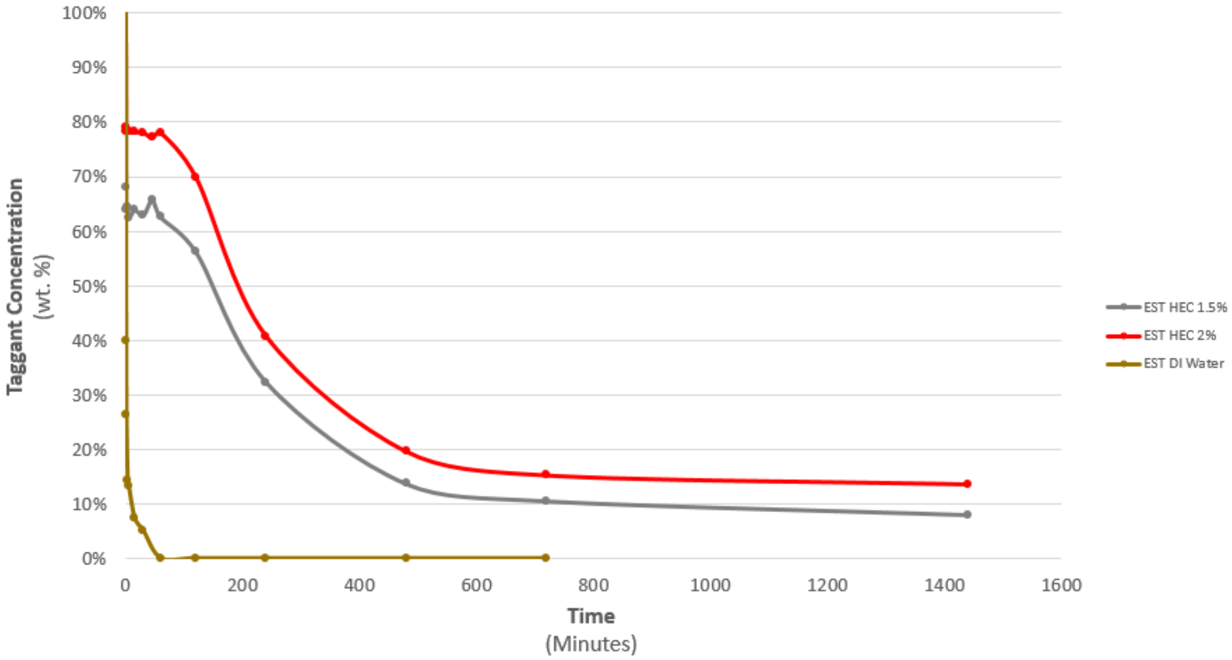

Figure 17: EST results for DI water, 1.5%, and 2% HEC over 24 hours.

Since 2% HEC is slightly more viscous than the 1.5%, the taggant concentration is consistently higher and therefore increases the suspension time slightly. The drop in suspension for DI water was swift (~15 minutes) and by the time the taggants have fallen out of suspension in water, they remained at a constant ~80% concentration and ~65% concentration for HEC 2% and HEC 1.5%, respectively.

5. Discussion

5.1 Fluorescence Penetration Test

Although the FPT is not a direct measure of the taggants' suspension time, it is a good qualitative test to determine which agents and modifiers show potential for significantly increasing suspension time. The obtained results indicate that the 2.5% and 3% HEC samples will keep taggants suspended the longest. However, due to their incredibly high viscosities, they are unusable for inkjet and flexographic printing so they were not used for further testing. These printing processes typically have viscosities ranging from 10-500 centipoise, but the 2.5% and 3% HEC suspensions showed viscosities of over 1000 centipoise [15]. The remainder of the tests were focused on the 1.5% and 2% HEC samples, because they demonstrated substantial increases in suspension time, but were not too viscous for use in inkjet and flexographic printing.

5.2 Emission Spectroscopy Test

The EST proved useful in providing quantified data for the analysis of the taggant suspension. The data matched what was expected to occur and also matched with FPT data. As time began, a huge decrease was typically found since large particles were likely falling out of suspension the fastest. After about a minute, the concentration remained fairly constant until an hour since the medium particles were falling, but lighter particles were falling slowly across the fiber optic which picked up a constant concentration of taggant overtime. Shortly after that hour, the concentration dropped again signifying the lighter particles were finally dropping below the fiber optic height (Figure 18).

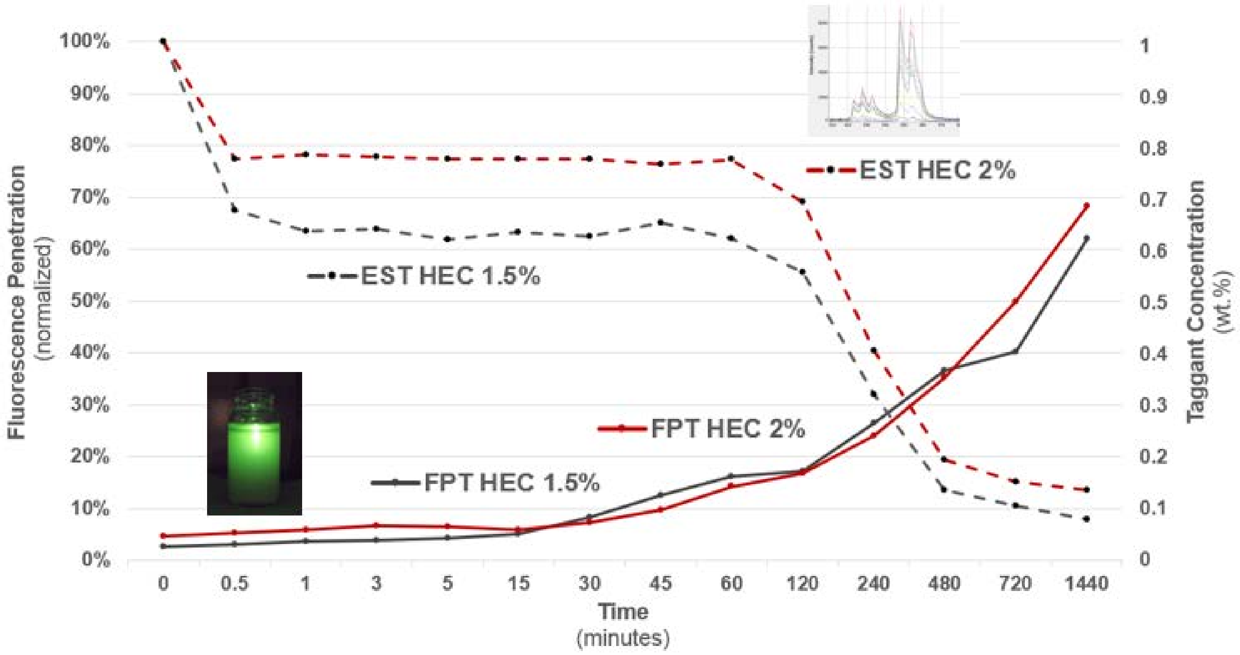

Figure 18: EST and FPT results for HEC 1.5% and 2% over a 24-hour period.
Note the time axis is non-linear

Due to the linear nature of the calibration equation, some flaws occurred where calculated concentrations went upwards of 100.1% loading. This was negligible but worth noting due to the equation not being a true representation of the relationship between fluorescent intensity and taggant concentration.

EST is an overall better test that provided more accurate results that is not subjective from the measuring of the fluorescence penetration. The EST is also quicker to use as a test once the calibration curve and equation are determined. However, it is more expensive and complicated to use due to the equipment involved in testing.

6. Conclusions

6.1 Recommendations

Steps need to be taken for further research to find more suspension agents that increase the time that the taggants stay suspended. The studies that are available are difficult to apply to the specific case of BrandWatch’s taggants. While some studies focus on suspension agents, they do not necessarily relate to lanthanide oxysulfide microparticles; whereas other studies focus on lanthanide oxysulfide microparticles, but do not look at the suspension of such particles in solutions. A further analysis of equipment can also be an area of research to show that certain lab equipment could be properly utilized to agitate the particles in a well-defined and cost effective manner that could open up this option for BrandWatch.

6.2 Conclusions

Hydroxyethylcellulose proved to be an effective means of increasing taggant suspension time by increasing the viscosity of the suspension. However, adding too much HEC can make the suspension too viscous for use in inkjet and flexographic printing. Additional research could be done to determine if combining HEC with other dispersing agents could increase suspension time without significantly affecting viscosity. Furthermore, two methods of testing suspension time were developed, the Fluorescence Penetration Test (FPT) and the Emission Spectroscopy Test (EST). The FPT delivers more qualitative results, while the EST provides quantitative data. With the EST a calibration curve was established for future use since the equation has been founded by previous work. Furthermore, a 3D printable rig was designed using SolidWorks for obtaining more consistent EST results.

6.3 Future Research

Although there is not much literature available on this specific subject, there are plenty of relevant articles related to the broader topics that the project is comprised of. Steps that are to be taken in increasing the suspension time include:

- Research turbidity and turbidity standards for a means of suspension time
- Arduino build can allow for a sensor to measure turbidity
- Ultrasonic Disruptor to de-agglomerate the suspended powder
- Charged zirconia nanoparticles (potentially microparticles) as a suspension agent
- Particle size variation, which will need to be further discussed with BrandWatch
- Polyelectrolyte Dispersants
- Analysis of pH effects on suspension times

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