

REVERSIBLE FORMATION OF SILVER CLUSTERS AND PARTICLES IN POLYMER FILMS

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ABSTRACT

The photoinduced formation of silver (Ag) clusters and particles in poly(vinyl alcohol) poly(acrylic acid) blend films is described. The photoreduction of the Ag^+ is achieved by subjecting the Ag^+ doped films to 350 nm photons. The formation of Ag clusters and particles is monitored using UV-VIS spectroscopy. Films treated with H_2O_2 exhibit bleaching of the UV-VIS signals corresponding to Ag clusters and Ag particles that were generated during the photoreduction. This paper describes the process for generating these films and provides results from the initial investigation into the formation and decay process observed.

1. INTRODUCTION

The United States Army has invested heavily in the last few years in nanotechnologies and flexible display technologies. The formation, funding and direction of the Institute for Soldier Nanotechnology (ISN) and the Flexible Display Initiative (FDI) by the United States Army reflects the Army's level of interest in these technologies and more importantly, the Army's apparent need for enabling technologies in these areas.

For centuries it has been known that colloidal suspensions of gold (Au) and silver (Ag) vary in color. It was not until 1907-1908 that Mie and Steubing published their results on the optical properties of gold colloids, which became known as simply Mie theory physically describing the phenomenon.^{1,2} They concluded that the size of gold particles had a profound influence on the

transmission of light through the medium containing the particles. They also reported that for gold particles < 50 nm, absorption dominates the optical properties and for gold particles > 50 nm scattering dominates the optical properties. By the 1920s, the theory was widely accepted, and since then scientists and engineers have relied on Mie theory to describe the interaction of light with metallic nanoparticles.

The work reported in this paper builds on the premise described by Mie and Steubing in the early 1900s. We have attempted to exploit the Mie nature of nanometer sized metal particles for use as chromophores in flexible substrates. The films in this study demonstrate the ability to "switch" in ambient conditions without further packaging. The possible application of this technology is a palette of extremely robust display materials for Army service electronics.

2. EXPERIMENTAL

Poly(acrylic acid) (PAA) ($\text{M.W.} = 2.0 \times 10^3 \text{ g mol}^{-1}$), poly(vinyl alcohol) (PVA) ($\text{M.W.} = 89-98 \times 10^3 \text{ g mol}^{-1}$), silver nitrate (AgNO_3) and silver perchlorate (AgClO_4) were purchased from Aldrich, methanol (CH_3OH), methyl sulfoxide (DMSO), 25 wt. % glutaraldehyde, 50 wt. % hydrogen peroxide (H_2O_2), and hydrochloric acid (HCl) were obtained from Fisher. The chemicals were used as received. All glassware was cleaned with *aqua regia* and rinsed with deionized water. Deionized water obtained from an ion exchange resin deionizer from U.S. Filter Service was used in all procedures. Glutaraldehyde-crosslinked films were made using a modified version

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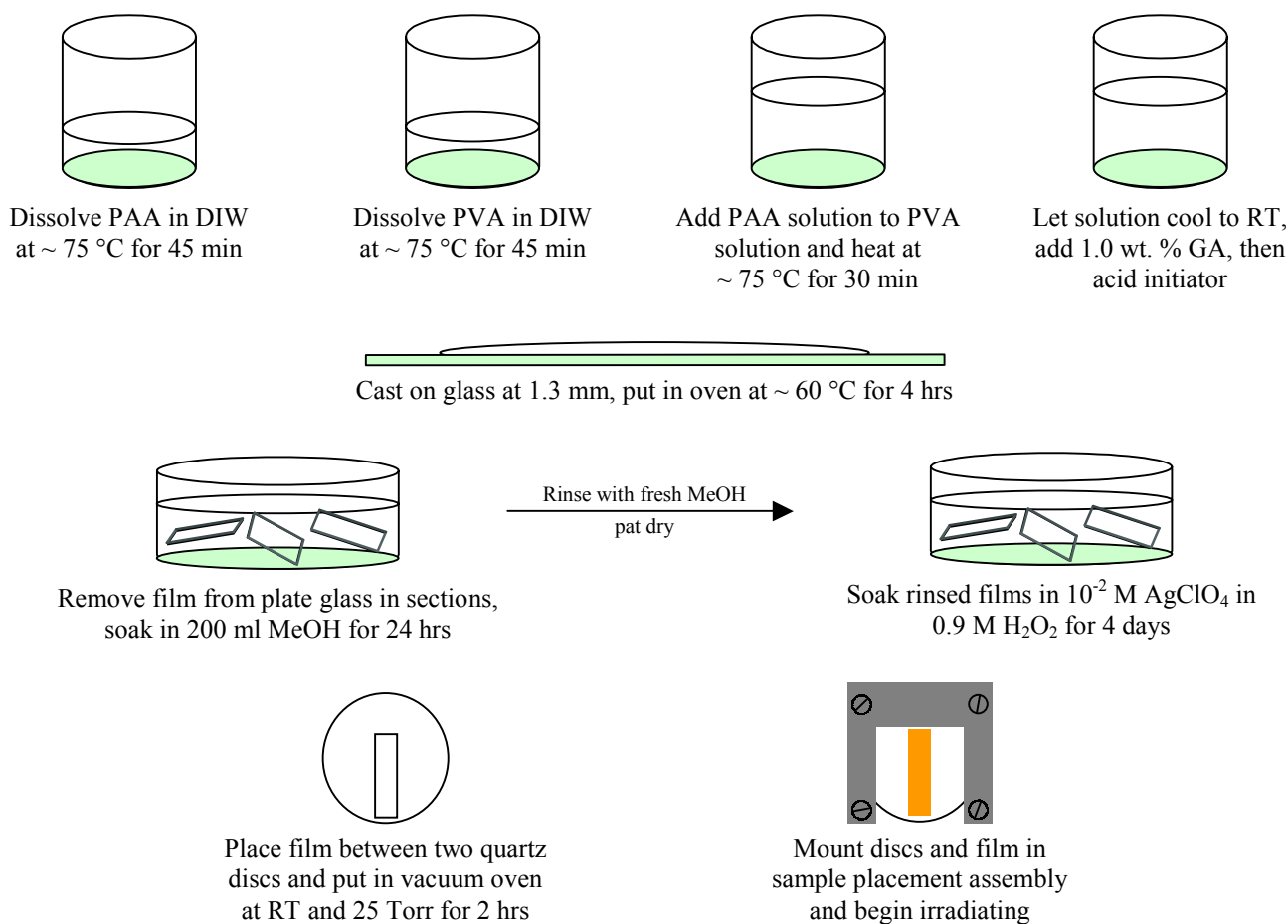


Figure 1. Experimental procedures leading to the production of flexible solid-state films capable of reversible formation of Ag clusters and particles.

of a method described in detail elsewhere.³⁻⁵ A brief summary of experimental procedures are depicted in Figure 1. Aqueous solutions of 5 wt. % PVA and 2 wt. % PAA prepared separately at 73 °C were combined after 45 min, and the resulting mixture was maintained at the elevated temperature for 30 min. The solution was then allowed to cool to room temperature; all steps were performed under constant stirring to ensure homogeneous mixing of the components. The solution was then treated with 3 mL of aqueous glutaraldehyde (1 wt. %, unless otherwise stated), followed by the addition of 3 mL of a 0.5 M HCl (or HNO_3) solution after 5 min while stirring. After two minutes of stirring, the mixture was poured onto clean glass substrates; uniform films were obtained using a Gardner knife (model AP-G08) with a setting of 1.3 mm. Heating the films in an oven at 57 °C for 4 h decreased the time required to crosslink the PVA. After heating, the films were sectioned into $\sim 1 \times 3$ cm samples. The crosslinking process was quenched by exposing the polymer samples to large volumes of methanol for 24 hrs. The films were immediately placed in 0.9 M H_2O_2 containing 1.0×10^{-2} M AgClO_4 for ~ 4 days (films not immediately used were stored in a freezer at -80 °C at this point). The films were removed from

the Ag^+ dopant solution and vacuum dried at room temperature and 30 Torr. The resulting films were insoluble in boiling water, optically transparent above 300 nm, and had an average thickness of 70 μm as determined with a TMI micrometer.

A cylindrical Rayonet 100 obtained from Southern New England Ultra-violet Company equipped with bulbs generating 350 (± 17) nm photons served as the photon source. The films were positioned vertically at the center of the Rayonet between two quartz discs. The temperature inside the reactor was 29 °C; the light intensity (I_0) was $4.5 \pm (0.5) \times 10^{-6}$ M (hv) min^{-1} as measured using a solution of Aberchrome 450 actinometer, and all films were irradiated in ambient atmosphere. UV-VIS measurements were obtained using a Shimadzu UV-2501-PC spectrophotometer.

3. RESULTS

Films produced using the described method are composed of 70.1 % PVA and 29.9 % PAA and were considered to possess optimum optical and mechanical properties.^{3,4} Upon exposure to UV light these films that

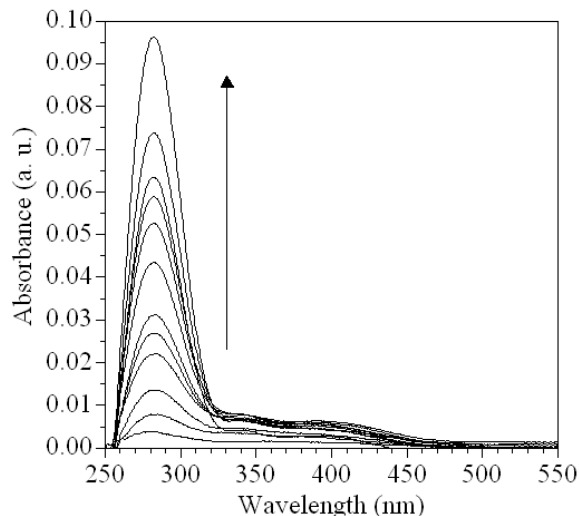


Figure 2. Evolution of UV-VIS absorption spectra during irradiation of Ag^+ doped, H_2O_2 containing film. Spectra were obtained after cumulative irradiation times of 2, 5, 10, 15, 20, 25, 35, 45, 55, 65, 75, and 105 minutes.

were doped with 1.0×10^{-2} M AgClO_4 produced UV-VIS signals between 250 nm and 500 nm, attributed to the presence of Ag clusters and Ag particles. The reduction of Ag^+ via radiation processes has been well documented in both solution⁶ and solid-state^{7,8} systems. It is universally accepted within the community that the surface plasmon resonance band for spherical silver particles < 20 nm is ~ 410 nm depending, of course, on host matrix. As Ag particles increase in size, this band generally red shifts as a result, conversely, as silver particles decrease in size, this band will often blue shift to shorter wavelengths. Absorption signals in the 250 - 350 nm range present in Ag containing systems have been attributed to the presence of Ag clusters of various sizes and charges.^{8,9} Determination of which cluster specie gives rise to which absorption signal is still widely debated in literature today. Researchers have varying degrees of certainty with respect to peak assignments due to the short lifetime of Ag clusters and the fact that the UV-VIS absorption signal positions are system dependent.

The UV-VIS spectra of a $\text{H}_2\text{O}_2/\text{Ag}^+$ -doped PVA-PAA film at various irradiation times is shown in Figure 2. The data in the figure reveals that the formation of Ag clusters dominates over the formation of particles in peroxide containing films as evidence of the signal at 280 nm and the absence of any other signal of any magnitude. This suggests that by the addition of H_2O_2 of sufficient concentration, the formation of large silver particles can be inhibited. Since the lifetime of Ag clusters is extremely short, this system will provide researchers a larger time window to study the processes leading to the formation of Ag particles. Identical films doped with 1.0×10^{-2} M Ag^+ (no peroxide) upon irradiation produced remarkably different UV-VIS spectra, as reported previously.³⁻⁵ Briefly, the predominant absorption signal

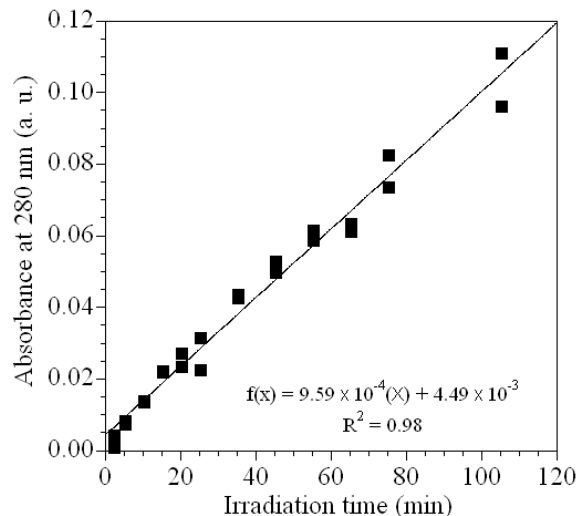


Figure 3. Absorbance at $\lambda = 280$ nm as a function of cumulative irradiation time with 350 nm photons. The slope of line represents the relative rate of cluster formation in the irradiated films.

in these films was at ~ 450 nm, although an absorption signal at 275 nm was also present at $\sim 70\%$ the intensity of the signal at 450 nm. This implies that in the films without H_2O_2 , particle formation is thermodynamically favored over cluster formation or simply cluster formation is the rate limiting process to particle formation.

Figure 3 is a plot of the change in the absorbance at 280 nm as a function of irradiation time for Ag^+ doped, H_2O_2 containing films. The plot also provides an insight as to the reproducibility of the system. The formation of the clusters responsible for this absorption (Ag_x^{y+}) follows an apparent zero-order rate law through 105 min or irradiation time. This observed adherence to the zero-order rate law is not unique to peroxide containing system. In previous studies of silver doped PVA-PAA blend films without peroxide,³ the photoreduction of Ag^+ to form clusters also followed an apparent zero order rate law until the absorbance at 280 nm reached ~ 0.15 , at which time the rate of cluster formation increased.

The simple substitution of the aqueous solution of Ag^+ with a peroxide containing solution of Ag^+ led to the realization that the PVA-PAA films could possibly be used for display applications. Figure 4 is a plot of the measured absorbance at 280 nm as a function of time. The time axis is spanning four different reaction steps (initial irradiation, initial decay, second irradiation, second decay) which represent two irradiation and decay cycles total. This data is the basis for the continued investigation of these materials for use in flexible displays and for use in three-dimensional information storage devices. The plot in Figure 4 shows an increase in the absorbance at 280 nm during the first irradiation step which is a result of the photoreduction of Ag^+ . After 105 min total irradiation time the film was placed in the spectrophotometer sampling chamber and the initial

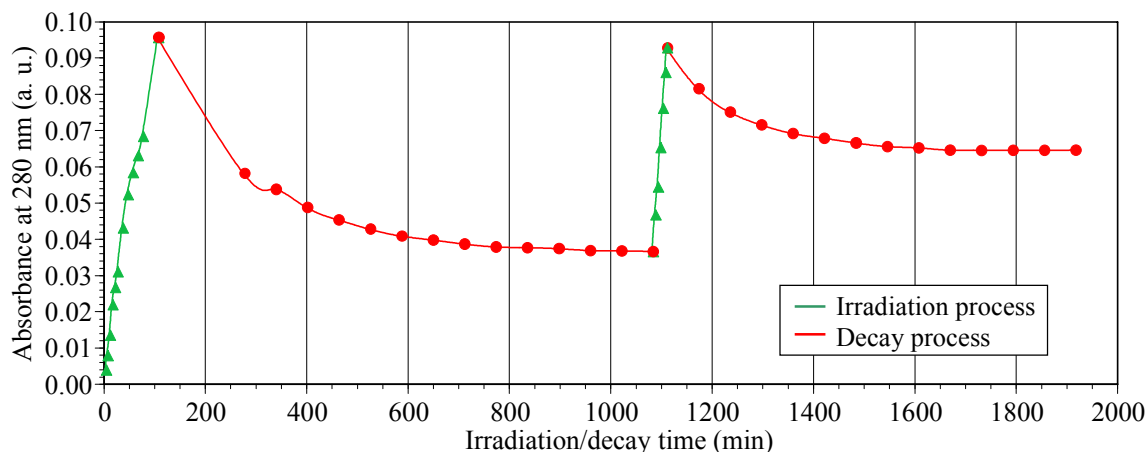


Figure 4. Absorption at $\lambda = 280$ nm as a function of time. The green data represents the absorbance during irradiation with 350 nm photons and the red data represent the subsequent dark reaction when the *in-situ* decay of the signal at 280 nm is observed.

“dark” or decay reaction was monitored. During the dark reaction bleaching of the 280 nm signal was observed. The signal decayed ~ 60 % of the original value when the initial irradiation was stopped. This decrease in the signal is caused by the incorporated peroxide in the films which oxidizes Ag clusters that were formed during the irradiation step. After the decay of the Ag cluster responsible for the 280 nm signal ceased (plateau in the initial decay data) the film was irradiated for a second time. Again, the 280 nm signal increased with increased irradiation time indicating the reformation of Ag clusters. The second irradiation step was stopped when the absorbance at 280 nm was equal to the absorbance after the first irradiation, ~ 0.095 . This was done so a qualitative comparison could be made between the two cycles since the concentration of Ag clusters would be

roughly the same at the onset of the decay steps. The Ag cluster signal bleached during the second dark reaction to ~ 30 % of the absorbance at the beginning of the second dark reaction.

Figures 5 and 6 are plots of the Ag cluster formation (irradiation) data and decay (dark reaction) data, respectively. The data in Figure 5 shows that both the initial and second photoinduced formation of Ag clusters follow an apparent zero order rate law. Figure 5 also indicates that the rate of Ag cluster formation in the second irradiation is an order of magnitude faster. There are two possible explanations for this observation; the peroxide concentration is lower as a result of the initial dark reaction which provides a less inhibiting (oxidative) film for the formation of the cluster or the system requires a “priming” step to achieve maximum performance

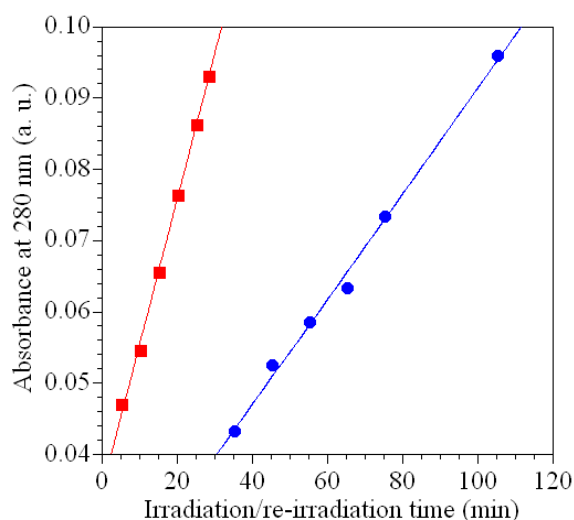


Figure 5. Absorbance at 280 nm at various times of irradiation. Blue data was collected during the initial irradiation step and the red data is a result of the second irradiation step which followed the initial dark reaction.

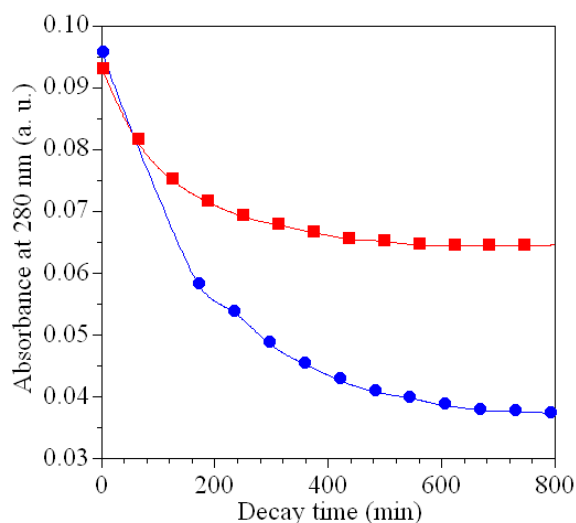


Figure 6. Absorbance at 280 nm at various times during dark reactions. Blue data was collected during the initial dark reaction step and the red data represents the second dark reaction step.

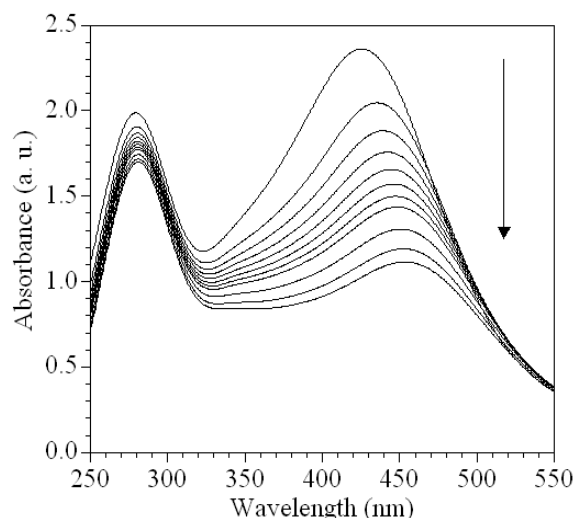


Figure 7. UV-VIS absorption spectra obtained during the third dark reaction (0 - 830 min) of the film in Figure 4. The third irradiation step was ~ 12 h in duration

during the photoreduction process. Figure 6 is a plot of the data obtained during the dark reactions. The plot indicates that the apparent initial rate of decay or oxidation of the clusters in both dark reactions is the same. The initial dark reaction appears to have been more effective at bleaching the signal at 280 nm at longer reaction times. This can be attributed to the proximity of formed Ag clusters to peroxide contained within the polymer films. During the initial decay cycle, the concentration of peroxide is arguably at the highest for a given dark reaction. This would imply that any formed Ag clusters would be in the closest proximity of oxidizing peroxide, and during the initial decay cycle, the absorption signal at 280 nm was reduced by $\sim 60\%$. During the second decay cycle the Ag cluster signal was reduced by $\sim 30\%$. This further suggests that the local concentration of peroxide relative to Ag clusters has decreased, yielding decreased effective range. This data coupled with the data and conclusions drawn from the formation steps imply that the peroxide concentration is high enough to have an inhibitive effect on the initial formation of Ag clusters, then the peroxide concentration decreases, through decomposition, during the initial dark reaction. This decrease in peroxide concentration is evident by the much faster formation kinetics during the second irradiation step, which is followed by a second decay step that, due to the decreased peroxide concentration, is less effective.

Figure 7 is the UV-VIS data collected for the third decay cycle. After the second decay cycle, the film was irradiated for 12 hrs to generate large particles of silver to observe the effects the incorporated peroxide would have on the larger particles. These spectra contain two absorption bands, one band at 280 nm which appears at shorter irradiation times and one centered at 425 nm. The 280 nm band is still attributed to Ag clusters and the band

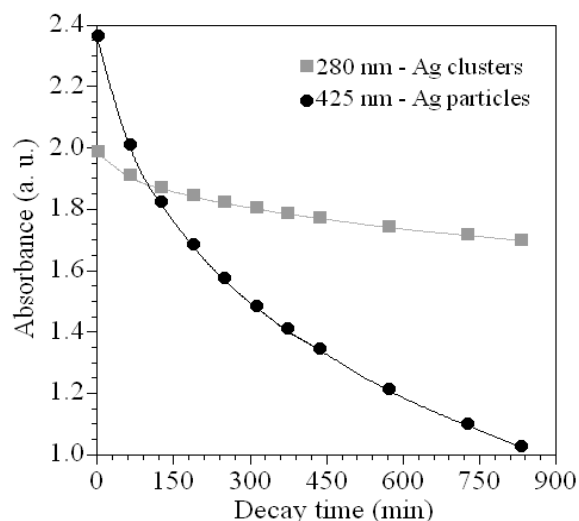


Figure 8. Absorbance at 280 nm (gray) and 425 nm (black) as a function of dark reaction time, the data was obtained from Figure 7.

at 425 nm is the surface plasmon resonance band of larger (10 – 16 nm) Ag particles. As the dark reaction proceeds, there is a noticeable decrease in the absorption for the particle signal. The signal also appears to be red shifting, this is not the case. The signal at 425 nm is most likely comprised of absorption bands of various sized Ag particles convoluted under a single peak. As the peroxide oxidizes the smaller particles the relative concentration of larger particles increases giving rise to the observed signal at 450+ nm.

Figure 8 is a plot of absorbance as a function of the dark reaction time in the third decay cycle. The data in the plot compares the apparent rate of decay of the clusters and particles after the third irradiation step. The peroxide does have an oxidative affect on the larger particles. The perceived decreased rate of cluster decay is believed to be a result of the probability of the larger particles being in close proximity of the peroxide, now at lower concentrations. Since the larger particles have a statistically higher probability of reacting with peroxide, products resulting from these oxidation reactions (Ag clusters) are likely to be produced increasing the absorption signal at 280 nm.

4. CONCLUSION

This research demonstrates the possibility of using metal particles in polymer films for Army display and information storage applications. The described system is robust and was demonstrated in ambient atmosphere without the need for additional packaging. Efforts are underway to determine a probable mechanism for both the formation and decay of the silver clusters and particles, improve the kinetics of formation and decay and optimize the operational range.

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