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The Influence of the Photosensitive Silver Halide/Silver Carboxylate Preparation Conditions on the Morphology of Thermally Developed Silver Particles

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An electron microscope study of the morphology of the silver particles forming in the image area from the photothermographic process shows that the shape and size of the silver crystals change depending on the method of preparation of the silver halide/silver fatty acid complex system. In the case of the in situ process, silver halide obtained by treating silver stearate with solutions of brominating agents (LiBr, $ZnBr_2$, or $HgBr_2$) during the photothermographic process yields silver filaments. In the case where the silver halide is preformed and then added during the preparation of the silver carboxylate, dendritic silver particles result during the photothermographic process.

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Introduction

Photothermographic materials are currently used in a wide range of practical applications. The main components of the thermally developed layer are silver halide and the silver complex of a fatty acid.[1,2] The construction incorporating these materials in order to produce a visible image is referred to as dry silver (DS), because no additional treatment of the material with developing and fixing solutions is required, and the image is obtained after thermal development (110 to 140°C) of the exposed film.

In the preliminary exposure step, the formation of catalytically active latent image centers takes place in the silver halide.[1,2] Then, silver deposits at these locations during thermal development, which leads to the formation of a visible image. In this case, the silver complex of a fatty acid (silver stearate or behenate), which is not photosensitive in the visible region of the spectrum, is the source of the silver particles formed. Thus, the DS material can be considered a photographic system with a physical thermal development process. Naturally, other chemical materials (for example, developer, toner, and sensitizer) are present in the layer of DS materials and essential to the optimum photographic characteristics.

In contrast to classical silver halide photography, essentially no data on the morphologic characteristics of the silver particles formed during thermal development of photothermographic materials are presently available in the literature. Therefore, investigations in this field are likely to be important for several reasons. For example, knowledge of the shape, size, and location of the sites of forming silver particles gives insight into the possible mechanism of photothermal development of DS materials. From the patent literature[3–5] it is known that the photographic characteristics of DS materials, such as optical density, depend on the way in which the silver halide/silver carboxylate is prepared. Our previous work has shown that electron microscopy can be used to develop this insight into fundamental photothermographic processes.[6]

In this work, we report that different methods of silver halide preparation give photothermographic materials that form silver having different silver particle morphologies. This change in silver morphology is fundamentally linked to the photographic characteristics of the resulting film.

Experimental

Silver Bromide Preparation. The synthesis of silver bromide was carried out in two different ways. In the first method, AgBr was obtained by the exchange reaction between silver stearate and a solution of the brominating agent (in situ AgBr):

$$n \cdot \mathrm{AgSt} + \mathrm{MBr}_n \rightarrow n \cdot \mathrm{AgBr} + \mathrm{MSt}_n$$

Solutions of LiBr, $ZnBr_2$, or $HgBr_2$ were used as brominating agents.[6] The second method yielded cubic AgBr crystals (500 Å), which were prepared by standard procedures.[7] A solution of potassium bromide and a separate solution of silver nitrate (1.8 mol/L) were added simultaneously to a solution of phthalated gelatin (Rousselot) dissolved in 1500 mL water at 32°C. The pAg was maintained at 2.0 ± 0.1 by a feedback loop.

Silver Soap Preparation. The synthesis of the in situ process is illustrated by silver stearate. Stearic acid (type 9718, Witco Co., USA), 100 g, was melted in 1.5 L of deionized water. Then a solution of 13.5 g of NaOH in 300 mL of water was added dropwise to the reaction mixture with vigorous stirring, followed by 3 mL of concentrated HNO_3 in 7 mL of water. The reaction mixture was allowed to cool to 55°C, and then a $AgNO_3$ solution (57.6 g in 300 mL of water) was added slowly. An example of silver bromide formation by the in situ process is given using zinc bromide. After

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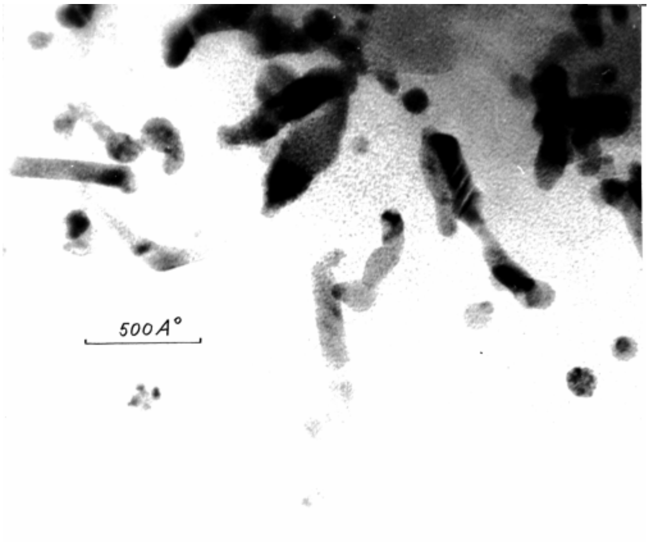


Figure 1. TEM micrograph of silver particles formed during the thermal development of exposed DS material. Silver halide was obtained by in situ treatment of AgSt with LiBr.

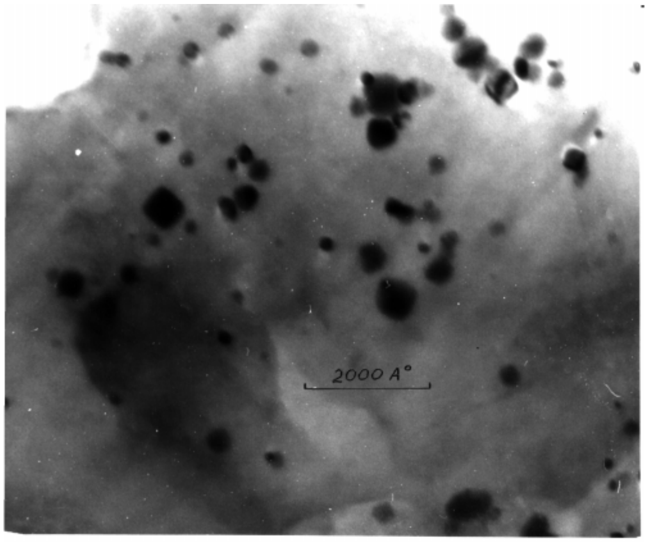


Figure 2. TEM micrograph of AgBr crystals present in DS material prior to the photothermal development process. Silver halide (100 to 500 Å) was obtained by in situ treatment of silver stearate with $ZnBr_2$.

20 min, a solution of $ZnBr_2$ (3.8 g in 100 mL of water) was added. This amount of $ZnBr_2$ theoretically converts 5 mol% of the AgSt to AgBr. The mixture was filtered, then the solid was stirred in 3 L of water, filtered and washed twice more in this manner. Finally the solid suspension was filtered and dried at 45°C for 3 days.

The preformed system was prepared by adding the preformed silver bromide to the sodium carboxylate reaction mixture (as described above) after the solution of NaOH had been added and the system reached 55°C. Only after this point was the $AgNO_3$ solution added. All procedures and solution concentrations were as described above, including the AgBr:AgSt ratio.

Photothermographic Film Preparation. The compositions obtained were used to prepare photothermographic materials, which contained, along with the silver halides and silver stearate, a hindered bis-phenolic developer, phthalazine, 4-methyl-phthalic acid, and a Butvar binder normally used in these types of constructions.[1] Typically, the silver carboxylate (345 g in 1300 mL 2-butanone containing 36 g of the binder) was homogenized (4000 psi), and portions were used for coating. To 240 g of this homogenate was added sensitizing dye, then, after 1 hour, 40 g additional binder, 10 g 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, and 0.95 g phthalazine, which was coated, to obtain 18 g/m^2 (dry). A protective topcoat (2 g/m^2) was prepared from 80 g 2-butanone, 7.7 g cellulose acetate butyrate, 0.26 g 4-methylphthalic acid, and 0.07 g tetrachlorophthalic acid anhydride.[7] In this way, the following DS materials were prepared:

1. in situ AgBr/AgSt composition.
2. preformed AgBr/AgSt composition without any other bromide source.
3. both preformed and in situ AgBr (prepared by treating the preformed AgBr/AgSt system with $ZnBr_2$).
4. a formulation with no silver halide.

The prepared DS films were exposed through a 0–4 wedge to light in the visible region (unfiltered EG&G xenon flash for 10^{-3} s) under the same conditions, with the exception of the DS material containing no silver halide, which was exposed to an ultraviolet source (500-W mercury vapor lamp at 20 cm for 10 s). Then the exposed films were developed at 124°C for 15 s. To carry out electron microscope (JEM-2000FX II) studies in the region of maximum optical density, thin cuts (1000 to 5000 Å) of each photosensitive layer were prepared, placed on a copper grid of the EM sample holder, and cooled with liquid nitrogen.

Results

The electron microscope studies revealed the following features of the morphology of silver particles formed during the thermal development of DS materials:

Morphology of Silver Particles Formed During Thermal Development of In Situ DS.

DS Material with In Situ Silver Bromide from LiBr Treatment of Silver Stearate. We found that after the thermal development of exposed in situ DS material, silver particles are formed of filaments up to 1000 Å long and 100 to 150 Å thick (Fig. 1). Apart from the silver filament crystals, this DS material also contains fine, round silver particles of 40- to 200-Å diameter randomly distributed in the photographic layer. Because the film contains silver halide crystals that are comparable in size to these particles, we could not determine if these particles were silver formed during the thermal development or if they were silver halide crystals. Some silver filament crystals exhibited striped contrast regions, a typical indication of twinning.

DS Material with In Situ Silver Halide from $ZnBr_2$ Treatment of Silver Stearate. Figure 2 shows an electron micrograph of the silver halide crystals present in the unexposed in situ DS material prior to development. The size of the AgBr crystals formed by treatment of silver stearate with $ZnBr_2$ ranges widely—from 100 to 500 Å. The morphology of the silver particles formed during the thermal development of exposed DS material shows that, as in the preceding case, silver filaments are formed (Fig. 3). The silver filament particles are 1000 to 1500 Å long and up to 200 Å thick. The round particles observed could be either silver or silver bromide.

Further analysis of the electron micrographs suggests that the silver filament crystals grow from the octahedral (111) faces of the silver halide crystals. In addition, we believe that the silver filaments form only as a result of the transfer and reduction of the silver ions of silver

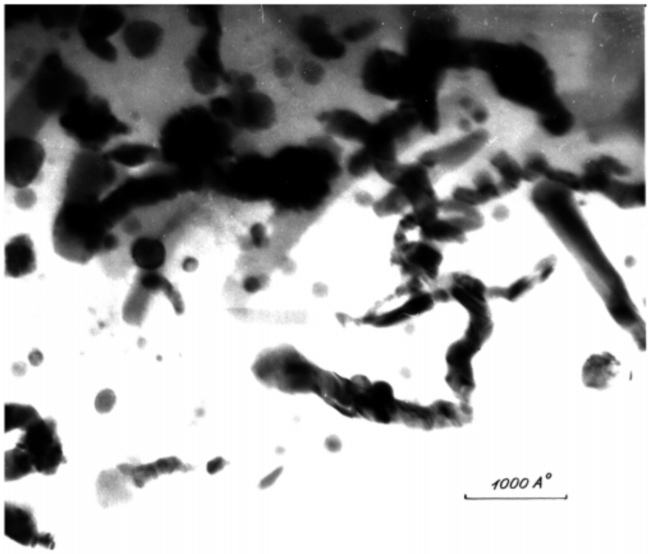


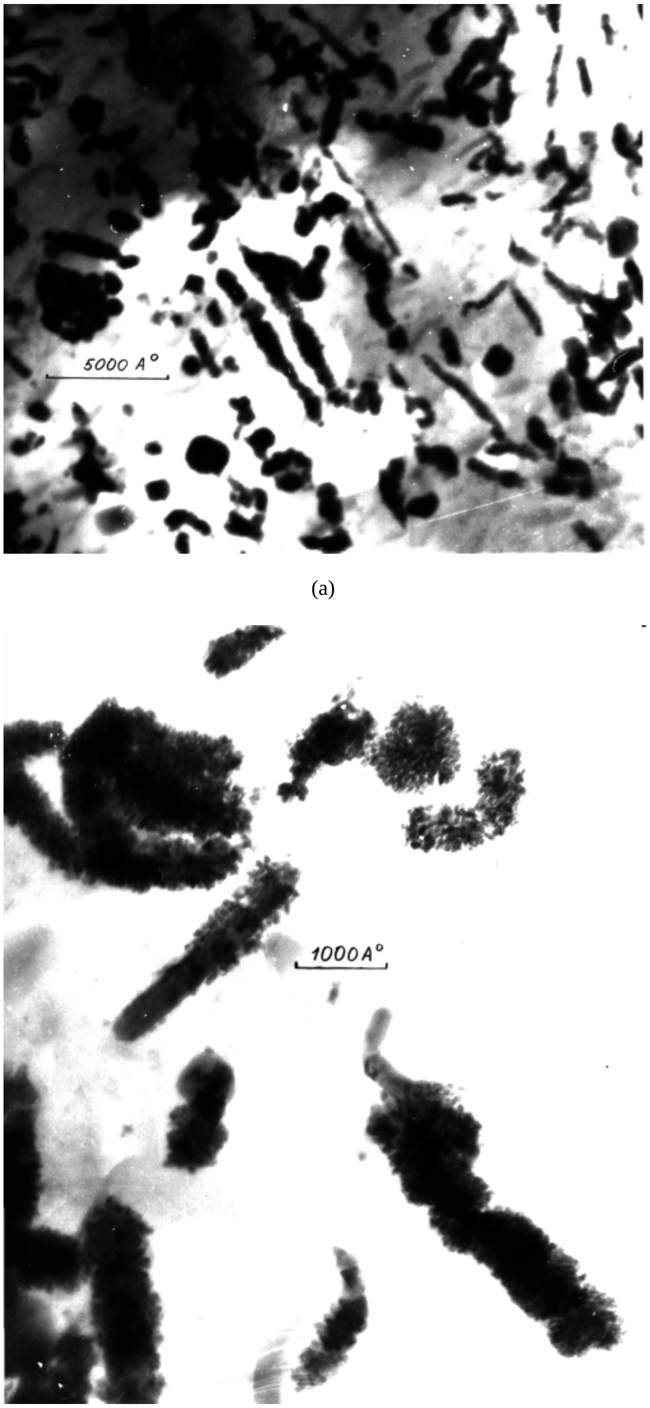
Figure 3. TEM micrograph of silver particles formed during the thermal development of exposed DS material. Silver halide was obtained by in situ treatment of AgSt with $ZnBr_2$.

stearate. This conclusion is the result of comparison of the silver filament crystals with the silver halide crystals prior to and after development. No changes in the size and shape of the silver halide crystals were observed.

DS Material with In Situ Silver Halide from $HgBr_2$ Treatment of Silver Stearate. The in situ system from $HgBr_2$ treatment of silver stearate was found to have both similarities and differences with the above in situ DS materials. The silver particles formed during the thermal development of exposed DS material are also filaments [Fig. 4(a)] 2000 to 5000 Å long and from 200 to 500 Å thick. In some cases, however [Fig. 4(b)], the filament surface is coated with 80- to 100-Å silver particles. In addition, the developed DS material contains aggregates of silver particles in the form typical of dendritic crystals. The dendritic crystals reach 2000 Å in diameter and are composed of very fine silver particles 30 to 50 Å across.

Morphology of Silver Particles Formed During the Thermal Development of DS Material Containing "Preformed" Silver Bromide. The morphology of silver particles formed during the photothermal processing of preformed DS material is predominantly dendritic, with crystals having a diameter of about 2000 Å [Fig. 5(a)]. The size of the silver crystallites ranges from 30 to 50 Å. Also, a comparatively small number of silver filament crystals formed. The silver developed in preformed DS material resembles the silver formed in the thermal development of the in situ DS material (prepared using mercury bromide), with the only difference that in preformed DS material dendritic silver crystals predominate, whereas in in situ DS material filamental crystals do.

The DS material containing both preformed and in situ AgBr, shows an increase in the concentration of filamental crystals in comparison with purely preformed DS material [Fig. 5(b)].

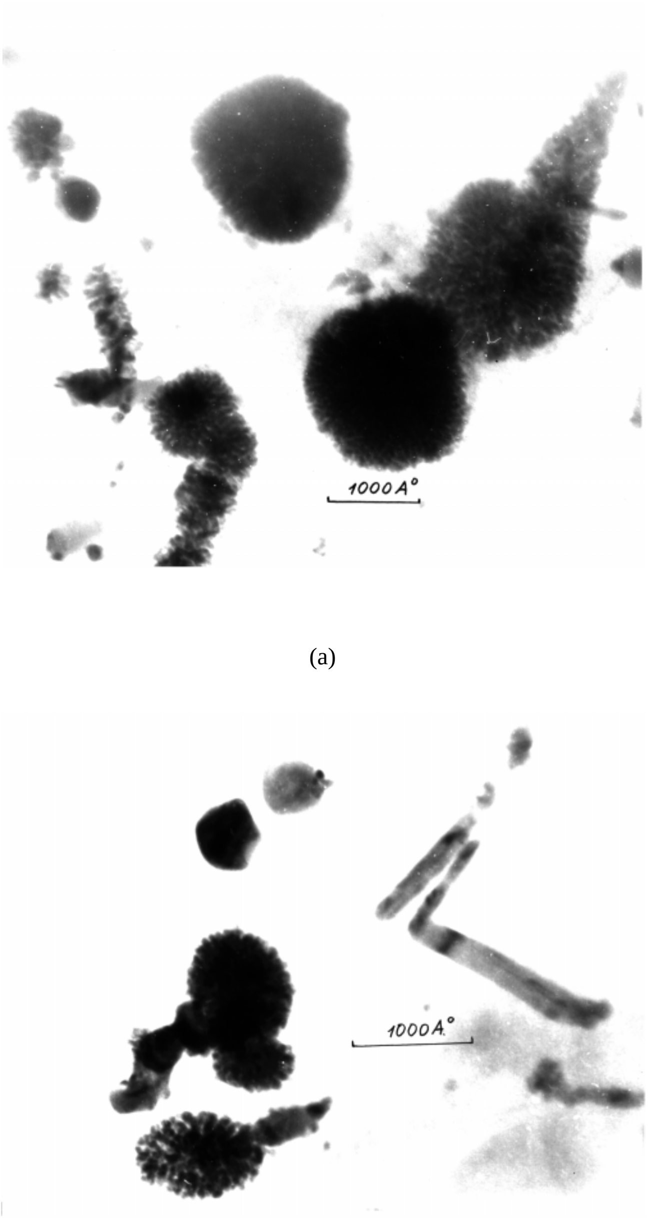


(a)

(b)

Figure 4. TEM micrograph of (a) silver filaments and (b) silver filaments coated with 80 – 100 Å silver particles, from thermal development of exposed DS material. The silver halide was obtained by in situ treatment of AgSt with $HgBr_2$.

Morphology of Silver Particles Formed in the Thermal Development of DS Materials Containing No Silver Halide. To gain better insight into the processes occurring during thermal development of DS materials, we prepared a material containing all of the main components of the photothermographic layer except silver halide. The most significant distinction of this film is that the absence of silver halide makes it impossible to obtain latent image centers by visible light exposure. Therefore, the formation of silver particles was studied both during the thermal development of this material and during the development at latent image centers that were obtained on exposure of the material to ultraviolet light. We found that the morphology of the silver particles formed during the thermal development of the unexposed material is virtually identical to the morphology of the silver particles formed during the thermal development of the film exposed previously to UV light (at the same optical density). Both the concentration of sil-



(a)

(b)

Figure 5. TEM micrograph of silver particles formed during the thermal development of DS material with (a) preformed AgBr and (b) preformed plus in situ AgBr.

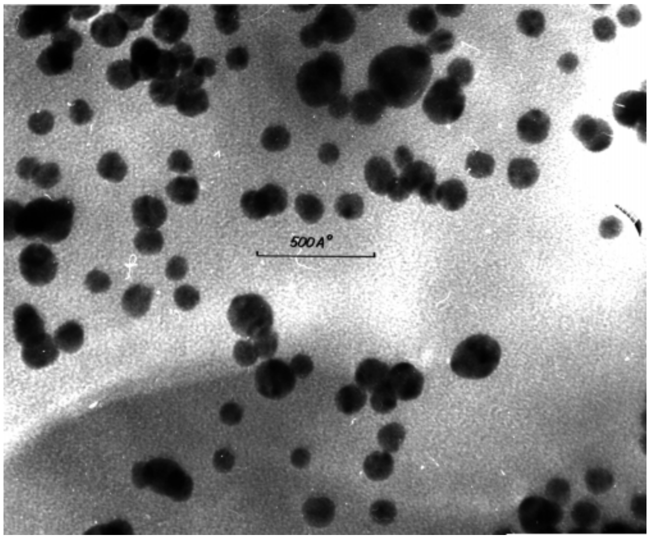


Figure 6. TEM micrograph of silver particles formed during the thermal development of unexposed DS material containing no silver halide.

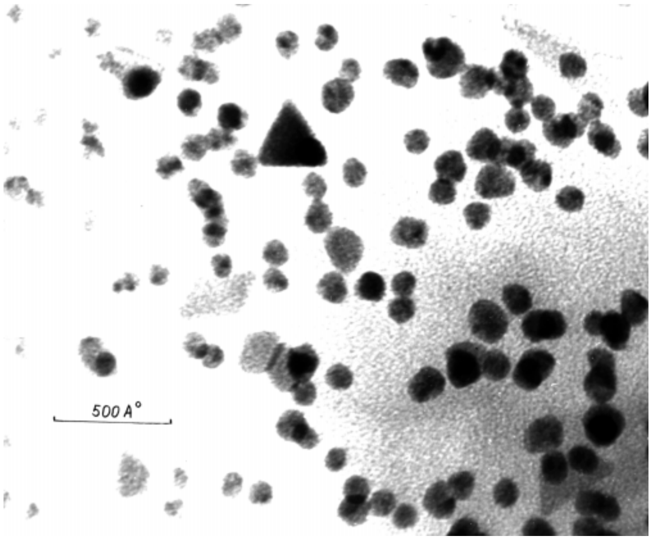


Figure 7. TEM micrograph of silver particles formed during the thermal development of UV-exposed DS material containing no silver halide.

ver particles formed and their sizes vary with the development time (optical density).

In the early steps of thermal development of the film, the silver particle sizes range from 10 to 20 Å, and after 5 min of development at 120°C silver particles are spherical and are on the order of 100 Å (Fig. 6). This change in the particle size is accompanied by a color change from light yellow to dark brown. The study of the formation of silver particles during the thermal development of the exposed DS material shows that the thermal development in the exposed regions of the film proceeds at a higher rate than in the unexposed regions. The morphologic characteristics of the process are similar to those of the thermal development of unexposed DS films. Silver particles in the exposed material (2 min of development at 120°C) are spherical and reach 100 to 160 Å. The only distinguishing feature of the photothermographic process is that the material contains silver particles having a regular habit and on the order of 200 Å (Fig. 7), which are somewhat larger than the spherical silver particles.

Discussion

These electron microscope studies show that the morphology of the silver particles formed during the thermal development of exposed DS materials essentially depends on the way in which the silver halide component of this system is prepared, that is, by the in situ or preformed method.

The developed silver is filamental when the DS material contains silver halide prepared by the in situ exchange reaction between silver carboxylate and a solution of brominating agent. If the DS material is prepared from previously synthesized silver halide crystals, the developed silver crystallizes mainly as 30- to 50-Å dendritic crystals.

Before proceeding to a discussion of the factors responsible for the morphology of silver particles, it is necessary to consider the data available on the morphology of silver particles after development in conventional silver halide photography.

The formation of silver filaments frequently occurs during physical development of silver halide crystals in conventional photographic film[8] and is one criterion that is indicative of the physical development process. Several mechanisms are proposed for the formation of the silver filament particles,[9] such as the orienting influence (epitaxy) of the silver halide surface. For example, in conventional physical development processes,[10,11] the filaments are displaced by silver atoms accumulating at the Ag/AgBr interface in the solid, which is responsible for the growth of silver filaments from this interface. Silver filament development by this latter route has been observed experimentally.[12]

Another mechanism for the growth of silver filaments assumes the progression of several steps. In the first step, an electron is transferred from the developer at the Ag/AgBr interface and imparts a negative charge to it. Then, in the immediate vicinity of the Ag/AgBr interface, dissolution of the AgBr crystal occurs. The Ag^+ ions in solution closest to the silver particle are neutralized on it to form silver atoms, which become part of the silver metal particle surface. This process occurs repeatedly at the Ag-metal/AgBr solution interface. In this process the formation of a gap between the growing silver filament crystal and the silver halide crystal is inferred. However, regardless of the sequence of steps in the growth of filament crystals, all the mechanisms[9] of physical development include the step of dissolution of the silver halide being developed. Under certain conditions the development process in conventional silver halide photography may also involve not only dissolution of the exposed crystals during development,[13] but also dissolution of unexposed silver halide crystals and transfer of silver ions to the developed regions of the image, insofar as the unexposed silver halide crystals may be dissolved in the developer to form complex compounds. These complex compounds can diffuse to latent image centers where they are reduced to the metal by a developer under the catalytic action of the AgBr/Ag interface.

Despite the apparent similarity in the morphology of developed silver particles in traditional silver halide photography and in situ DS material, the latter shows a number of distinguishing features. The most important of these distinguishing features are as follows:

1. No dissolution of silver halide on which the silver filament crystals grows is observed during development.
2. No dissolution of unexposed silver halide crystals is observed.

The data obtained suggest the following sequence in the formation of silver filament crystals in the thermal development of the in situ DS material. As in the case of traditional silver halide photography, a developer and the Ag(latent image center)/AgBr/AgSt interact upon thermal development by the reversible reaction:

$$\text{Red} \leftrightarrow \text{Ox} + e^-$$

Electrons transferred from the developer are captured at the silver latent image center on the silver halide crystal, giving rise to a negative surface charge. The presence of this negative charge promotes the reduction of silver ions at the latent image center. Since no change in the size and habit of silver halide crystals occurs during thermal development, the silver carboxylate contact with the halide appears to be the source of reduced silver ions. In this case, it is likely that the transfer of silver ions occurs due to dissolution of the silver carboxylates by the toning agents added to the photothermographic formulation during heating.

As shown above, the morphology of silver particles is significantly different in the development of preformed DS material and the DS material containing no silver halide. Although the source of this difference is not yet fully understood, we propose that several interrelated causes are responsible for the formation of dendritic crystals in the development of preformed DS materials. The most important of these causes underlying the different morphologies may be that different structures at the interfaces between the silver halide and silver carboxylate control the morphology of silver particles during the thermal development of preformed and in situ DS materials. Therefore, a change in the structure of the interface between the silver halide and the silver carboxylate may bring about changes in the size and quantity of latent image centers formed in the preliminary exposure step of the DS material.

The significant role of the AgSt/AgBr interface is further supported by the ultraviolet experiment in which development proceeds at latent image silver centers formed on the silver stearate. In this case, the morphology of silver particles (discrete silver particles up to 200 Å) formed during the development of this silver carboxylate construction containing no Ag/AgBr interface is very different from the morphology of silver particles in both preformed and in situ materials. It is known that the morphology of the developed silver in conventional silver halide photography is affected by the Ag/AgBr interface structure. For example, the morphology changes from filamental in direct development (controlled by the Ag/AgBr interface structure) to large crystalline in development after fixing (which is not dependent on an interface structure). Consequently, differences in the morphology of the silver formed at different AgSt/AgBr interfaces are reasonable on the basis of conventional silver halide photographic materials.

Another factor that may significantly influence the crystallization of silver particles during development may be differences in the concentration of silver ions reduced at the AgSt-Ag/AgBr interface in preformed and in situ DS materials. The shape of crystals formed during crystallization from solutions or melts depends strongly on the concentration of crystallizing components. In this case, depending on the conditions of crystallization, well cut crystals or dendritic crystals can be obtained.[14]

All of these facts point to the significant role of the AgSt/AgBr interfaces in the thermal development of photothermographic materials.

Conclusions

Electron microscope studies show that the differences observed in the photographic characteristics of preformed and in situ silver halide in photothermographic materials are associated with the different morphology of metallic silver particles formed in the development process. In the in situ process of AgBr preparation, thermal development yields primarily silver filaments. In the preformed process thermal development produces mainly dendritic silver particles. The most likely explanation for observed differences is that the interfaces formed between the silver halide and the silver fatty acid complex have different structures.

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References

1. (a) D. A. Morgan, *J. Imaging Technol.* **13**: 4 (1987); (b) D. H. Klosterboer, in *Neblette's Eighth Edition*: *Imaging Processes and Materials*, J. M. Sturge, A. Shepp, and V. Walworth, Eds., 1989.
2. J. W. Shepard, *J. Appl. Photogr. Eng.* **8**(5): 210 (1982).
3. W. J. Miller and R. W. Baxendate, US Patent 4,820,617 (1989).
4. M. J. Simons, US Patent 3,839,049 (1973).
5. D. Morgan and B. Shely, US Patent 3,457,075 (1969).
6. B. Bokhonov, L. Burleva, W. C. Frank, J. R. Miller, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. M. Winslow and C. Zou, *J. Imaging Sci. Technol.,* **40**:85 (1996).
7. C. Zou, J. B. Phillip, S. M. Shor, M. C. Skinner, and P. Zhou, US Patent 5,434,043 (1995).
8. H. I. Metz, *J. Photogr. Sci.* **20**: 119 (1948).
9. T. H. James, Ed., *The Theory of the Photographic Process,* Macmillan Publishing Co., New York, 1977.
10. R. W. Gurney and N. F. Mott, *Proc. Roy. Soc. London* **164A:** 151 (1938).
11. N. F. Mott. *Photogr. J.* **88B**: 119 (1948).
12. A. Küster, *Z. Wiss. Phot.* **43**: 191 (1948).
13. G. C. Farnell, *J. Photogr. Sci.,* **21**: 148 (1973).
14. B. K. Vainshtein, Ed., *Modern Crystallography,* Nauka, Moscow, **3**, 1980.