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Photothermographic Materials with Tabular Silver Iodide Grains

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Abstract. *It has been revealed in this study that the sensitivity of newly developed composite grains with tabular silver iodide grains as hosts and epitaxially formed silver bromide microcrystals as guests is high enough in photothermographic materials to realize a blue medical x-ray film-screen system in combination with BaFBr:Eu fluorescent radiographic intensifying screen. Beside the fact that the quality of the system image is comparable with that of conventional ones, the image stability as well as the haze of the new system is satisfactory, in spite of the fact that the new system uses photothermographic materials, since the grains used as photosensors are fixed during thermal development. © 2007 Society for Imaging Science and Technology.*
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INTRODUCTION

In our studies presented at ICIS'06, we have elucidated that nanoparticles of silver iodide in photothermographic materials have high sensitivity for blue diode laser light, and that the fog density of the developed layers of the materials does not increase under room light illumination of 25°C, relative humidity 60% for 30 days, since the nanoparticles are fixed during thermal development.[1] We have also studied ionic and electronic properties of silver iodide grains to obtain guiding principles for design of photothermographic materials.[2]

Photothemographic materials[3] are ecofriendly, since they do not need wet processing with chemical solutions, but only dry processing. However, they are used only in big hospitals as printing materials in computed radiographic systems for medical use. Most small hospitals, which cannot afford computed radiographic systems, still have to continue to use x-ray films which need wet processing, since photothermographic materials with camera speed have not yet been introduced commercially. The camera speed materials need silver halide grains, which are much bigger than those for the printing media as photosensors.

In usual photothermographic materials, silver halide grains are not fixed during dry processing and therefore induce haze and increase of fog density of developed layers under room light illumination. No camera speed photothermographic material has ever been commercialized until now, since the haze and the increase in the fog density are enhanced by the increase in the size of silver halide grains.

We have now developed photothermographic materials with tabular silver iodide grains, which are camera speed in sensitivity towards blue light and are fixed during thermal development. One of the aims of this paper is to describe the formation, sensitization, covering power enhancement, and fixation of tabular silver iodide grains during thermal development.

We have also found that a radiographic intensifying screen made of europium-doped barium fluorobromide[4] (BaFBr:Eu) exhibits fluorescence with sufficiently high intensity in the wavelength region of the exciton absorption band of silver iodide grains. Thus we could realize a blue regular medical x-ray dry film-screen system by use of photothermographic materials with tabular silver iodide grains and a radiographic intensifying screen composed of BaFBr:Eu. An aim of this paper is to describe this newly developed system.

EXPERIMENTAL

Tabular silver iodide grains in an emulsion were prepared by means of a usual controlled double jet method with pAg kept constant during the precipitation of the grains in the presence of a silver halide solvent (3,6-dithia-1,8-octanediol) in an aqueous gelatin solution.[5] Figure 1 shows the electron micrograph of the grains obtained. They were composed of a mixture of β and γ phase of silver iodide; most of them were tabular in shape, 1.4 μm in average equivalent circular

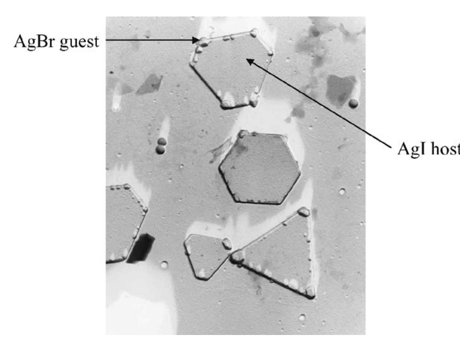

Figure 1. Transmission electron micrograph of carbon-replicated tabular silver iodide grains with epitaxitially formed silver bromide microcrystals. Minute spheres are latex with 0.2 μm in diameter.

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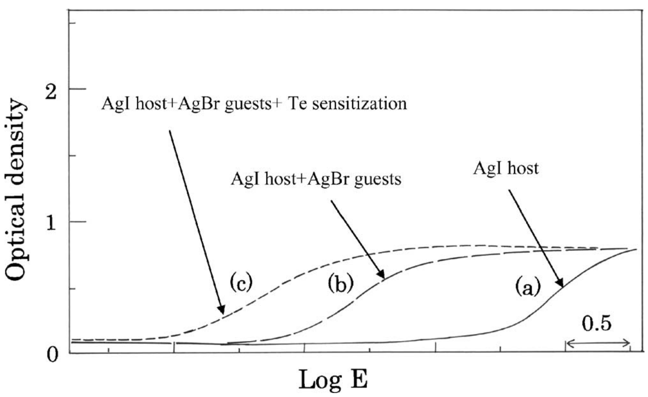

Figure 2. Characteristic curves of (a) tabular silver iodide grains, (b) with epitaxially formed silver bromide microcrystals, and (c) with the microcrystals and tellurium sensitization centers, in photothermographic materials in the absence of any nucleating agent.

diameter of main surface, 0.12 μm in average thickness, and 0.68 μm in equivalent sphere diameter. Guest silver bromide microcrystals were epitaxially formed on host silver iodide grains by means of a controlled double jet method. The molar ratio of the amount of the guest to that of the host was 10%. Then, the grains were chemically sensitized with bis-(*N*-methyl-*N*-phenylcarbamoyl)-telluride as a sensitizer to give tellurium sensitization centers on the grain surface.[6]

Silver behenate microcrystals were prepared and dispersed in water with polyvinyl alcohol as a binder.[7,8] Silver behenate (source of silver ions), bis-phenol (developing agent), polyhalide (antifoggant), substituted phthalazine, phthalic acid (silver ion carriers and toners), and water dispersion of SBR latex (binder) were mixed in the form of an aqueous liquid dispersion. After an emulsion with tabular silver iodide grains was introduced into this liquid dispersion, it was coated on both sides of PET film base and dried to give samples of the water-based photothermographic material.[7–9]

The characteristic curves of the samples, prepared as described above, were obtained by usual light sensitometry with a tungsten lamp as a light source and a blue filter, and by medical x-ray sensitometry with the newly developed radiographic intensifying screen composed of BaFBr:Eu.[4(b)] The exposed samples were developed at 121°C for 24 sec. A nucleating agent incorporated in the material improved the covering power of developed silver images.

RESULTS AND DISCUSSION

Sensitization of Tabular Silver Iodide Grains

Photographic sensitivity of tabular silver iodide grains in photothermographic materials was considerably lower than that extrapolated from the sensitivity of silver iodide nanoparticles[1] according to the proportionality of sensitivity to grain volume.[2] As shown in Figure 2, the sensitivity of tabular silver iodide grains was significantly increased by epitaxially formed guest microcrystals of silver bromide on the grains. In addition, tellurium sensitization[6] further increased the sensitivity of the grains.

Figure 3 shows the reciprocity law behavior of three kinds of tabular silver iodide grains. As seen in this figure,

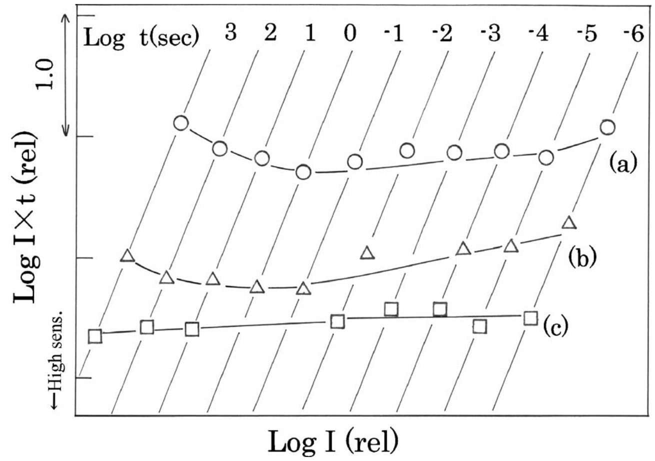

Figure 3. Reciprocity law behavior in photothermographic materials (a) with tabular silver iodide grains, (b) those with epitaxially formed silver bromide grains, and (c) those with the microcrystals and tellurium sensitization centers. The ordinate $I \times t$ refers to the exposure required to give the optical density of 0.2 above fog for the developed layers of the materials.

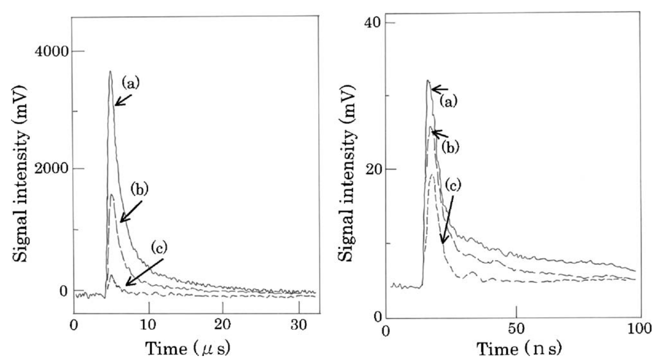

Figure 4. Time-resolved photoconductivity with photoelectrons as carriers in terms of the signal intensity of 35 GHz microwave photoconductivity measurements (right) and with positive holes as carriers in terms of the signal intensity of radiofrequency photoconductivity measurements (left) of (a) tabular silver iodide grains, (b) those with epitaxially formed silver bromide microcrystals, and (c) those with the microcrystals and tellurium sensitization centers.

tabular silver iodide grains themselves exhibited low sensitivity with low-intensity reciprocity law failure, while those with guest silver bromide microcrystals exhibited enhanced sensitivity with both low-intensity and high-intensity reciprocity law failure. Tellurium sensitized tabular silver iodide grains with guest silver bromide microcrystals exhibited the highest sensitivity among them with no reciprocity law failure.

Figure 4 shows the time-resolved photoconductivity of the tabular silver iodide grains.[2] The photoconductivity with positive holes as carriers in the grains in terms of the signal intensity of the radiofrequency photoconductivity measurement was decreased by the guest silver bromide microcrystals and tellurium sensitization centers. The photoconductivity with photoelectrons as carriers in the grains in terms of the signal intensity of the 35 GHz microwave photoconductivity measurement was also decreased by the guest microcrystals and tellurium sensitization centers.

It is considered that the mismatch in lattice structure introduced at the heterojunction between host silver iodide

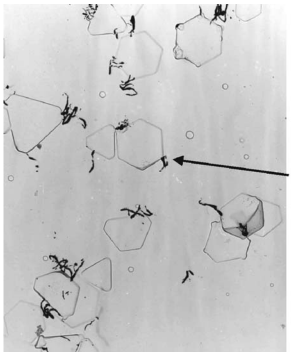

Figure 5. Electron micrograph of tellurium sensitized tabular silver iodide grains in conventional materials, which were exposed and subjected to arrested development by use of a liquid developer D-19 at 20°C for 30 min.

and guest silver bromide causes the formation of dislocations acting as shallow electron traps. In addition, the increase in the silver ion concentration in the vicinity of the grains in an emulsion due to the presence of epitaxitially formed silver bromide microcrystals enhance the reaction of positive holes with the surroundings of the grains.[1] These conditions should increase the sensitivity of the grains by enhancing charge separation.

Electron traps provided by tellurium sensitization centers should be effective in increasing the efficiency of latent image formation. It is inferred that tellurium sensitization centers are formed in contact with guest silver bromide microcrystals, since silver telluride clusters which are formed with excess tellurium sensitizer and large enough to be observable by means of a transmission electron microscope are observed in contact with the guest silver bromide microcrystals, as shown in Figure 5.

Figure 6 shows the fraction of silver halide grains bearing latent image centers in conventional emulsion layers in terms of the optical density of the layers, which were treated by Frei's buffer solutions[10] with redox potential indicated on the abscissa and developed. The examination was made with silver bromide grains, silver iodide ones, and tabular silver iodide ones with epitaxitially formed silver bromide microcrystals. The redox potential, at which the optical density is one half, is regarded as the oxidation potential of latent image centers.

We have considered that the developability of latent image centers on silver iodide grains is improved by the formation of the epitaxitially formed silver bromide microcrystals, since the oxidation potential of latent image centers on the silver iodide grains with the microcrystals was more positive than that of the centers formed on the silver iodide grains without the silver bromide microcrystals, and similar to that of the centers formed on silver bromide grains. Although these experiments were carried out in a conventional material with wet processing, it is assumed that the obtained result is also valid in photothermographic materials.

We could thus obtain highly sensitive tabular silver iodide grains owing to the enhancement of charge separation by introducing dislocations into the grains, the increase in silver ion concentration in the vicinity of the grains, the stabilization of latent image centers by epitaxitially formed silver bromide microcrystals on them, and the enhancement of latent image formation by tellurium sensitization.

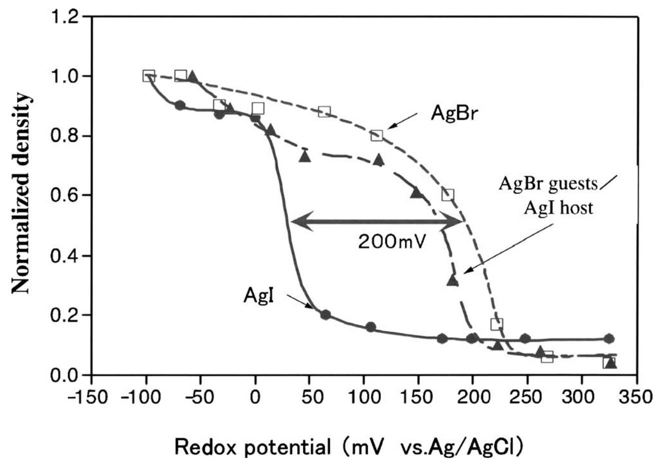

Figure 6. Normalized optical density regarded as the fraction of grains having latent image centers on the surface in a coated layer which was exposed to render all the grain developable, treated in a buffer solution with redox potential indicated on the abscissa, and developed. Latent image centers were formed on silver bromide grains (open squares), silver iodide ones (filled circles) and tabular silver iodide ones with epitaxially formed silver bromide microcrystals (filled triangles).

Improvement in Covering Power of Silver Images and Fixation of Tabular Silver Iodide Grains

Since the source of silver ions for an image composed of silver clusters in a coated layer of a photothermographic material is not a silver halide grain, but silver carboxylate, the amount of silver halide is not simply related to the maximum density of the developed layer. The maximum density (D_{max}) of a characteristic curve of a coated layer with a certain amount of silver halide decreases by increasing the size of silver halide grains in it, since the number of the silver clusters decreases, and covering power thus decreases with increasing the size of silver halide grains.

We have therefore attempted to use nucleating agents to obtain photothermographic materials with high D_{max}. Some of such well-known nucleating agents as hydrazine and acrylonitrile actually increased D_{max} when they were added to photothermographic materials,[11] as seen in Figure 7 which shows characteristic curves of layers with varying amounts of a nucleating agent. Along with this phenomenon, many minute silver clusters were observed near developed silver grains on tabular silver iodide grains in the electron micrographs of the cross sections of developed layers of photothermographic materials with nucleating agents. It is proposed that the oxidation of nucleating agents by oxidized developing agents gave active species responsible for the formation of development centers during thermal development. In addition, the covering power of a silver image was enhanced by the formation of these minute silver clusters, which are smaller in size and larger in covering power than the developed silver grains.

We have found that tabular silver iodide grains as well as nanoparticles of silver iodide[1] are fixed in photothermo-

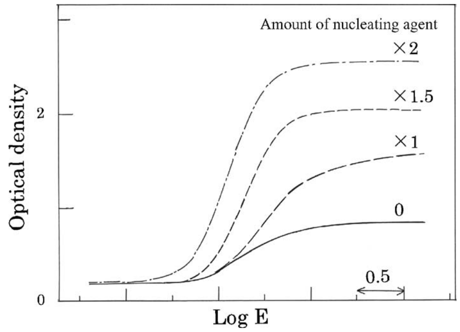

Figure 7. Characteristic curves of coated layers of tabular silver iodide grains in photothermographic materials to which a nucleating agent was added in varying amounts.

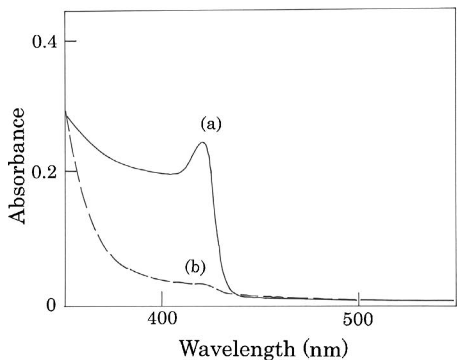

Figure 8. Absorption spectra of coated layers of tabular silver iodide grains in photothermographic materials (a) before and (b) after thermal development.

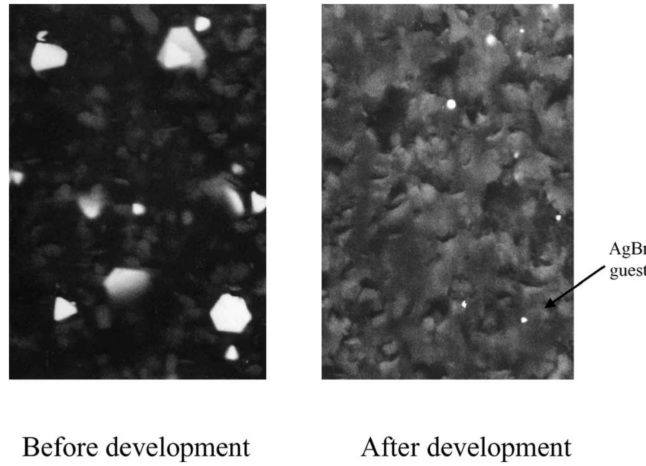

Figure 9. Electron micrographs of coated layers of photothermographic materials before (left) and after (right) thermal development. Note that minute dots in the right figure are remaining silver bromide microcrystals, which were originally formed epitaxially on tabular silver iodide grains, and that tabular silver iodide grains are present in the left figure and absent in the right figure.

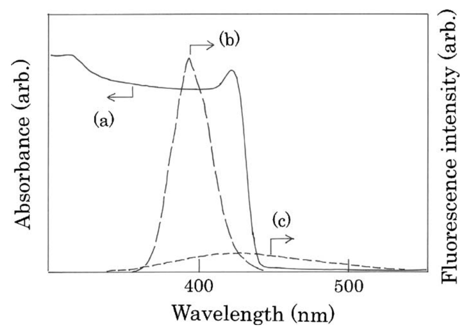

Figure 10. Absorption spectrum of (a) silver iodide and fluorescence spectra of radiographic intensifying screens composed of (b) BaFBr:Eu and (c) $CaWO_4$.

graphic materials during thermal development. As shown in Figure 8, the exciton absorption band of tabular silver iodide grains in photothermographic materials disappeared during thermal development, as was already observed in the materials with the nanoparticles. On the other hand, as shown in Figure 9, guest silver bromide microcrystals formed on the tabular grains were not dissolved and remained in developed layers of photothermographic materials. Fortunately, the amount of the remaining silver bromide microcrystals was not large enough to bring about the appearance of haze and the increase in fog density of developed layers under room light illumination.

BaFBr:Er radiographic intensifying screen and Blue Regular Medical X-ray Dry Film-Screen System

Radiographic intensifying screens with calciumtungstate ($CaWO_4$) have been used for blue regular medical x-ray conventional film-screen systems.[12] We have discovered that a radiographic intensifying screen made from europium-doped barium fluorobromide[4] (BaFBr:Eu) exhibits the fluorescence with very high intensity in the wavelength region of the exciton absorption band of silver iodide grains (i.e., blue-violet region), as shown in Figure 10.

Blue regular medical x-ray conventional film RX-U® made by FUJIFILM Corporation is composed of silver iodobromide grains, which are as large as 0.93 μm in average equivalent sphere diameter, and twenty times more abundant in a molar basis than silver halide grains in our photothermographic film with the tabular silver iodide grains in this study. Although the total amount of silver included in our photothermographic materials as tabular silver iodide grains and silver carboxylate microcrystals is one half of the total amount of silver in RX-U®, our materials gave the same $D_{\max}$ as RX-U®.

We combined both the photothermographic materials, as described above, with optimally sensitized tabular silver iodide grains, and the radiographic intensifying screen composed of BaFBr:Eu to give a new medical x-ray film-screen system. It has been found that this new system has the same system sensitivity as that of the conventional system with wet processing film RX-U® and $CaWO_4$ radiographic intensifying screen, as shown in Fig. 11.

System granularity and system sharpness are nearly the same between our new system and the conventional system with RX-U® and $CaWO_4$, as shown in Fig. 12 and Fig. 13. The developed films of the new system are free from haze and show no increase in fog density under room light illumination.

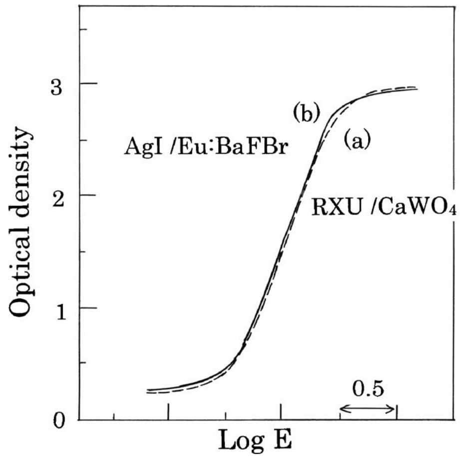

Figure 11. Comparison of characteristic curves between (a) a conventional system with medical x-ray blue sensitive film RX-U® and $CaWO_4$ radiographic intensifying screen and (b) the new system with the photothermographic film and BaFBr:Eu radiographic intensifying screen as described in this paper. Note that curves (a) and (b) were obtained by wet and dry processing, respectively.

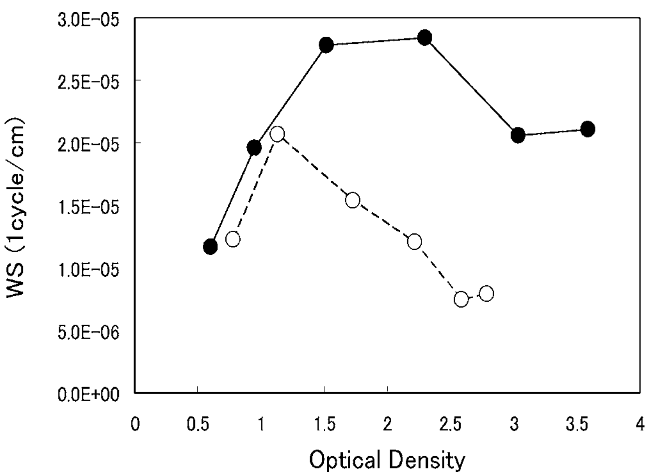

Figure 12. Comparison in system granularity between the new AgI/BaFBr:Eu system (open circles) and the conventional RX-U®/$CaWO_4$ system (closed circles).

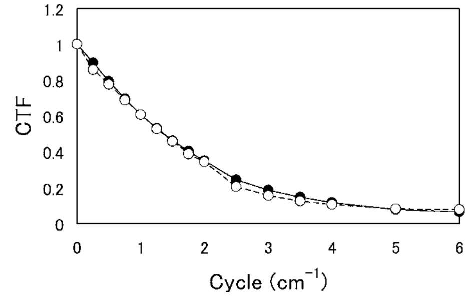

Figure 13. Comparison in system sharpness between the new AgI/BaFBr:Eu system (open circles) and the conventional RX-U®/$CaWO_4$ system (closed circles).

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REFERENCES

[1] H. Mifune, K. Yamane, T. Ohzeki, F. Nariyuki, K. Watanabe, M. Yoshikane, M. Nakanishi, T. Maekawa, and T. Funakubo, “Photothermographic materials with nanoparticles of silver iodide”, J. Imaging Sci. Technol. **51**(3), 207 (2007).
[2] T. Tani, H. Mifune, S. Yamashita, S. Aiba, T. Ohzeki, and K. Yamane, “Ionic and electronic properties of silver iodide grains”, J. Imaging Sci. Technol. **51**(3), 202 (2007).
[3] M. R. V. Sahyun, J. Imaging Sci. Technol. **49**, 337 (2005).
[4] (a) M. Sonoda, M. Takano, J. Miyahara, and H. Kato, Radiology **148**, 833 (1983). (b) K. Yamane and K. Kohda, US Patent Application 2005-74707A1 (2005).
[5] T. Ohzeki and E. Okutsu, US Patent Application 2004-131983A1 (2004).
[6] K. Morimura, H. Sasaki, T. Kojima, M. Ihama, S. Yamashita, T. Tani, and H. Mifune, “Characterization of sulfur, selenium and tellurium sensitization centers and sensitization mechanisms”, *Proceedings of The 2005 Beijing International Conference on Imaging: Technology and Application for the 21th Century* (Chinese Academy of Sciences, Beijing, 2005) p. 56.
[7] H. Tsuzuki, A. Hatakeyama, and K. Nakajima, “The aqueous-coated photothermographic material”, *Proc. ICIS’02: The 20th International Congress of Imaging Science* (SPSTJ, Tokyo, 2002) p. 27.
[8] K. Yamane and S. Yamashita, “The role of silver halides in photothermographic materials with a water dispersible binder”, *Proc. ICIS’02, The 29th International Congress of Imaging Science* (SPSTJ, Tokyo, 2002) p. 29.
[9] T. Funakubo, US Patent 7,144,692 B2 (2006).
[10] E. A. Frei, Photogr. Korresp. **105**, 5,21,37 (1969).
[11] T. Ohzeki, US Patent Application 2005-26093A1 (2005).
[12] A. G. Haus and J. E. Cullinan, “Screen film processing system for medical radiography: A historical review”, Radiographics **9**, 1203 (1989).