

Recent Progress in Understanding the Mechanisms of Development of Photothermographic Imaging Media

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Abstract

We have reviewed and analyzed recent research on the chemistry of development of grayscale, silver carboxylate-based photothermographic imaging media. Areas of investigation have included morphological studies on the developed image silver, kinetics and activation parameters for development, computational models of the development process, and electrochemistry of the developing agents. With knowledge of development chemistry inferred from these studies it is possible to construct phenomenological models for characteristic curves of photothermographic media and ultimately engineer desired sensitometric responses.

Summary

Photothermographic imaging materials comprise a class of media on which imagery or data are recorded optically to form an invisible pattern, i.e., latent image, which is rendered visible by application of heat. While exposure techniques vary, depending on application, the heating is usually accomplished by passing the exposed media over a heated roller. Alternative heat sources, such as microwave heating, resistive heating, and thermostatted fluorochemical baths, have been discussed in the patent literature.

All the chemical components required to confer light sensitivity and enable development are usually contained within the photothermographic composition. Photothermographic materials are therefore thermodynamically unstable and, as a result, shelf stability of photothermographic products and stability of the images produced in these media have required major product development efforts by the various manufacturers. The stabilizers and antifoggants added to this end may have significant effects on the course of the development chemistry.

Most modern photothermographic compositions involve at least three components:

1. a light sensitive compound, usually silver halide;
2. a reducible silver salt, often the silver salt of a long-chain carboxylic acid such as silver behenate; and
3. reducing agents capable of reducing the second component on application of heat to form the metallic silver image.

The steps of photothermographic imaging involve exposure of the imaging material, followed by heating to activate the development chemistry. Unlike traditional silver halide films and papers, photothermographic media are not "fixed" to remove light sensitive components which would otherwise cause the material to darken when handled in ambient light. Instead, in modern photothermographic materials the light sensitive silver halide is present in sufficiently low concentration

that, given the low covering power of print-out silver, its subsequent photochemical darkening is inconsequential.

We have reviewed and analyzed recent research on the chemistry of development of grayscale, silver carboxylate-based photothermographic imaging media. [1] It is now generally accepted that all image silver comes from the silver carboxylate phase. The overall reaction scheme encompasses the following steps:

1. Dissolution of silver carboxylate by action of silver complexing agents.

2. The resulting soluble complexes, particularly silver(I) phthalazine complexes, then diffuse to a reaction center, initially provided by latent image, in a medium comprising either molten carboxylic acid (byproduct of the complexation reaction) or binder, highly plasticized by the carboxylic acid.

3. The diffusion range creates a "sphere of influence", which can be observed by TEM, surrounding the development center in solvent-based materials. A corresponding sphere of influence is not necessarily observable in water-based materials, however.

Morphological studies of developed silver suggest: (a) two stages of development giving rise to filamentary and dendritic silver deposits, respectively, and (b) in solvent-based, but not water-based, media a considerable degree of secondary nucleation, occurring over the course of the reaction. Thermal development follows autocatalytic kinetics, and exhibits a large activation enthalpy, along with a positive entropy of activation; both parameters are inconsistent with a diffusion limited rate of development. In the solvent-based systems studied, secondary nucleation has been proposed to provide positive feedback and be rate-determining, consistent with modern theories of phase formation and crystallization. Both solvent-based and water-based systems exhibit exposure dependent induction periods, which suggests an entropic basis for photocatalytic image development.

The electrochemistry of hindered phenolic developing agents has also been studied. Two-electron oxidation is characteristic of these compounds, with a deprotonation step, which is rate determining, occurring between the two single electron transfers. Thus silver ions may be reduced in pairs, to form relatively stable Ag_2 species, which would facilitate the secondary nucleation process.

With knowledge of development kinetics it is possible to construct phenomenological models for the characteristic curves of photothermographic media. In solvent-based materials operation of secondary nucleation results in a development rate, subsequent to the induction period, that is exposure independent. Contrast is consequently independent of development time. On the other hand models predict that development rate is exposure dependent for water-based

materials, and that contrast correspondingly increases with development time.

References

- [1] M. R. V. Sahyun, "Photothermographic Development Mechanisms in Silver Carboxylate Imaging Materials", *J. Imaging Sci. Technol.*, 49, 337-347 (2005).

Author Biography

M. R. V. Sahyun received his A.B. degree from the University of California—Santa Barbara and his Ph.D. in physical chemistry from UCLA. He has held career positions with the US Public Health Service and 3M Corporate Research, and has served on the faculty of the University of Wisconsin—Eau Claire. He is a Fellow and Senior Member of IS&T, and is currently Editor of the Journal of Imaging Science and Technology. Research interests include photothermography, nonlinear optical spectroscopy, and image archiving.