Variations in the Morphology of Image Silver Particles in Thermally Developed Photographic Materials

Boris B. Bokhonov and Lilia P. Burleva

Institute of Solid State Chemistry, Novosibirsk, Russia

David R. Whitcomb▲

Eastman Kodak Company, Oakdale, Minnesota

Photothermographic imaging systems based on silver halide and silver carboxylates have been utilized for a wide variety of imaging applications for many years. We have been investigating the morphology of silver particles formed in the image area of photothermographic imaging systems in order to understand the forces that affect their morphology. Because the size, shape, morphology and silver particle distribution within an image area affects the overall optical properties of the imaging material, control of these properties should lead to improved photographic responses of the materials. We have found in this investigation that there are multiple factors that influence the overall morphology of the silver particles, and show how morphological properties are changed by different conditions, e.g., the nature of the materials used, including the toners (succinimide, phthalimide, phthalazine), phenolic developers, and related components.

Journal of Imaging Science and Technology 43: 505–508 (1999)

Introduction

Photothermographic materials based on silver halide and silver carboxylates, $[Ag(O_2C_R)]_2$ (R = 13-21) are complicated systems comprising more than a dozen components.[1] The most important of these components are the silver halide/silver carboxylate composition, (such as silver stearate, silver behenate, or similar carboxylates and their mixtures), toner, developer, and binder.[1,2] Changes in the composition, such as component concentrations, type of components, and the preparation and development conditions, all have a substantial effect on sensitometric characteristics of these photographic materials. The effect of these different conditions on the sensitometry can be related to the different chemical reactions occurring during the development process. Consequently, fluctuations in the chemical reactions can lead to substantial changes in the morphology of the silver particles formed in the image areas.

The developing process of the photothermographic material is autocatalytic in nature[3,4] and occurs via the following two steps. First, exposure initiates the formation of catalytically active latent image centers by photocatalytic activation of the photosensitive component, AgX. Second, thermal development causes the formation of silver particles at these latent image centers through the reduction of silver ions from the silver carboxylate. The resulting silver particles form the visible image. It should be noted that very little is known regarding the morphology of the developed silver at this time however, and understanding of the processes that occur during thermal development of the photographic material is still lacking. In other words, the changes occurring in the silver carboxylate during thermal development (its reductive transformation into a silver particle) remain unknown.

Previously, we have shown that the morphology of the silver particles forming in the image area depends on the method of preparation of the silver halide/silver fatty acid complex system.[5–7] The shape and size of the metallic silver crystals change depending on whether the silver halide is incorporated into the imaging composition by the *in situ* or *ex situ* preparation process. When silver halide is obtained by treating the silver carboxylate with a solution of a brominating agent, such as LiBr, $ZnBr_2$, or $HgBr_2$, the process is termed *in situ*. Under these conditions, the photothermographic imaging and thermal development process yields silver filaments (see Fig. 1).

The photothermographic process in which silver halide is prepared separately and then added to the silver carboxylate formulation, termed the *ex situ* or preformed process, produces dendritic silver particles (see Fig. 2).

The goal of the present work was to further understand those factors that influence the morphology of the silver particles formed during thermal development of the photothermographic material.

Experimental

Photothermographic Film Preparation

The silver carboxylate and preformed silver bromide were obtained as described earlier[2,5] to prepare the

Original manuscript received December 15, 1998

▲ IS&T Member

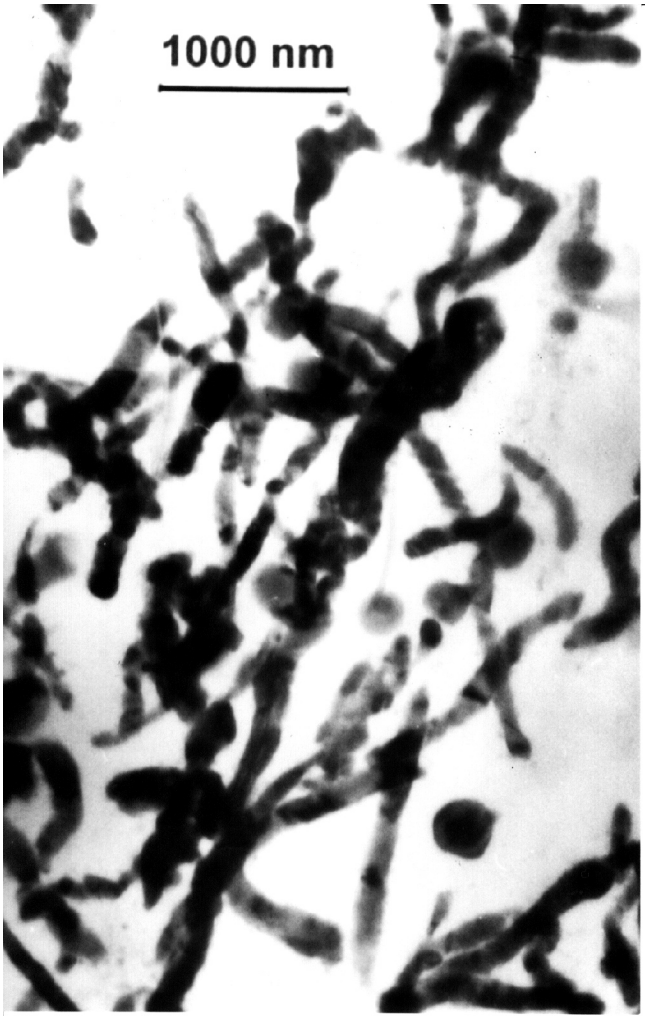


Figure 1. Silver filaments obtained from *in situ* prepared photothermographic imaging material.

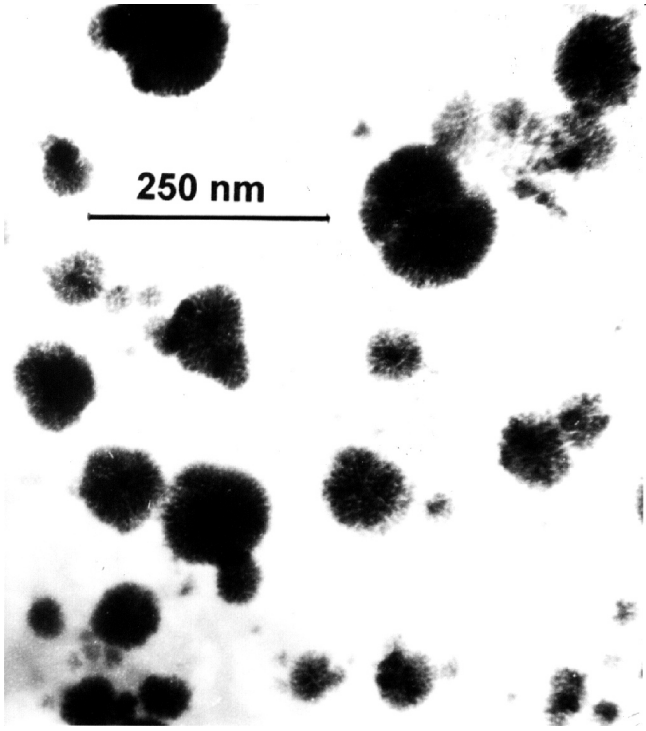


Figure 2. Dendrites obtained from photothermographic films prepared from the *ex situ* (preformed) silver halide grains.

photothermographic materials. In this way, the following photothermographic materials were prepared:[2,6]

1. Formulation with no silver halide.
2. Both preformed and *in situ* AgBr, prepared by treating the preformed AgBr/AgSt system with $ZnBr_2$, modified by use of (a) AgBr T-grains instead of cubic AgBr and (b) various types of toners.

The photothermographic films were exposed through a 0-4 optical density step tablet to light in the visible and near-UV region (unfiltered EG&G xenon flash for 10^{-3} s) under the same conditions, with the exception of the photothermographic material containing no silver halide. The silver halide free film was exposed to an ultraviolet source (500-W mercury vapor lamp at 20 cm for 10 sec.). The UV absorption/senstivity of silver carboxylate has been reported.[8,9] The exposed films were developed at 124°C for 15 s.

T-grain AgBr crystals (diameter = 1.1 – 1.5 μm, thickness = 0.2 – 0.25 μm) were prepared by Yu. Breslav, Imation Corp., Ferrania, Italy.

Electron Microscopy

SEM and TEM investigations of AgSt and AgBr crystals were carried out using a JEM-2000FXII microscope equipped with a scanning ASID-20 device at an accelerating voltage of 200 kV. TEM samples were prepared by selecting a section of the D_{max} region of the photothermographic films that were embedded in 3M Scotchcast™ Electrical Resin. The samples appeared "bubbly" under microscopic examination. The resulting epoxy blocks were then microtomed with a Leica ultracut UCT microtome at room temperature to a 200 nm thickness. The samples were collected on hexagonal carbon coated copper grids. The grids were introduced into the TEM on a cooling holder. All preparations were performed under red light, including transport and insertion into the microscope. These TEM studies used a liquid nitrogen single-tilt holder operating at its minimum temperature (–160°C) to avoid, as much as possible, radiation damage by 200 kV electrons. Most microtomed samples could be observed for over an hour without change under these conditions.

Results

Morphology of Silver Particles Formed During Thermal Development of a Photothermographic Film Without Silver Bromide. In order to most completely understand the processes occurring in the thermal development of photothermographic imaging film samples, we prepared a material containing all of the primary components of the photothermographic layer but without the silver halide. The most significant difference between this photothermographic film and those containing the silver halide is the fact that the absence of the silver halide prevents the formation of a latent image center upon visible light exposure. Consequently, we investigated the formation of silver particles resulting from both thermal development of the film and development of latent image centers that were generated by UV irradiation.

Depending on the thermal development time (optical density) of unexposed film we observed that the concen-

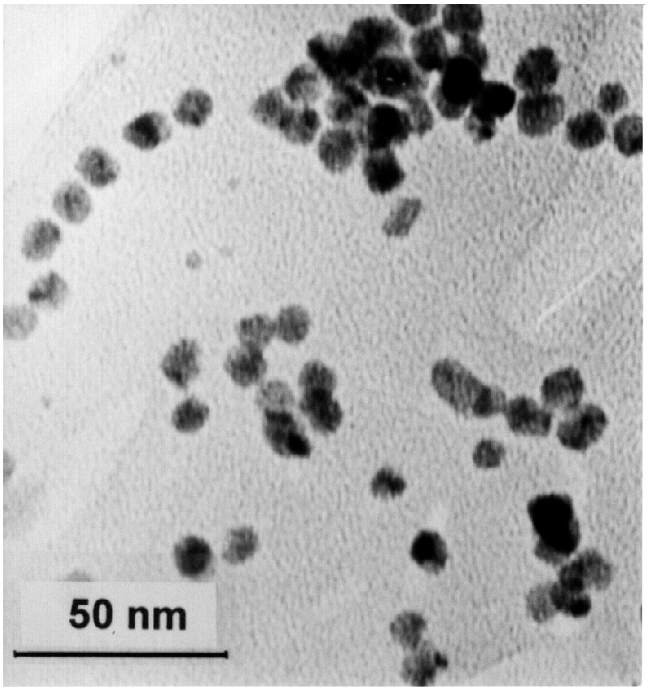


Figure 3. TEM micrograph of silver particles formed during thermal development of unexposed photothermographic film containing no silver halide.

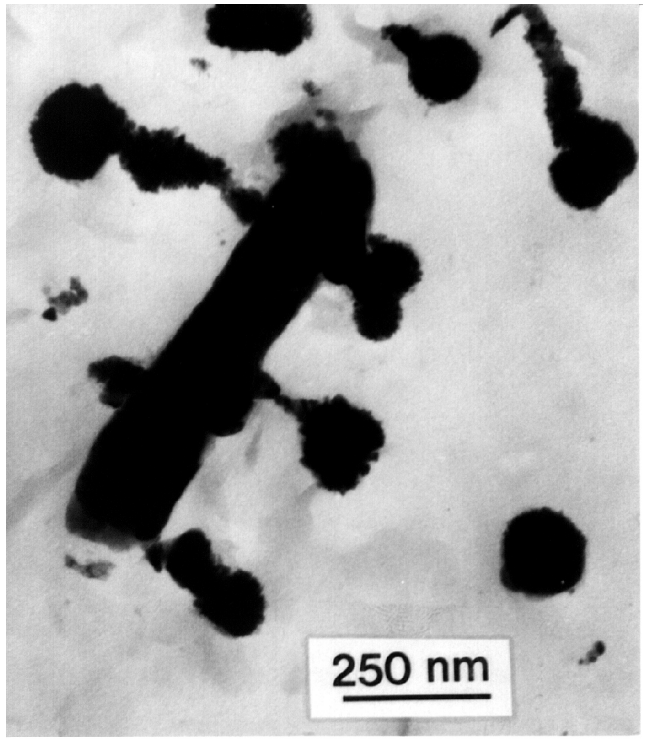
tration of the formed silver particles changed along with their size. Similar results were also reported in samples containing silver bromide.[3] At the initial stages of thermal development (120°C) the silver particles formed were from 10–20 Å in size, but after 5 min of development the silver particles became rounded and on the order of 100 Å, as shown in Fig. 3. These size changes of the developing particles are accompanied by a change in the color of the photothermographic film from yellow to a dark brown.

The morphology of the silver particles obtained upon thermal development of the UV exposed film, at a single optical density, was essentially the same for all the silver particles. In addition, thermal development in the exposed region of the film proceeds at a faster rate than in the unexposed area. The morphology of the precipitating silver particles is completely analogous to that observed upon thermal development of a UV-unexposed, AgBr free, photothermographic film. The silver particles in the UV exposed and developed AgBr free material (2 min of thermal development at 120°C) also are rounded and are in the 100–160 Å size range.

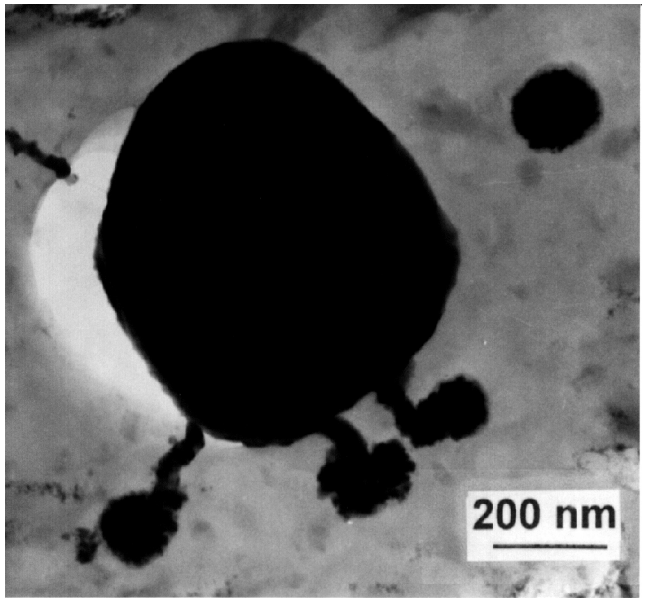
Morphology of Silver Particles Formed During Thermal Development of a System Containing Both "In Situ" and Preformed AgBr.

Systems with AgBr T-grains. We significantly changed the AgBr size and shape in the initial AgBr/Ag carboxylate composition to see how it may affect the morphology of silver particles in the developed film. In the case of photothermographic materials containing T-grains, we found that in practically every example, the formation of silver particles both as dendritic and as filamentary particles was observed.

By comparison, it was shown earlier[5] that developed photothermographic materials, containing cubic preformed AgBr, in the maximum optical density area was predominantly dendritic silver particles. Only a small number of filamentary crystals was observed in this area.



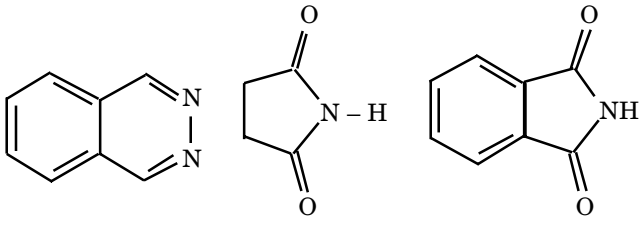
(a)



(b)

Figure 4. TEM micrograph of dendritic and filamentary silver particles in thermally developed photothermographic material film, a) edge-on view of a AgBr T-grain, b) T-grain crystal rotated 90°.

The consequence of these steps that result in the formation of filamentary and dendritic silver during the photothermographic process is most clearly observed in films prepared from T-grain silver halide crystals. The growth of silver particle filaments from the T-grain AgBr crystal surface (111) is observed, while at the terminus of a filament crystal, as a rule, crystallization of fine silver particles as dendritic crystals is observed (see Fig. 4). The size of dendritic silver clusters in the developed material is 100 – 150 nm.



a b c

Figure 5. Photothermographic toners; a) phthalazine, b) succinimide, c) phthalimide.

Photothermographic Film Formulations Containing Different Toners. Earlier it was mentioned[1] that use of different toners in photothermographic materials can lead to substantial changes of the photographic characteristics. In previous work[6] we showed that filamentary and dendritic silver particles are formed in a developed photothermographic material with phthalazine as a toner, as shown in Fig. 5.

In the present work we expanded our investigation into photothermographic materials (both *in* and *ex situ*) containing succinimide and phthalimide as toners. We found that, unlike photothermographic materials with phthalazine as a toner, only the formation of filamentary silver crystals was observed. These particles were up to 400 nm long and several tens of nm thick, as shown in Fig. 6.

Discussion

The electron microscope investigations of the morphology of silver particles formed during the photothermographic process revealed several important properties of these materials.

In most cases, the formation of dendritic and filamentary crystals is observed during the development of the photothermographic film. Under standard concentrations of components, the size of the dendritic crystals formed was 100–200 nm.

a) In many cases, both dendritic and filamentary crystals can be formed at the same surface of silver halide crystals.
b) Filamentary crystals also appear to be a source of dendritic silver in so far as formation of dendritic silver particle crystal is observed at the terminus of the growing filamentary crystal.

The substantial role of toner in the development process of photothermographic material is confirmed by the fact that the change of a toner has a clear effect on the morphology of the developed silver. It was found that using succinimide or phthalimide as a toner instead of phthalazine leads to the formation only of filamentary silver. It is most likely that the observed changes in the morphology of the silver crystals can be related to either different rate of formation of the silver carboxylate complexes with succinimide and phthalimide compared to phthalazine, or with the different chemical properties of these complexes, compared to the properties of the complex formed in the interaction of silver carboxylate with phthalazine. The structures of complex compounds formed between silver and phthalazine based toners used in the photothermographic composition have been reported.[10–13] These types of silver/toner complexes are proposed to be intermediates in the silver particle formation during development.

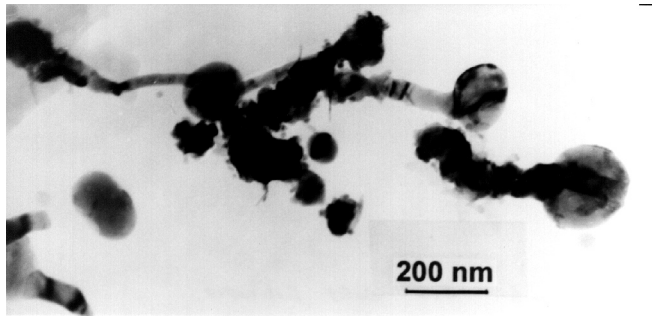


Figure 6. TEM micrograph of filaments in thermally developed photothermographic films with succinimide or phthalimide toners.

Conclusions

We have shown that the formation of silver particles is, in many respects, determined by the presence of certain components in the system, especially those near the latent image centers. However, it is still not yet possible to outline unambiguously the mechanisms underlying the formation and growth stages of dendritic or filamentary crystals. In other words, while the morphology of the silver particles formed during development are most likely determined by the relation between the rates of complex compound formation in the interaction of toner with silver carboxylate and the rate of its reduction by the developer at a latent image or fog center, this relationship is not yet well defined.

Acknowledgments. We gratefully acknowledge the preparations by Drs. Yu. Breslav and C. Zou (Imation Corporation) of the T-grain AgBr and silver carboxylate samples containing the T-grain AgBr, respectively.

References:

1. D. H. Klosterboer, in *Imaging Processes and Materials*, Neblette's Eighth Edition, J. M. Sturge, V. Walworth, A. Shepp, Eds., Van Nostrand-Reinhold, New York: Chap. 9, 279 (1989).
2. C. Zou, J. B. Phillip, S. M. Shor, M. C. Skinner, and P. Zhou, US Patent 5,434,043, 1995.
3. S. E. Hill, M. B. Mizen, M. R. V. Sahyun, and Yu. E. Usanov, *J. Imag. Sci. Technol.* **40,** 568 (1996).
4. M. B. Mizen, *IS&T 50th Annual Conference*, IS&T, Springfield, VA, 1997, p. 34.
5. B. B. Bokhonov, L. P. Burleva, W. C. Frank, J. R. Miller, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. M. Winslow, and C. Zou, *J. Imag. Sci. Technol.* **40,** 85 (1996).
6. B. B. Bokhonov, L. P. Burleva, W. C. Frank, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. M. Winslow, and C. Zou, *J. Imag. Sci. Technol.* **40,** 417 (1996).
7. B. B. Bokhonov, L. P. Burleva, D. R. Whitcomb, and M. R. V. Sahyun, *Micr. Res. Technol.* **42,** 152 (1998).
8. V. M. Andreev, Yu. G. Golitzin, Yu. I. Mikhailov, and V. V. Boldyrev, *Izv. Sib. Otd., Akad. Sci. SSSR, Ser. Khim. Nauk.* **2,** 64 (1983).
9. B. B. Bokhonov, B. I. Lomovskii, V. M. Andreev, and V. V. Boldyrev, *Izv. Sib. Otd., Akad. Sci. SSSR, Ser. Khim. Nauk.* **5,** 8 (1984).
10. D. R. Whitcomb and R. D. Rogers, *Inorg. Chim. Acta* **256,** 263 (1997).
11. D. R. Whitcomb and R. D. Rogers, *J. Chem. Cryst.* **25,** 137 (1995).
12. D. R. Whitcomb and R. D. Rogers, *J. Chem. Cryst.* **26,** 99 (1996).
13. D. R. Whitcomb, US 5,491,059 (1996).