In situ X-ray Investigation of Metallic Silver Phase Formation from Silver Myristate Thermal Decomposition and from its Reduction in Photothermographic Films

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In situ investigation of metallic silver formation, resulting from the thermal decomposition of silver myristate and from the thermally induced reduction of silver myristate incorporated into a photothermographic imaging construction, shows that the metallic silver formed is different in the two systems. The thermal decomposition of this silver carboxylate produces larger metallic silver crystallites than the thermally induced reduction process, which can be attributed to the silver growing within the constraints of the solid state crystal lattice in the former, compared to the transport of silver ions to the development sites in the latter. The conversion of silver ions to metallic silver in the decomposition process occurs only after the silver carboxylate crystallites pass through several solid state phases.

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Introduction

Silver carboxylates of the general formula $[Ag(O_2C_nH_{2n-1})]_2$, where n = 12-22, are one of the basic components of photothermographic materials, which is the source of silver ions for metallic silver formation during the thermal development process. The reduction of the silver ions to metallic silver results in the formation of the visible image.^{1,2}

Significant effort has gone into understanding the properties of photothermographic materials and the individual components used in those compositions. The remaining question is, however, which of the chemical reactions occurring in the thermal development process is responsible for the formation of the visible image. This is particularly true for the metallic silver particle formation and growth. Despite the same final solid product, metallic silver, the chemical reactions in the thermal decomposition of silver carboxylates and the thermally induced reduction of silver ions during the development of photothermographic materials are completely different.

While the thermal decomposition of silver carboxylates proceeds according to:

Corresponding Author: David Whitcomb, David.whitcomb@kodak.com ©2005, IS&T—The Society for Imaging Science and Technology $[\mathrm{Ag}(\mathrm{O_2C_{2(n-1)}H_{2(2n-1)}})]_2 \rightarrow 2\mathrm{Ag} + 4\mathrm{CO_2} + 2\mathrm{C_{2(n-1)}H_{2(2n-1)}} \ (1)$

with the formation of metallic silver and paraffin as solid products, the photothermographic material development occurs by a more complicated process, which can be stated by the following simplified two-step process:¹⁻³

- 1. At the first stage (light exposure), latent image centers are formed on the silver halide.
- 2. During the second stage (thermal development, 110–130°C), catalytic reduction of silver ions occurs at the latent image centers to form silver crystal particles.

It is generally agreed that the non-light sensitive silver carboxylate is the source for formation of silver particles initiated at the latent image center, and transport of silver ions takes places via silver complexes formed with the other film components (developers, toners, or antifoggants), which can be illustrated as:^{1,2}

a. Conversion of silver carboxylate to a silver complex, which has higher mobility in the reaction medium (using silver stearate, AgSt as an example):

$$AgSt + HL = [AgL] + HSt$$
 (2)

b. Diffusion of the silver complex to the development center where it is reduced to metallic silver:

[AgL] + HDeveloper = Ag(0) + HL + Developer(ox) (3)

where L may be compounds such as phthalic acid or phthalazine. $^{2,4-9}$ Thus, photothermographic materials

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can be thought of as a photographic system with a thermally induced physical development process.

Comparison of this proposed thermal development mechanism (silver crystal growth) to traditional silver halide photography must include the AgX crystals in the photothermographic process because the latent image center is formed there. However, the silver halide crystals in the photothermographic process only serve a catalytic function during development, while the liquid phase physical development step in traditional photography not only develops the silver halide crystals having a latent image center, but also dissolves the unexposed AgX crystals. This is completely consistent with the conclusions in our previous investigations where it was shown¹⁰⁻¹² that there is no change in the size and habit of the silver halide crystal during the thermal development of the photothermographic material. These results demonstrate that the source of silver ions is the reduction of silver carboxylate crystals, not the silver halide.

However, recent publications regarding phase composition changes in the development process of photothermographic media have raised doubts that the initial silver ions forming the visible image are only from the silver carboxylate phase.^{13,14} Thus, it was argued that the reduction of model compounds of AgSt/AgBr with PHZ, 4MPA, and developer, generated a significant (~45%) decrease in the X-ray reflection intensity of the silver halide, which in the opinion of the authors, was involved with the formation of metallic particles.

Further understanding is needed of the structures and morphology changes in the silver carboxylate systems that form metallic silver, i.e., in the thermal decomposition process of silver carboxylates as well as during the thermally induced reduction of photothermographic materials. The nature of the products of the chemical reactions can be expected to affect the formation of metallic silver, and these insights may also provide novel routes to improve both the silver carboxylate source as well as the properties of the photothermographic films.

With this objective, we carried out in situ X-ray investigations on silver myristate, as an individual compound as well as incorporated into a photothermographic film formulation, at various diffraction angles whereby it was possible to determine the change in the solid phase composition and structure of the silver carboxylate and silver halide:

- a) In the small angle region (SAX, $2\theta = 0.4-15^{\circ}$), the change of the interlayer distance d_{001} for the silver carboxylate can easily be determined, and from the peak heights and shapes it is possible to analyze the formation and growth of the silver particles.
- b) In the large angle region (WAXS, $2\theta = 24-54^{\circ}$), the change of the silver carboxylate substructure can be established. In addition, this region is very sensitive for observing metallic silver and silver halide, and can be used to follow their formation or decomposition.

Results

The in situ investigation of the formation of silver particles was carried out by thermal decomposition of silver myristate and thermally induced reduction of the silver myristate in a photothermographic material using methods and materials previously described.^{12,15} Silver myristate was selected as the silver ion source in these experiments because its phase transitions occur at lower temperatures than with either silver stearate or silver behenate, the typical silver carboxylate sources in photothermographic materials, making it easier to monitor the reactions experimentally. The four carbon difference compared to silver stearate was also considered a convenient chain length differential corresponding to that between silver stearate and silver behenate. Thus, C_{14} , C_{18} , and C_{22} can be compared as a series. This investigation showed that the phase changes during thermal decomposition, compared to thermally induced reduction, are significantly different.

In situ X-ray Investigation of the Phases ForÒmed during Silver Myristate Thermal Decomposition

The change in the SAXS patterns for silver myristate in the in situ heating process from 20 to 200°C is shown in Fig. 1(a). Heating silver myristate from 20 to 180°C produces a series of phase transformations, that is, the reflections of the high temperature phase are shifted as the temperature is increased, corresponding to decreasing interlayer distances in the silver carboxylate structure. At least six structurally different phases can be distinguished (Fig. 1(b)).

It should be noted that there is an intermediate phase in the X-ray pattern (Fig. 1(b), curves 2–5), in which there are at least two series of layer reflections that we believe are indicative of the formation of a twodimensional structure.

The layer reflections disappear from the diffraction pattern as the temperature is heated above 200°C, and is accompanied by a corresponding increase in the SAXS intensity, the maximum of which is at $2\theta \sim 1.116^{\circ}$ (Fig. 1(c)). In addition, lower intensity peaks centered at $2\theta \sim 2.21^{\circ}$ and ~ 3.15° (Fig. 1(d)) were detected, which corresponds to the second- and third-order reflections of the largest intensity maximum intensity at $2\theta \sim 1.116^{\circ}$.

The in situ WAXS investigation of the thermal decomposition of silver myristate (Fig. 2) shows that heating to 110° C results in only a minimal change in the reflection intensities of silver myristate. At temperatures above 110° C the reflections of the crystalline phase disappear, and starting at 180° C the diffraction pattern shows broad reflections (111) and (200) of metallic silver (Fig. 2), the intensity of which increases with temperature.

In Situ X-ray Investigation of Phase Formation in the Thermal Development of Silver Myristate Photothermographic Film

The in situ X-ray investigation of the formation of phases during the development of photothermographic materials prepared with silver myristate showed that, in contrast to the thermal decomposition of pure silver myristate, heating the photothermographic material does not shift the silver myristate peak positions. At the same time, the d-layer peak intensities decreased (001) while the SAXS peak intensities increased (Fig. 3). This X-ray pattern change behavior in the thermal development process is associated with the beginning of the change in the phase compositions. This change is seen to begin as early as 80°C and is completed by the temperature of the first phase transition (120°C). The low temperature onset should not be related to the silver carboxylate phase changes, but may be attributed to the polyvinylbutyral resin binder, which has a low Tg (62-72°C). However, it should be noted that the in situ WAXS investigation showed that metallic silver peaks can be detected as low as 80°C (Fig. 4). As the temperature increases (development time) the silver WAXS peak intensities increase.

It is important to point out that the in situ investigation of the thermal development of the photothermographic



Figure 1. SAXS data for silver myristate: heating $20-200^{\circ}$ C (a); six phases can be detected in the heating process (b); single phase above 200° C (c); second- and third-order reflections of the largest intensity maximum intensity at $2\theta \sim 1.116^{\circ}$ (d).

film showed no additional peaks from any kind of intermediate phase, that is, the reaction products do not produce any detectable new solid phase components. In addition, the intensity of the silver halide peak (200) up to and after the development of the photothermographic film remained unchanged (Fig. 4), indicating no size change in this solid state species.

Comparison of the half-widths of the (111) and (200)silver peaks at the decomposition temperature of the silver carboxylate (Fig. 2) and the thermally induced development of the photothermographic film (Fig. 4) produced unequivocal evidence that, during the development process, the overall size of the silver clusters are significantly larger than the particles formed in the thermal decomposition of pure silver carboxylate. For example, the typical silver nanoparticle cluster is 50–100 nm (an agglomeration of 3–5 nm primary particles) compared to 5–10 nm, respectively. Therefore, we can conclude that the first phase



Figure 2. WAXS data for silver myristate: heating 20_200°C.



Figure 3. SAXS data for silver myristate photothermographic film: heating $20 - 200^{\circ}$ C

transition in silver myristate is not silver formation but is related to a transition from a crystalline to a liquid crystalline state. This conclusion is supported by small diffraction angle data at temperatures above 110°C in which the regular order of the layers is preserved, and in the 24–54° angle region where the silver carboxylate reflections have disappeared. This conclusion is also consistent with the Martensitic transition assignment previously made for the first thermal transition in AgSt.¹⁶

It should also be noted that the formation of the metallic silver phase upon decomposition of the silver myristate is preceded by the formation of a series of intermediate mesophases, and the silver particles form ordered structures, several maxima of which are observed in the SAXS.

The in situ investigation of the thermally developed photothermographic film confirms that the silver phase begins to form at 80°C and is accompanied by decreasing intensities of the d layer peaks of silver myristate along with the simultaneous increase of the SAXS intensity. It must be stressed that the formation and growth of the silver phase does not lead to changes in the intensities of the silver halide peaks, which clearly demonstrates that the silver particles are formed from the reduction of silver ions originating from the silver carboxylate, not from the silver halide.

Overall, the silver myristate results are in good agreement with the data we previously reported.^{10-12,15} There, it was shown that the thermal decomposition of individual silver stearate crystals generates silver particles within the boundaries of the silver ion layers in the silver carboxylate lattice. In our opinion, this controlled formation of the silver particles during thermal decomposition corresponds to the observed diffraction maxima in the SAXS.

The morphological characteristics of the silver particles formed during the development of photothermographic films depend significantly on the route by which the AgX/ AgCarboxylate components were prepared, and the same morphology was observed whether the chain length was C_{14} , C_{18} or C_{22} . For the in situ photothermographic film filamentary silver crystals were predominantly observed, while spherical aggregates comprised of spherical silver nanoparticles were predominantly observed from films



Figure 4. WAXS data for silver myristate photothermographic film: heating $20 - 200^{\circ}$ C

containing silver carboxylates prepared in the presence of silver bromide grains, as observed previously.^{10–12,15} The size of the filamentary crystals and the nanosized particles in the developed photothermographic film is greater than that of the particles resulting from thermal decomposition of the silver carboxylate, which can be clearly seen by the corresponding half-widths of the metallic silver peaks, respectively.

We have shown that the variation of the diffraction patterns on photothermographic film development and the thermal decomposition of the silver myristate is the result of variations in the chemical reactions in these two processes. During the thermal development of the photothermographic film, the silver particles form by reduction of the soluble intermediate silver complexes, which incorporate various ligands present in the film formulation. In addition, the variations in the morphological and structural characteristics of the silver myristate can be attributed to the reduction of the silver ions occurring at the latent image center on the silver halide. Formation of metallic silver at the latent image centers can also explain the orientation effects on the formation and growth of the silver particles, e.g., the formation of the filamentary crystal or nanocrystalline, spherical aggregates. In the case of thermal decomposition of individual compounds, such as silver myristate, the layered structure of the silver carboxylate crystal controls the growth of the silver particles.

Conclusions

In situ investigation of metallic silver formation, resulting from the thermal decomposition of silver myristate and from the thermally induced reduction of silver myristate incorporated into a photothermographic imaging construction, shows that the metallic silver formed is different in the two systems. The thermal decomposition of this silver carboxylate produces larger metallic silver crystallites than the primary silver nanoparticles in the thermally induced reduction process, which can be attributed to the silver particles forming within the constraints of the solid state crystal lattice in the former, compared to the transport of silver ions to the development sites in the latter. The conversion of silver ions to metallic silver in the decomposition process occurs only after the crystallites have proceeded through several solid state phases. In addition, the formation of metallic silver in the photothermographic formulation is the result of the silver ion originating from the silver carboxylate being reduced, with no evidence for the silver ion from the silver halide being involved.

The formation of ordered, nanosized products during the thermal decomposition of silver myristate from the ordered intermediate phase is not well understood. Additional investigation is needed of other silver carboxylate decompositions under similar conditions, such as other long-chain derivatives of silver carboxylates, as well as other metal carboxylates.

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References

1. P. Cowdery-Corvan and D. R. Whitcomb, Phothermographic and Thermographic Imaging Materials, *Handbook of Imaging Materials*, A. Diamond and D. Weiss, Eds., (Marcel Dekkers, New York, 2002) p. 473.

- D. H. Klosterboer, *Thermally Processed Silver Systems, Neblette's Eighth Edition: Imaging Processes and Materials*, J. M. Sturge, V. Walworth and A. Stepp, Eds. (Van Nothtrand-Reinhold, New York, NY, 1989) pp. 279–291.
- NY, 1989) pp. 279–291.
 T. H. James, *The Theory of the Photographic Process*, 4th ed., (Macmillan, New York, NY, 1977)
- T. Maekawa, M. Yoshikane, H. Fujimura, and L. Toya, J. Imaging Sci. Technol. ISSN: 1062-3701, 45, 365 (2001).
- 5. D. R. Whitcomb and M. Rajeswaran, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **47**, 107 (2003).
- D. R. Whitcomb and R. D. Rogers, J. Chem. Crystallogr. 25, 137 (1995).
- 7. D. R. Whitcomb and R. D. Rogers, Inorg. Chim. Acta, 256, 263 (1997).
- 8. D. R. Whitcomb and W. C. Frank, US Patent 5,466,804 (1995).
- 9. D. R. Whitcomb and W. C. Frank, US Patent 5,350,669 (1994).
- B. B. Bokhonov, L. P. Burleva and D. R. Whitcomb, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **43**, 505–508, (1999).
- B. B. Bokhonov, L. P. Burleva, D. R. Whitcomb, and M. R. V. Sahyun, Microsc. Res. Tech. 42, 152 (1998).
- B. B. Bokhonov, L. P. Burleva, W. Frank, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. Winslow, and C. Zou, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **40**, 417 (1996).
- P. L. Potapov, D. Shryvers, H. Strijckers, and C. Van Rost, J. Imaging Sci. Technol. ISSN: 1062-3701, 47, 115 (2003).
- 14. H. Strijckers, *J. Imaging Sci. Technol.*, ISSN: 1062-3701, **47**, 100 (2003). 15. B. Bokhonov, L. Burleva, Yu. Usanov, and D. R. Whitcomb, *J. Imag.*
- *Sci. Technol.* ISSN: 1062-3701, **45** (2001) 259.
- B. B. Bokhonov, L. P. Burleva, A. A. Sidelnikov, M. R. Sharafutdinov, B. P. Tolochko, and D. R. Whitcomb, *J. Imaging Sci. Technol.* ISSN: 1062-3701, 47, 89 (2003).