Probing the Nature of Developed Ag in Photothermographic Media

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Abstract

The fundamental imaging element in photothermographic media is nano-sized Ag^0 particles, formed from the thermally induced reduction of silver ions. In the Kodak DryView laser imaging system media, the developed Ag^0 imaging elements contain a mixture of dendritic and filamentary silver. Using a temperature series (105-140 °C) arrested-development study, the latter was found to be ribbon-like, crystalline, and dispersed with microtwins. Dendritic silver, however, was seen to develop at a higher temperature, and reached its maximum size at 122 °C, the condition normally used in the thermal processing of Kodak DryView films. Its morphology resembled a cluster containing numerous loosely packed Ag⁰ nanoparticles. At higher temperatures, it gradually collapsed and condensed into a smaller polycrystalline aggregate. With increasing temperature, its degree of structural order gradually increased and was the highest at 140 °C.

Introduction

A primary component of photothermographic (PTG) imaging materials, based on silver carboxylates, is the toner that enables the golden-brown color of Ag^0 , which is formed from the thermal decomposition of silver carboxylates to be blue-black.^{1,2} This color control is critical for a commercially acceptable product. Current PTG materials use phthalazine (PHZ) in conjunction with a co-toner, phthalic acid (PA), Fig. 1, or their derivatives—a combination originally discovered nearly thirty ago as toners to be used in these systems.³

Historically, one difficulty has been a lack of understanding of the specific roles of these types of toners and co-toners in the PTG imaging processes, which



Figure 1. (a) Phthalazine (PHZ), and (b) Phthalic acid (PA).

inhibits the rationale for design of improved materials. Some of the coordination chemistry of these toners has been reported,^{4,5} and several papers discussing the general reaction mechanisms have appeared.^{6,7} Since at least two types of metallic silver particles, dendrites and filaments are formed,^{8,9} what is needed is a detailed explanation of how the controlling factors involve various components in the formulation. The filamentary shape has been recently investigated,¹⁰ and some correlation to the filaments observed in conventional black and white photography can be made. The dendritic form, however, is unique to PTG imaging systems and has been attributed to originate primarily on silver bromide prepared separately from the silver soap, while the filaments were attributed to in situ silver bromide.⁸ The roles of the toners must be accounted for, if this tendency is accurate.

The novelty of the dendritic composition of metallic Ag^0 and the silver high efficiency of PTG constructions, compared to conventional silver halide, suggests a connection that would be worth exploring. This is particularly true when considering the fact that the dendritic form is comprised of Carey Lea-sized silver nanoparticles,¹¹ which by themselves do not give a neutral black visual density. We now report the results of our

investigation into the dendritic form of metallic silver from an arrested-development, temperature series. We show how the dendritic silver contributes to the light absorption properties of the image area and lay the groundwork for providing better understanding of the silver particle formation that will lead to new and improved imaging materials.

Experimental

Commercial Kodak DryView laser imaging system film¹² containing silver carboxylates and preformed silver bromide, along with other imaging components, was used for this study. All materials were exposed at similar conditions with a scanning laser sensitometer incorporating an 811 nm laser diode. The samples were developed using a heated roll processor for 15 s in the 105–140 °C temperature range.

The microstructures of these films were examined by transmission electron microscopy (TEM). Film cross-sections were prepared in a Leica Ultracut S microtome using a diamond knife, and thin sections were wet-transferred onto a carbon-coated Cu grid. All electron beam imaging and analysis were gathered with the sample kept at liquid nitrogen temperature in a JEM-2000FX instrument, as has been described elsewhere¹³. High-resolution lattice imaging was performed in a JEM-2010F TEM.

X-ray diffraction (XRD) measurements were made using a Rigaku Bragg-Brentano diffractometer equipped with a copper-rotating anode, diffracted-beam monochromator, and scintillation detector. All diffraction data were collected at ambient temperature. Samples were analyzed in the D-max region after actinic radiation exposure and thermal processing. Crystallite size was determined using the Scherrer technique¹⁴ with National Institute of Standards and Technology (NIST) Silicon 640b being used as the instrument profile standard.

Results

The D-max optical density for PTG media, processed at various temperatures, was found to go through maxima at about 122 °C, Fig. 1, which is the development temperature used for DryView system. While the optical density for 110 °C (it barely rose above D-min) could intuitively be ascribed to a lack of chemical reactivity at the lower temperatures, and the increase in optical density that peaked at 122 °C might be due to increased reaction between the coated components in the imaging layer, such reasoning cannot be used to reconcile with the rapid drop in optical density for processing temperatures above 122 °C. An anomalous change in Ag morphology was suspected.



Figure 1. Optical density of PTG films developed at temperatures ranging form 110–140 °C, 15 s.

Examining the morphology of developed Ag⁰ using TEM provided novel insights into their formation characteristics. At the lowest temperature studied (105 and 110 °C, 15 s), developed Ag⁰ took on primarily a filamentary morphology, each emanating from a AgBr cube, Fig. 1(a). As filamentary Ag⁰ has been seen in both chemically and physically developed imaging media systems, their analysis was carried using a combination of energy-dispersive spectroscopy (EDS) and lowmagnification imaging methods, similar to those reported by others.^{10,15} Only a minority of the AgBr particles had any discernible Ag filaments, and they were narrow (~10 nm) and short (0.1-0.2 µm). Upon increasing the temperature to 115 °C, while filamentary Ag⁰ was still prevalent, the first sign of dendritic Ag^0 , a collection of nanoparticles adhering to the outer surface of Ag filaments, was observed, Fig. 2(b). These were usually seen on the filament tip farthest away from the AgBr. Increasing the processing temperature to 122 °C resulted in two major changes to the developed Ag⁰ morphology. First, most of the Ag⁰ took on a distinct "broccoli" shape, made up of a filamentary "stem," capped with a dendritic "head", Figure 2(c). The latter is an agglomerate of isolated Ag⁰ nanoparticles, each 3-5 nm in size, in close proximity but separated from each other, not unlike a sponge ball. The average size of these agglomerates was the highest at 122 °C, Table 1. The dendrite agglomerate density was qualitatively determined by counting their presence in a given volume of film, whose area was the field of view, and whose thickness was estimated from the color of the microtomed sections.¹⁶ For our experiments, the imaged sections were greyish-silver in color when viewed under an optical microscope, and they correspond to a thickness of ~60 nm. At 130 and 135 °C, a gradual but detectable decrease in dendritic Ag⁰ size was evident, Figs. 2(d) and 2(e), and Table 1. In addition, the dendrites started to exhibit a "blotchy" morphology in which portions of the dendrite agglomerate appeared with a different contrast. This transformation continued and appeared complete by 140 °C, as dendritic Ag^0 became compact and polycrystalline, Fig. 2(f). Apparently, the higher processing temperatures gradually caused the dendritic, spongy Ag^0 to sinter and condense into spherical Ag^0 polycrystals, ~ 60-80 nm in size.

Table 1. Temperature-time processing conditions of PTG coatings, showing changes in D-max optical densities and dendritic Ag⁰ properties.

Process T (°C)	Process time (s)	Optical density at D-max	Average dendrite size (nm)	Dendrite density (#/µm ³)
110	15	0.5	n/a	n/a
115	15	2.3	n/a	n/a
122	15	3.8	0.2	23
130	15	3.5	0.15	21
135	15	2.9	0.1	22
140	15	2.4	n/a	n/a



Figure 2. Morphology of developed Ag0 at various processing T. (*a*) 110 °C, (*b*) 115 °C, (*c*) 122 °C, (*d*) 130°C, (*e*) 135 °C, and (*f*) 140 °C.

Detailed examination of developed Ag^0 in the 122 °C, 15 s processed PTG film by high-resolution lattice imaging revealed another structural difference between dendritic and filamentary Ag^0 . Whereas low magnification images of the former suggested an agglomerate of isolated nanoparticles, lattice images revealed that each nanoparticulate is made up of a collection of microcrystalline domains. In a given nanoparticle, ordered domains existed as neighbours, with each only ~2–5 nm wide, Fig. 3. In between, amorphous regions made up of either void or organic coatings were present, and presumably served to passivate the Ag^0 surfaces. By contrast, the Ag^0 filament contained longerrange structural order, with lattice lines that spanned the entire width of the filament, typically ~30–50 nm in dimension, Fig. 4. Along most filaments, while different lattice orientations could be found with some that showed a twinning relationship, lattice lines were present throughout. This difference in microstructure was consistent with the relatively strong diffraction contrast seen in filament vs the weak contrast in dendrites when both were images side by side at different tilt angles.



Figure 3. High-resolution lattice image of dendritic Ag° developed at 122 °C,15 s. showing the short range structural order within a given nanoparticles of a dendritic cluster.



Figure 4. High-resolution lattice image of filamentary Ag^o showing the extent of structural order across the width of a filament.

X-ray diffraction analysis of developed Ag^0 was carried out by studying the peak profile of the (111) Ag^0 diffraction peak at 38.15° 2-theta, Fig. 5. The average crystallite size, a measure of long-range structural order as calculated by its full width at half maximum, was low at 110 °C but gradually increased with increasing temperatures, and reached the maximum at 140 °C. This suggests the higher temperatures caused Ag⁰ to sinter from short-range ordered crystallites to polycrystals with longer-range structural order.



Figure 5. (111) Ag^o diffraction peak for PTG films developed at (a) 115 °C, (b) 122 °C, (c) 130 °C, (d) 135 °C, and (e) 140 °C. Observed intensities.

Discussion

Key features on the formation of dendritic Ag⁰ in PTG media has been uncovered by probing its structural and morphological characteristrics in the 105–140 °C thermal processing range. The combination of electron microscopy and X-ray diffraction data has unraveled several structural evidences relevant for explaining the observed variations in its optical density behavior.

The initial, sparse appearance of dendritic Ag in the 115 °C range, coupled to its fully developed state at 122 °C, and finally to its gradual collapse into a condensed polycrystalline form in the 130-140 °C range, not only correlates well to the observed optical density maxima at 122 °C but also provides key attributes for forming a relevant mechanism to account for the optical properties of PTG film, based on a Ag carboxylate construction. The formation of this unique form of Ag⁰ clearly point to a careful balance of semi-crystalline, nanoparticulate agglomerates that are surface passivated to produce their spongy morphology. Its collapse at the higher temperatures also points to a narrow range of stability that is likely controlled by the chemistries in the PTG formulation. The lack of any significant change in particle density between 122-135 °C, Table 1, suggests that its nucleation density has not changed significantly but, rather, the condensation of dendritic agglomerates took place in dendrites preformed at the lower temperatures. The collapse of this morphology at temperatures of only

130–140 °C would seem anomalous, considering the melting point of Ag is 962 °C but might point to sintering as the passivant starting to decompose by 130 °C,¹⁷ or to melting point depression caused by the small size of the dendrites.¹⁸

The other, filamentary form of Ag⁰ is observed to first form at a lower temperature than dendritic Ag⁰, and it is invariably nucleated from the surface of a AgBr crystal. It is likely that the crystal surface, playing the role of an underlying structural template, may cause a lowering of the filamentary formation temperature. The propensity of silver with its face-centered-cubic structure is also well known for twinning across its (111) crystallographic face, a feature commonly observed in the current study. This propensity to form microtwins makes it ambiguously difficult to conduct meaningful micro- or nano-diffraction studies on individual filaments, if diffraction studies are performed on areas away from the $Ag^0/AgBr$ interface. The crystallographic relationships initiated at the AgBr template surface may not propagate very far into the growing Ag⁰ filament before one or more twinning events occur, and each structural switch would change the original interfacial orientation. The lack of such information in the current literature point to the need for a future study to directly unravel this AgBr/Ag⁰ relationship.

While a comprehensive description of the Ag development process is not yet available, several features reported here will need to be incorporated to better understand the various roles played by the chemistry built into the PTG film. They include: 1) the formation of two types of Ag^0 , 2) chemical passivation of the silver surface that apparently degrades at a low temperature, and 3) the maximum size of dendrite in a narrow temperature range. A more detailed description of the Ag^0 development process is being created for a separate publication.

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