Photothermographic Materials with Tabular Silver Iodide Grains

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Abstract

The sensitivity of composite grains with tabular silver iodide grains as hosts and epitaxially formed silver bromide grains as guests in photothermographic materials was high enough to realize blue regular medical X-ray film-screen system in combination with BaFBr:Eu fluorescence radiographic intensifying screen.

Introduction

In our previous papers[1,2], we have elucidated that nano-particles 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 never increases under room light illumination because the particles are dissolved during thermal development. We also studied ionic and electronic properties of silver iodide grains for obtaining adequate guiding principles to design the grains.

Photothermographic materials having camera speed without suffering from the haze and increase in the fog density of developed layers under room light illumination have not yet been realized till now. We have developed the photothermographic materials with tabular silver iodide grains, which have camera speed for blue light. This paper is undertaken to describe the formation, sensitization, covering power enhancement and fixation of tabular silver iodide grains during thermal development. We have also found that radiographic intensifying screen made of BaFBr:Eu has high fluorescent intensity in the wavelength region of the absorption band of silver iodide grains. Thus, we could realize blue regular medical X-ray dry film-screen system by use of photothermographic materials with tabular silver iodide grains and BaFBr:Eu radiographic intensifying screen.

Experimental

Tabular silver iodide emulsion grains were prepared by means of a usual controlled double jet method with pAg kept constant in the presence of silver halide solvent (3,6-dithia-1,8-octanediol) in an aqueous gelatin solution. The obtained grains had average equivalent circular diameter of main surfaces of 1.4µm, average thickness of 0.12µm, and equivalent sphere diameter of 0.68µm. Guest silver bromide grains were epitaxially formed on host silver iodide ones by means of a controlled double jet method. The ratio of the amount of the guest to that of the host was 10 mole %. Then, the grains were chemically sensitized with bis-(N-methyl-N- phenylcarbamoyl)-telluride as a tellurium sensitizer[3].

Silver behenate microcrystals were prepared and dispersed in water with polyvinyl alcohol as a binder. Silver behenate (source of silver ions), bis-phenol (reducing agent), polyhalide (anti-foggant), alkyl-substituted phtalazine, phthalic acid (silver ion carriers and toners), and a 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 the above-stated liquid dispersion, the dispersion was coated on a PET film base and dried to give a water-based photothermographic material[4]. The characteristic curve of the above-stated material was obtained by exposing it to a tungsten lamp through a blue filter or by medical X-ray sensitometry with radiographic intensifying screen. The exposed material was developed at 121℃ for 24 sec. A nucleating agent was used to improve the covering power of developed silver images.

Results and Discussion

1. Sensitization of Tabular Silver Iodide Grains

Photographic sensitivity of tabular silver iodide grains in photothermographic materials was considerably lower than that expected from the extrapolation of the sensitivity of silver iodide nano-particles according to the proportionality of sensitivity with grain volume[1]. As shown in Fig. 1, the sensitivity was significantly increased by epitaxially forming guest grains of silver bromide on tabular silver iodide grains. The guest grains were deposited on the corners and edges of the tabular grains. Tellurium sensitization increased the sensitivity of the grains.

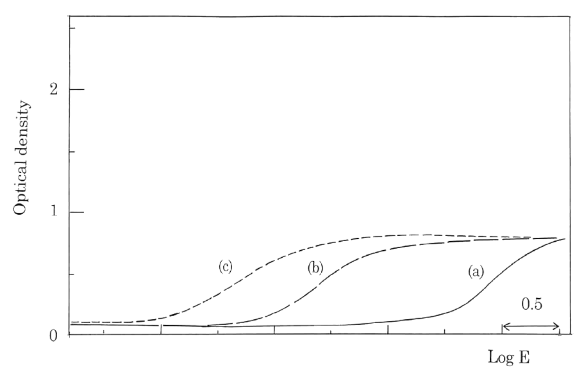

Figure 1. *Characteristic curves of tabular silver iodide grains without any treatment (a), the grains (a) with epitaxially formed silver bromide grains (b), and the grains (b) with tellurium sensitization treatment (c) in photothermographic materials in the absence of any nucleating agent*

It was inferred that tellurium sensitization centers are formed in contact with guest silver bromide grains, since silver telluride clusters, which were formed with excess amount of tellurium sensitizer and observed by means of transmission electron micrograph, were in contact with the guest grains. In addition, latent image centers thus formed were also in contact with the guest grains. As described in the previous paper[2], the formation of the guest silver bromide grains on tabular silver iodide grains decreased the concentrations of both photoelectrons as indicated by the signal intensity of the 35GHz microwave photoconductivity and positive holes as indicated by the signal intensity of the radiowave photoconductivity. It is considered that electron traps are provided by lattice defects at the interface between guest silver bromide grains and host silver iodide ones, and that the increase in the silver ion concentration due to the presence of silver bromide enhances the reaction of positive holes with the surroundings of the grains. These conditions should increase sensitivity by enhancing the charge separation. Effective electron traps provided by tellurium sensitization increase the efficiency of latent image formation. In addition, it is considered that the developability of latent image centers is improved by the formation of the guest silver bromide grains, since the oxidation potential of latent image centers in contact with the guest silver bromide grains were more positive than that formed on silver iodide ones and similar to that formed on silver bromide grains as shown in Fig.2.

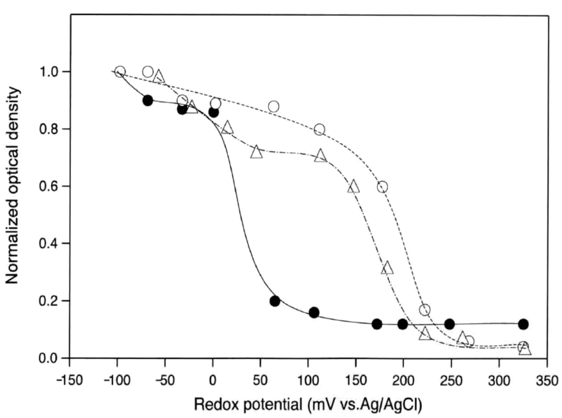

Figure 2. Normalized optical density in proportion to the fraction of grains with residual latent image centers in a buffer solution with redox potential on the abscissa for latent image centers formed on silver bromide grains (open circle), silver iodide ones (filled circle) and tabular silver iodide ones with epitaxially formed silver bromide grains (triangle).

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

The maximum density (Dmax) of the characteristic curve of tabular silver iodide grain was raised by adding nucleating agents to photothermographic materials. Along with this phenomenon, many minute silver clusters were observed near developed tabular silver iodide grains in the electron micrographs of the cross-sections of the coated layers. It is considered that the covering power of a silver image was enhanced by the formation of these minute silver clusters. Blue regular medical X-ray conventional film RX-U® made by Fuji Photo Film is composed of silver iodobromide grains, which are as large as 0.93μm in average equivalent sphere diameter, and twenty times more abundant in mole than silver halide grains in our photothermographic film. Although the total amount of silver included in our materials as silver iodide and silver carboxylate is one half of the total amount of silver in RX-U®, our materials gave the same Dmax as RX-U®.

It was found that, not only nano-particles of silver iodide[1], but also tabular silver iodide grains were dissolved during thermal development. On the other hand, guest silver bromide grains formed on the tabular grains were not dissolved and remained in developed layers of photothermographic materials. The remained silver bromide grains, however, didn't bring about the appearance of the haze and the increase in the fog density of the developed layers under room light illumination.

3. Blue Regular Medical X-ray Dry Film-Screen System

Radiographic intensifying screen with $CaWO_4$ has been used for blue regular medical X-ray conventional film-screen system. We discovered that radiographic intensifying screen made from BaFBr:Eu has very high fluorescence intensity in the wavelength region of the absorption band of silver iodide grains (i.e., blue-violet region), as shown in Fig.3.

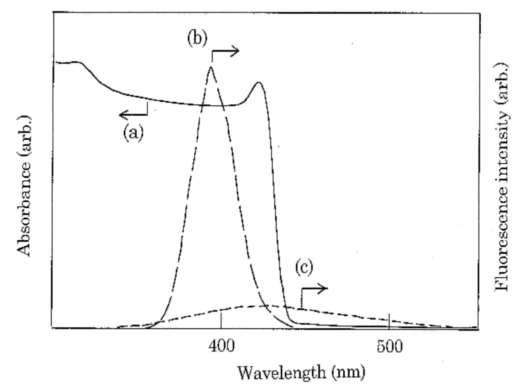

Figure 3. Absorption spectrum of silver iodide (a) and fluorescence spectra of BaFBr:Eu radiographic intensifying screen (b) and $CaWO_4$ one (c).

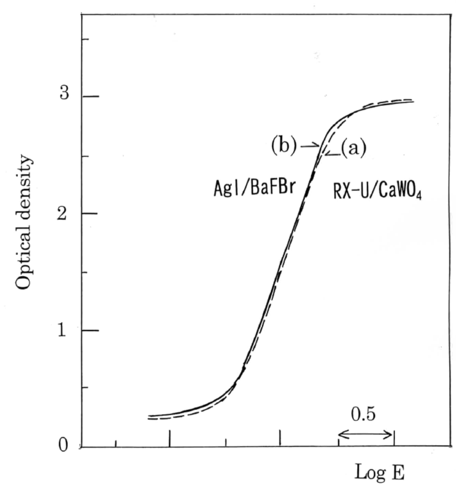

Figure 4. Characteristic curves of the conventional system with medical X-ray blue sensitive film RX-U® and $CaWO_4$ radiographic intensifying screen (a) and the new system with the photothermographic film and BaFBr:Eu radiographic intensifying screen described in this paper (b).

We combined the above-stated photothermographic materials with optimally sensitized tabular silver iodide grains and the radiographic intensifying screen with BaFBr:Eu for medical X-ray film-screen system. It was found that this new system with the above-stated photothermographic film and BaFBr:Eu radiographic intensifying screen had 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.4. The developed films of the new system are free from haze and increase in the fog density under room light illumination.

References

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Author Biography

Takeshi Funakubo received his M.S.degree in Chemistry from Tokyo University in 1992. Since 1992 he has been a member of Ashigara Research Laboratories and Materials Research Division, Fuji Photo Film Co.,Ltd.