Photothermographic Materials with Nano-particles of Silver Iodide

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Abstract

It has been found that nano-particles of silver iodide is highly sensitive to blue light in photothermographic materials, and can be fixed during thermal development. Accordingly, the fog density of developed layers of photothermographic materials with silver iodide nano-particles never increases under room light illumination.

Introduction

Photothermographic materials with silver carboxylates as sources for silver ions have made remarkable progresses in recent years. Nano-particles of silver iodobromide and silver bromide have been used for their photo-sensors. However, un-exposed nano-particles remain in the materials after thermal development, and are responsible for fog formation owing to the printout of the remaining nano-particles under room light illumination. Yamane, one of the present authors, has made a trial to use nano-particles of silver iodide for photothermographic materials as photo-sensors, taking into account the fact that silver halide grains in the photothermographic materials are treated at such a high temperature as to cause the phase transition from β and γ phases to α-phase of silver iodide, which exhibits much higher sensitivity than the β and γ phases in conventional photographic materials[1], in addition to the facts that the absorption coefficient of silver iodide is much larger in blue region than that of silver bromide, and that silver iodide grains exhibit high performance at low pAg circumstance[2,3]. After some trials, we have discovered unexpectedly that nano-particles of silver iodide are fixed during thermal development, and are not therefore responsible for the increase in fog density of developed layers under room light illumination. In this study, we also report that silver iodide nano-particles are smaller in size and higher in blue sensitivity than silver iodobromide ones in photothermographic materials for use of medical X-ray image display film.

Experimental

Nano-particles of silver iodide with average equivalent circular diameters of 40nm and 29nm were prepared by a controlled double jet method in an aqueous gelatin solution with controlled pAg value. Nano-particles of cubic silver iodobromide with average edge length of 42nm and iodide content of 3.5mol% were also prepared for reference. Microcrystals of silver behenate were dispersed in an aqueous polyvinyl alcohol solution. Silver behenate acting as a source for silver ions, bis-phenol as a reducing agent, poly-halide as an anti-foggant, alkyl-substituted phtalazine and phthalic acid as silver ion carriers and toners, and water dispersion of SBR latex as a binder were mixed to form an aqueous liquid dispersion. Then, nano-particles of silver halide were introduced into these liquid dispersions, and the dispersions were coated on PET film bases to give water-based photothermographic materials[4]. We obtained the characteristic curves by exposing the materials to a xenon flash lamp through a blue band pass filter or to blue diode laser light and developing them at 121℃ for 24sec. The conventional materials composed of the above-stated nano-particles of silver halide and gelatin were also prepared, and processed with a liquid developer composed of pyrogallol[2] as a developer agent at 38℃ for 60min after they were exposed to light.

Results and discussions

1. Photographic Response of Nano-particles of Silver Iodide in Photothemographic Materials

Nano-particles of silver iodide in conventional emulsions were not sensitive to light at such pAg values (e.g., 8 and so on) as usual in conventional emulsions composed of silver bromide grains, and became to be sensitive to light at low pAg values. Their sensitivity steeply increased with decreasing pAg values, as already reported in the literatures[5,6]. On the other hand, all the nano-particles of silver iodide in emulsions with variation of pAg (i.e., 8, 6 and 3) became to exhibit similar sensitivities when they were introduced into photothermographic materials, and had similar sensitivity to that of the grains in the conventional material with pAg of 4. Although nano-partilces of silver iodide in the conventional emulsions with pAg of 6 severely suffer from low-intensity reciprocal law failure (LIRF), the decrease in pAg (i.e., the increase in silver ion concentration) in the emulsions greatly diminished their LIRF. Silver iodide nano-particles in photothermographic materials also suffered from LIRF, which was similar to that in conventional emulsions with pAg of 4. It is considered that the silver ion concentration in our photothermographic materials corresponds to that in conventional emulsions with pAg of about 4.

The signal intensity of positive holes in nano-particles of silver iodide in a conventional emulsion as measured by means of a radiowave photoconduvtivity method[3] decreased with increasing the silver ion concentration in the emulsion. On the other hand, the signal intensity of photoelectrons of the nano-particles in a conventional emulsion as measured by means of a 35GHz microwave photoconductivity was nearly independent of the silver ion concentration.

Reducing agents with substituents adsorptive to nano-particles of silver iodide increased the photographic sensitivity and at the same time decreased the signal intensity of positive holes in photothermographic materials. Silver iodide nano-particles were smaller in size and higher in intrinsic sensitivity than silver iodobromide ones owing to the fact that the absorption coefficient of the former in intrinsic wavelength (i.e., blue) region is ten times larger than that of the latter.

As described in the previous paper[3], there are some difficulties for silver iodide to achieve high sensitivity. Namely, silver iodide grains are characterized by rapid capture of photoelectrons by many interstitial silver ions in the grains, and the recombination of the captured electrons with highly active positive holes in the grains. The rates of formation and development of latent image centers on silver iodide grains should be the smallest among silver halide grains, since its solubility is the lowest, and its silver potential is the most negative among silver halides in water. However, the increase in silver ion concentration around the grains effectively depresses the activity of positive holes, and improves the developability of latent image centers on the grains. The condition with high concentration of silver ions in the presence of silver carboxylate as the source of silver ions makes silver iodide nano-particles highly sensitive in photothermographic materials.

2. Fixation of Silver Iodide Nano-particles during Thermal Development in Photothermographic Materials

Un-exposed nano-particles of silver iodobromide and silver bromide remain in photothermographic materials after thermal development. The fog density of developed layers thus increases owing to the printout of the grains under room light illumination. We have discovered that nano-particles of silver iodide in photothermographic materials can be fixed during thermal development. This discovery was proved by the observation that the exciton absorption band characteristic of silver iodide at ca. 420nm disappeared after thermal development as shown in Fig.1. The disappearance of silver iodide particles during thermal development was also confirmed by the electron-microscopic observation of the cross sections of developed layers. Accordingly, the fog density of developed materials does not increase under room light illumination, as shown in Fig.2.

It has been found that silver behenate and phtalazine play key roles in thermal fixation of silver iodide nano-particles. Amorphous silver behenate formed at elevated temperature dissolves silver iodide nano-particles. Phtalazine decreased the temperature for the phase-transition of silver behenate from waxy and sub-waxy state to amorphous one. Phtalazine itself makes complexes with silver iodide nano-particles at elevated temperature. It is considered that silver iodide nano-articles are dissolved rapidly owing to the above-stated collaboration functions of silver behenate and phtalazine at elevated temperature during thermal development. Although we have not yet found definitely the necessary conditions required for the compounds with ability dissolve silver iodide during thermal development, it is inferred that highly hydrophobic organic compounds contain those compounds, since silver iodide is hydrophobic.

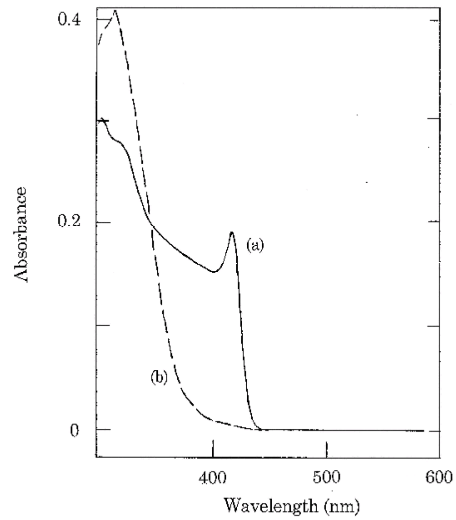

Figure 1. *Absorption spectra of layers of photothermographic materials with silver iodide grains before (a) and after (b) thermal development*

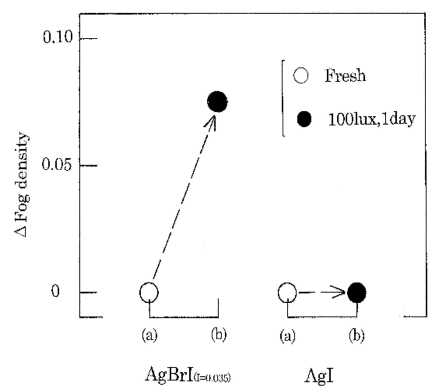

Figure 2. *Change in the fog density of developed layers of photothermographic materials with silver iodobromide grains (left) and silver iodide ones (right) under room light illumination with 100lux for 1 day*

3. High Sensitivity of Silver Iodide Nano-particles in Photothermographic Materials for Blue Diode Laser Light

Nano-particles of silver iodide were higher in blue sensitivity and smaller in size than those of silver iodobromide in photothermographic materials. Silver iodide is more suitable than silver iodobromide in preparing small particles to increase the concentration of particles and therefore the concentration of development centers without increasing the amount of silver halides in photothermographic materials. Since photothermographic materials are used for medical X-ray image display films with red or infrared diode lasers as light sources, nano-particles of silver iodobromide are spectral sensitized with organic sensitizing dyes. The use of dyes brings about such problems as the instability of sensitizing dyes on silver iodobromide grains under heavy storage conditions, and the stain due to the dyes remaining after thermal development especially when large amount of dyes is used to achieve high sensitivity.

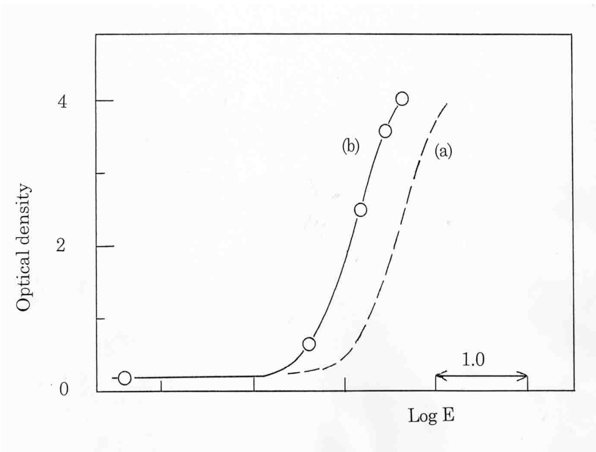

Figure 3. *System characteristic curves of the target (a) and silver iodide particles of 29nm diameter (b) for a blue diode laser, which was set instead of a red laser light in medical dry laser imager DRYPIX 7000® made by Fuji Photo Film*

In recent years, blue diode laser technologies have made big progresses. By use of nano-particles of silver iodide together with a blue diode laser, which emits at ～400 nm and is commercially available, we could realize the photothermographic materials, which had high system sensitivity as shown in Fig. 3, when the above diode was set up instead of a red laser in medical dry laser imager DRYPIX 7000® made by Fuji Photo Film. Since the fog density of developed materials never increased under room light illumination, an obtained image was very stable under illumination.

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Author Biography

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