Silver Formation, Particle Size Distribution, and Morphology in Photothermographic Systems

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Abstract

Spectroscopic measurements of photothermographic systems at development temperatures show how silver particles form during the course of the development process. In standard systems, development follows autocatalytic kinetics. Systems containing infectious developers exhibit more unusual kinetics which do not generally fit simple mathematical models.

In standard photothermographic systems, silver particles have an average diameter of approximately 0.10 μm. The diameter is reduced to 0.04 μm and the particles are significantly more spherical in the presence of an infectious developer. Intermediate sizes and morphologies are possible with low levels of infectious development. Particle size and morphology correlates to light absorption and silver covering power. Spectroscopic measurements show how particle size changes during the course of the development process.

Introduction

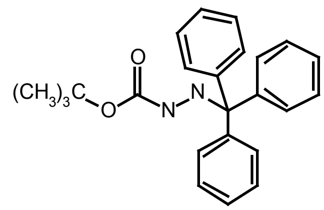
Photothermographic systems, including DryView™ medical imaging film from Imation Corp., use light-sensitive silver halide to catalyze the reduction of light insensitive silver salts, such as long-chain silver fatty acids. Silver production in such a system further accelerates the devel-opment reaction via an autocatalytic reaction, equation (1).

$$\frac{dX}{dt} = k_{auto}[A_0 - X][X + X_0] \qquad (1)$$

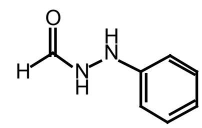
In this equation, k_{auto} is the autocatalytic rate constant, A_0 is the limiting reagent, X_0 is related to the latent image, and X is the product of the development reaction. The integrated form of equation (1) provides a direct relationship between the product X, which is related to density, and k_{auto}, equation (2).

$$X = \frac{A_0 X_0 \left[e^{k_{auto} t (A_0 + X_0)} - 1\right]}{A_0 + X_0 e^{k_{auto} t (A_0 + X_0)}} \qquad (2)$$

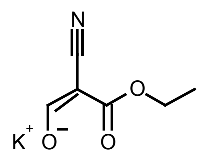
The development process also provides the capability to initiate other reactions such as those responsible for high contrast infectious development. Such a system provides a dry solution to graphic arts imagesetting requirements.[1] In these systems the infectious developer may be a trityl hydrazide (**I**),[2] a formylarylhydrazine (**II, IV**)[2], or an acrylonitrile (**III**).[3] Silver soaps containing infectious developers typically require significantly less silver to reach a given density than films without infectious developers.



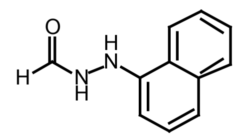
I



II



III



IV

In this paper, we wish to provide kinetic details on several photothermographic systems, including systems containing infectious developers. We will also describe the morphology, size distribution, and optical properties of the resulting silver particles.

Results and Discussion

Development Rate

Photothermographic development typically takes place at temperatures near 122°C. This process follows auto-catalytic kinetics, Figure 1. In the autocatalytic rate equat-ion, density is used as an approximation for the amount of product.

Values for X_0 obtained through fitting the autocatalytic rate equation to experimental data should approximate the Ag initially present in the latent image. Instead, calculated autocatalytic fits generally yield X_0 values between 0.001 and 0.1. These X_0 values suggest that small silver clusters are more reactive than large silver particles and that silver reactivity decreases during the development process.

In DryView, the autocatalytic activation energy for silver formation is 33.2 Kcal/mole in unexposed films and 32.8 Kcal/mole in exposed film. This activation energy is essen-tially independent of exposure. Aged and unaged DryView samples showed little variation in development kinetics.

Once underway, DryView film development can proceed for a significant time during the film cooling process, which requires approximately 30 s. Measurements of density changes show that these post-processor changes can be as great as 20 % at low exposure levels.

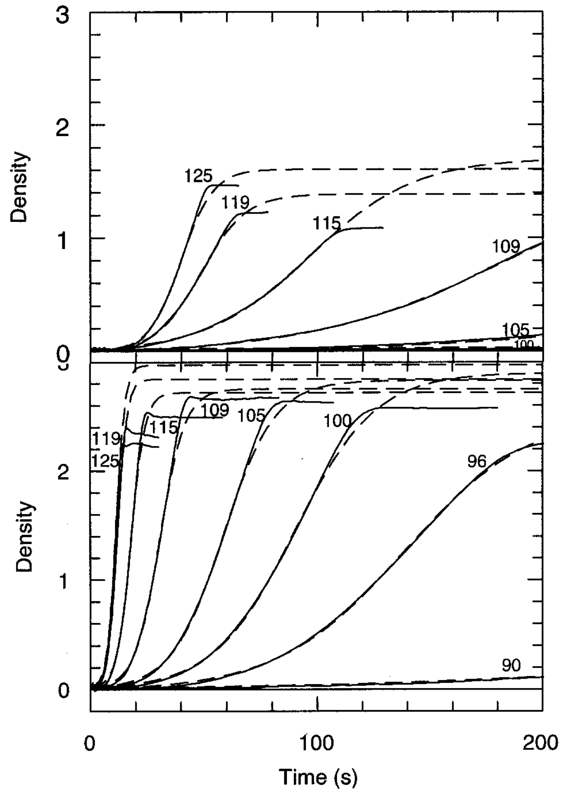


Figure 1. DryView development kinetics (———) and calculated autocatalytic curves (— — —). Processing of unexposed (top) and exposed (bottom) films was carried out in a fluorochemical bath at the temperature (°C) indicated next to each curve. Density was measured at 1000 nm.

Photothermographic development in systems containing infectious developers also follows autocatalytic kinetics during the initial phases of development. However, the deviation from ideal behavior at long development times prevents determination of thermodynamic parameters for high contrast systems, Figure 2. Decreased densities after initial development at high temperatures may be due to aggregation of small silver particles.

Films containing even low levels of infectious developers showed decreased densities at long development times, Figure 3. These films have contrasts between standard films and films containing higher levels of infectious developers. For example, a typical photothermographic film containing **IV** at a codeveloper to soap ratio of 0.0015 has a contrast of 6, rather than 4 in standard films or greater than 20 in high contrast systems. In addition films con-taining low levels of infectious developers have significantly higher silver efficiency than standard films. Infectious devel-opment is not an all or nothing proposition in photo-thermographic systems.

Silver Formation

The silver formed during development of high contrast photothermographic films containing **III** has a greater visible absorbance, relative to infrared, than the silver formed in standard photothermographic films such as DryView, Figure 4. Most likely, this difference is a consequence of the smaller particle size and less effective absorption of longer wavelengths. Mie scattering calculations confirm this dependence of light absorption on size for these Ag particles.

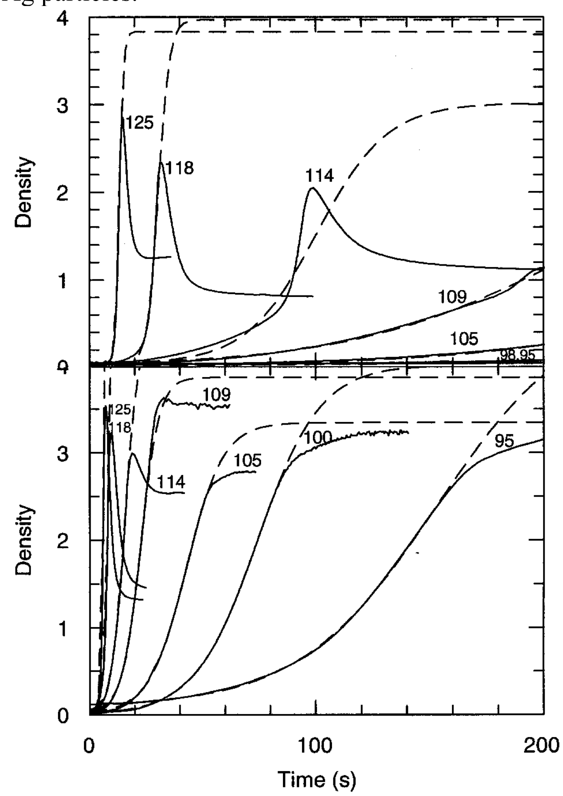


Figure 2. Photothermographic development kinetics (———) and calculated autocatalytic curves (— — —) for a high contrast film containing Nonox and II at a 1:1 ratio at the development temperature (°C) indicated next to each curve. Both unexposed (top) and exposed (bottom) films are shown. Density was measured at 1000 nm

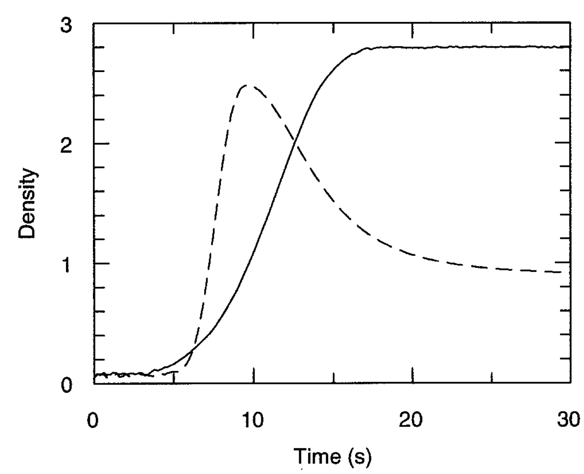


Figure 3. Development kinetics at 125°C in a fluorochemical bath for photothermographic films without infectious developer (———) and containing IV at a ratio to soap of 0.0015 (— — —). Density was monitored at 1000 nm.

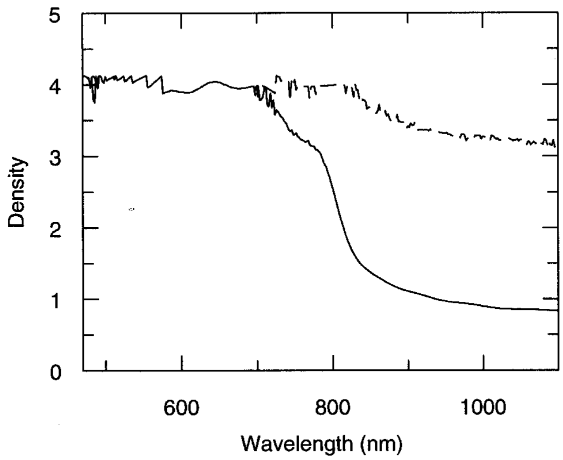


Figure 4. Spectral absorbance of high contrast film (———) and DryView (— — —). Films were exposed for 5 s at an intensity of 1 on a 3M Model 179 Contact Printer-Processor and developed for 15 s at 124°C. Films developed for 23 s showed similar absorbances.

Different silver morphologies are readily apparent in different photothermographic systems, Figure 5.

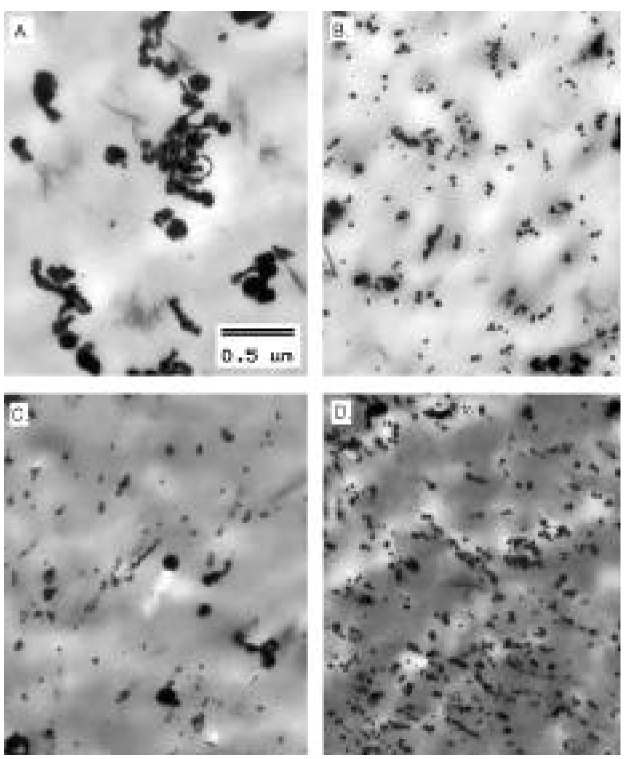


Figure 5. Electron micrographs of silver particles in photothermographic systems containing no infectious developer (A), II (B), I (C), and III (D). These electron micrographs are at a magnification of 30,000 and show a representative portion of the complete electron micrograph.

Electron micrographs confirm that photothermographic systems containing small levels of infectious developers show both development processes, Figure 6. In these systems silver particles are significantly more disperse than in standard systems.

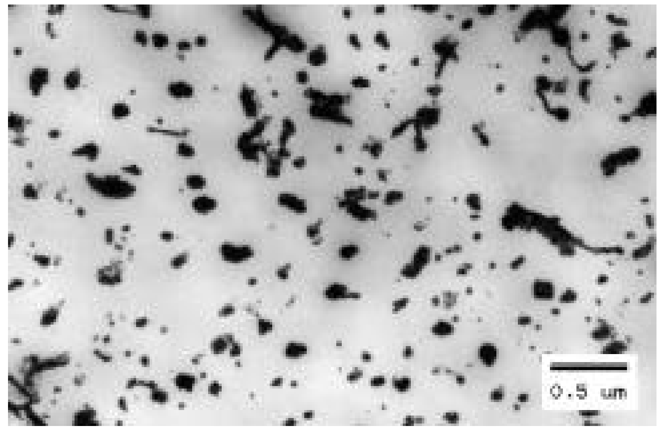


Figure 6. Electron micrograph of photothermographic film containing a low level of IV. The codeveloper to soap ratio was 0.00147, with a coating weight of 1.54 g Ag/m^2.

Particle size analysis quantifies the difference in silver particle size between different photothermographic systems. Infectious development results in particles which are significantly more spherical and significantly smaller, Table 1. Graphically, the peak in particle size is inversely dependent on the level of infectious developer, Figure 7.

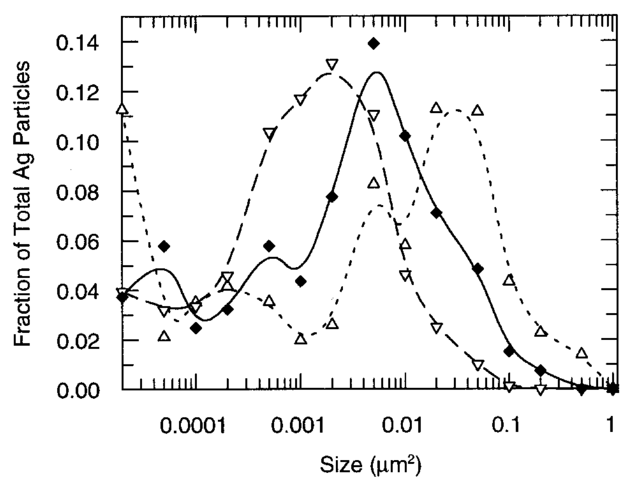


Figure 7. Particle size distribution for various development systems including standard development (Δ), high contrast infectious development (∇), and low contrast infectious development (♦). The particle size distribution for high contrast infectious development represents the average for formulations containing I, II, and III. The sum of the fraction of total silver particles is 1.00 for each curve.

Table 1. Characterization of silver particles in different photothermographic systems.

Sample	Dry-View	I	II	III	IV
Shape[a]	0.69	0.79	0.77	0.79	0.78
Feret D (μm)[b]	0.10	0.037	0.038	0.039	0.067
Area (μm^2)	0.018	0.0022	0.0019	0.0018	0.0069

[a] *Shape is 0 for a line and 1 for a circle according to the formula* Shape = $4\pi x$Area/Perimeter^2.

[b] *Feret D is the diameter of a circle in μm with a cross sectional area equivalent to the particle of interest.*

Conclusions

Image formation in DryView and other photothermographic systems follows autocatalytic kinetics. Infectious developers provide a means to modify silver particle morphology in these photothermographic systems. These developers result in a more uniformly distributed silver image and result in improved silver efficiency.

Acknowledgments

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References

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2. a. S. M. Simpson, L. S. Harring, U.S. Patent No. 5,558,983 (1996); b. S. M. Simpson, L. S. Harring, U.S. Patent No. 5,496,695 (1996).
3. T. J. Murray, S. M. Simpson, U.S Patent 5,545,515 (1996).