JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 47, Number 2, March/April 2003

Image Formation Mechanisms in Photothermographic Silver Imaging Media

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Different theories have been proposed on the mechanisms that control the latent image formation and the image formation upon thermal development of photothermographic materials based on silver halide and silver carboxylates. The purpose of this study is to get closer to reaching a general consensus on the actual mechanisms involved. Evidence is provided which calls the concept of an epitaxial interface between silver halide and silver carboxylate into question, as well as its photochemical reactivity. Instead an alternative mechanism for latent image formation is proposed. Tribromomethyl-substituted compounds are present in all commercial materials as antifoggants or printout stabilizers. In this study, an important role in the mechanism of thermal development is attributed to these tribromomethyl-substituted compounds. An arrested development study was conducted using TEM. The results of all these investigations led to a novel theory for the mechanisms of underlying image formation in photothermographic materials.

Journal of Imaging Science and Technology 47: 100–106 (2003)

Introduction

Thermally developable, photosensitive imaging systems based on silver halide and silver carboxylates, otherwise known as photothermographic materials, require that the photosensitive silver halide (AgX) is in “catalytic proximity” with the silver organic salt (AgOS) to ensure good performance. It is generally accepted that the latent image on silver halide acts as a catalyst for the reduction of silver ions which primarily come from the silver carboxylate in the proximity of this latent image and not from the silver halide itself.[1,2] This catalytic proximity is also described in many patents[3] in the period 1994-2000 as an “intimate physical association” between silver halide and silver carboxylate. A particular picture (Fig. 9 in Ref. 4) taken during an electron microscopy study led to the belief that an epitaxial interface exists between AgX and AgOS. Furthermore it was suggested that this interface plays an important role in the latent image formation, i.e., as a photochemically reactive interface.[5,6] It was stated that at the interface between silver bromide and silver carboxylate, initially formed metallic silver atoms grow into silver clusters capable of nucleating physical development.[5,7] This offered an explanation of why chemically unsensitized silver halide in photothermographic materials, compared with a classical wet silver halide material, had been proven to be so efficient in avoiding the expected recombination of an electron and a hole upon exposure to light.[8] Sahyun stated that the interface effectively separates electron-hole pairs photogenerated in the silver halide phase.[5] One of the objectives of this investigation was to ascertain the nature of this epitaxial interface, as well as whether this interface was photochemically reactive.

After imagewise exposure, the photothermographic material is uniformly heated to develop the latent image into a visible image. As already mentioned it is generally accepted that the latent image catalyzes the reduction of silver ions/complexes. However, it is still not completely clear how this development reaction proceeds.

At present, the ideas around the mechanism of thermal development can be summarized as follows: toning agents, such as phthalazine and phthalic acid, react with the silver carboxylate to form silver complexes[2,9,14] which then migrate in a fatty acid melt to the latent image on AgX, where they are reduced to metallic silver by a reducing agent. The fatty acid is formed as a by-product of the reaction of toning agents with the silver carboxylate.[10] At the development temperatures used in photothermographic systems this fatty acid is present as a liquid phase. The size and number of the latent image/fog centers control the catalysis of the reduction reaction and hence the resulting image.

In order to obtain a good sensitometric response, it has been found, that, in the design of “modern” (meaning free of a mercury stabilizer) photothermographic materials, it is virtually impossible to omit a tribromomethyl-substituted compound. Omitting this tribromomethyl stabilizer (TBMS) generally results in strongly fogged materials. When the amount of TBMS present in the material is increased, then the development conditions (temperature/time) have to be increased to obtain an identical sensitometry. However if the development temperature and/or development time are increased too much, then the material is again strongly fogged. It is possible to state that for a certain range of development temperature and time, the concentration of TBMS in the material creates a “window for

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Original manuscript received October 31, 2002

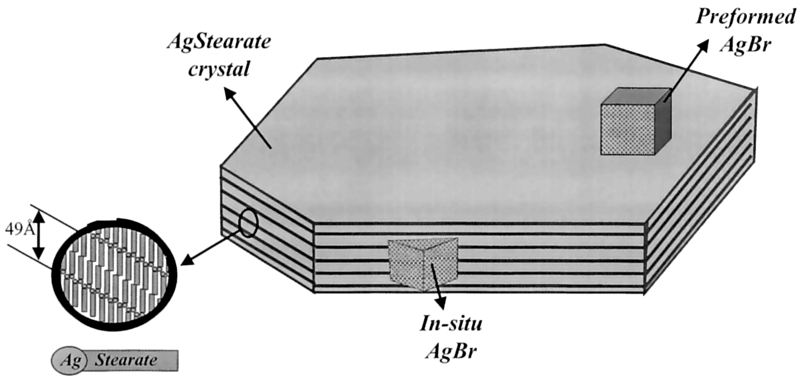


Figure 1. Drawing of *in situ* and *ex situ* silver halide in physical contact with the layered structure of a silver carboxylate.

imagewise development". These tribromomethyl-substituted compounds have been described in many patents[11] as antifoggants or post-processing stabilizers and are present in all commercial materials. Yet, no role is attributed to these compounds in the mechanism of thermal development of photothermographic materials. It was decided to investigate how the concentration of TBMS in a photothermographic material changes as a function of exposure and development conditions. These investigations led to some surprising results and ideas for a novel mechanism of thermal development. An arrested development study with TEM on an imagewise exposed photothermographic material was conducted. Examination of these images recorded by TEM, together with the previous results and concepts, makes it possible to propose a novel theory for the image-forming mechanism in a photothermographic material.

Experiments and Discussion

Epitaxial Interface

The silver carboxylates used in photothermographic materials have a needle- or plate-shaped crystal morphology. They are anisotropic since they consist of silver ionic layers separated by long hydrocarbon chains.[16] The result is a layered structure as shown in Fig. 1.

The silver halide can be introduced into a photothermographic composition in different ways. The addition of a halidizing agent to the silver carboxylate results in the formation of silver halide, which is known as *in situ* silver halide. This *in situ* silver halide occurs mostly on the lateral faces of the silver carboxylate crystal.[4]

Alternatively preformed silver halide can be added during the silver carboxylate synthesis. In this case the silver halide grains are located on the 1,0,0 plane of the silver carboxylate crystal. For photothermographic materials coated from aqueous media the easiest way of combining both silver compounds is by simply mixing a silver carboxylate dispersion with a silver halide dispersion. In both, "*ex situ*" silver halide grains are present.

As can be seen in Fig. 1 the silver halide crystals are drawn in contact with the silver carboxylate. In the literature it is proposed that for a silver halide to be catalytically active, there has to be a physical contact which may consist of an epitaxial character.[12]

By definition, an epitaxial interface requires at least one common crystal plane between the two different crystal lattices.[13] Bokhonov, Burleva, Whitcomb and Sahyun[12] suggested a model with epitaxy between *in situ* silver bromide and silver stearate. (Fig. 17 in Ref. 12) The drawing shows a cross-section where a row of silver atoms are common between the silver bromide and the silver stearate. If the drawing is expanded in the 0,0,1 direction for AgX, another common row of silver atoms is found, at a distance of approximately two times the paraffin chain.

The following experiment was then conducted: *in situ* silver bromide was prepared by adding potassium bromide at a concentration of 10 mol % with respect to silver behenate. The *in situ* silver bromide crystals in contact with silver behenate were then visualized using transmission electron microscopy. Using small spot size and a slightly convergent beam, the electron microdiffraction patterns were determined for different silver halide crystals. The specimen was oriented in order to obtain a good diffraction pattern for one of the silver halide crystals. Diffraction patterns were then obtained from the other silver halide crystals without changing the orientation of the specimen.

In the event of a strong epitaxial relationship, the *HKL* of the silver organic salt should be parallel to the *H'K'L'* of the silver halide and the *UVW* of the silver organic salt should be parallel to the *U'V'W'* of the silver halide, since the *UVW* directions are in the *HKL* planes and the *HKL* planes are interface planes. The obtained diffraction patterns should be the same for all the crystals.

This was not the case as illustrated by this example. When for example, crystal 2 is 1,1,0 oriented, the orientation of crystal 1 is close to the 1,0,0 direction. However, the crystals 3 and 4 were oriented in a different way from the other two crystals. This means that the epitaxial relationship was not strong. Alternatively, the epitaxy could be partial, it means that only the relation *HKL* of the silver organic salt was parallel to the *H'K'L'* of the silver halide (*HKL* are the interface planes). In this case only one row of reflections would be the same on all diffraction patterns and this row should be perpendicular to the interface. Again it was not what was observed. Taking into account the shape of the silver halide crystals, it seemed that we could expect at least a partial relation. This was consistent with the obtained electron microdiffraction patterns. It could be argued that the possible presence of a small (< 10 nm) transition zone between the silver carboxylate and AgX lattices could remain undetected in this experiment, but even then it is to be expected that in the case of epitaxy, this zone and the subsequent silver halide lattice should have a definite orientational relationship with the silver carboxylate lattice. This is not what has been found.

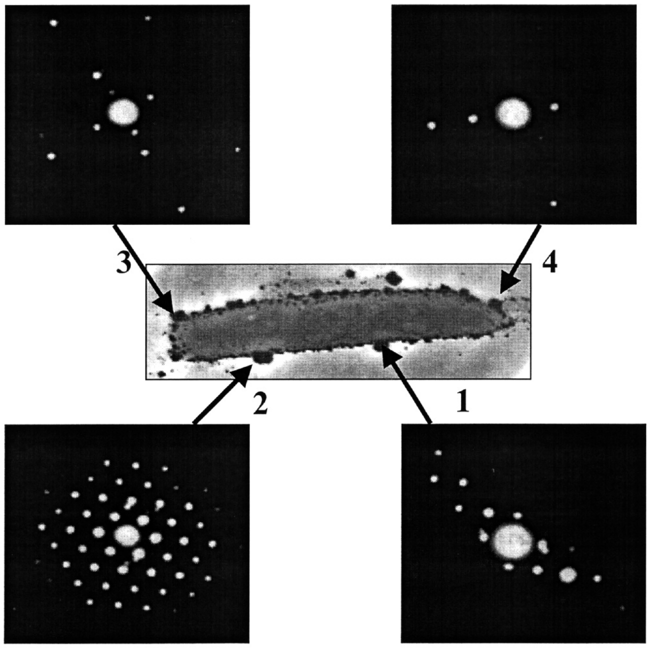
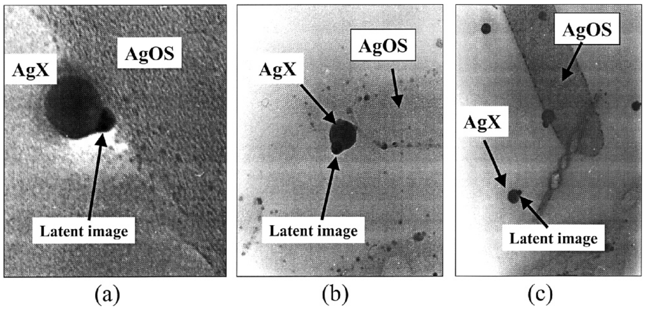


Figure 2. TEM-image of 4 *in situ* silver bromide crystals in physical contact with silver behenate and their corresponding microdiffraction patterns.



(a) (b) (c)

Figure 3. Location of latent image on silver halide (a) at the edge of the interface between silver halide and silver carboxylate (AgOS); (b) on a surface of silver halide other than that which is in contact with silver carboxylate; (c) on a silver halide with no visible contact with silver carboxylate.

Latent Image Formation

It was already been mentioned that the epitaxial interface between silver halide and silver carboxylate has to be regarded as a photochemically reactive interface, leading to the separation of a Ag° phase which is capable of nucleating physical development. These silver clusters are thus latent image specks which can catalyze the reduction and should be situated in the interfacial zone. The latent image obtained after a "normal exposure" only consists of a few silver atoms. These clusters are too small to be directly observable. Samples on a copper grid were prepared with preformed silver bromide with an average grainsize of 70 nm in combination with silver behenate. The silver bromide was precipitated in an ethanol solution of polyvinylbutyral by simultaneous addition of lithium bromide and silver nitrate. To increase the size of the latent image silver clusters these samples were then overexposed for 24 hours using daylight. As a control, a sample comprising just silver behenate was exposed to the same conditions. No formation of metallic silver was observed. With the help of scanning transmission electron microscopy, it was possible to produce a very small beam and to carry out pointwise X-ray analysis (EDX) to verify that the clusters were in fact silver crystals and not silver bromide or other silver compounds.

If a photochemically reactive interface between AgX and the silver organic salt were to exist, it would be expected that the latent image would be formed in this interfacial zone. To be able to catalyze the reduction reaction, the latent image should be formed at the edge of the heterojunction otherwise it would be inaccessible to for the reducing agent, unless the epitaxial contact is broken during thermal development. Some evidence for the latent image formed at the edge of the heterojunction can be found using TEM as shown in Fig. 3(a).

In the micrograph it can be seen that a latent image was situated on the edge of the interface between the silver halide and the silver organic salt, but a latent image at the interface edge was certainly not the general case. From examining a lot of TEM pictures it was possible to draw two conclusions. First, a latent image could be formed on an AgX crystal face other than that which made contact with the organic silver salt. This is shown in Fig. 3(b) in which the latent image was found on silver halide crystal surfaces even opposite to the interfacial zone. More surprisingly was the second conclusion: a latent image could be formed on an AgX crystal with no visible contact with the organic silver salt. This is shown in the picture in Fig. 3(c) in which no organic silver salt made contact with the silver halide; still a silver cluster could be observed on the silver halide.

These results raised the next question. If the latent image formation was not controlled by the photochemically reactive AgX silver organic salt epitaxial interface, then which mechanism was responsible?

The formation of *in situ* silver halide by halidization of silver carboxylate is possible due to a large difference in solubility products. Mixing silver bromide and silver behenate results is an equilibrium in which minimal bromide ions are present in the dispersion, i.e., a state of very low pAg. This causes the silver halide surface to be positively charged by adsorbed silver ions. These charges can be compensated by components present in the dispersion such as gelatin, carboxylate ions, spectral sensitizer, etc.

An easy way to demonstrate the surface charge of the silver halide is by making use of certain spectral sensitizing dyes such as the dye of Fig. 4.

As shown in Fig. 5 with a cubic 0.4 μm cubic silver bromoiodide the absorption spectrum is determined by the charge of the AgX surface. It was demonstrated that the λ_{max} of the spectral sensitizer (40% surface coverage) adsorbed on this cubic AgBrI grain changed from 660 nm to below 560 nm by lowering the pAg.

The same effect was obtained by mixing the AgBrI with a silver behenate-dispersion in water. An AgBrI (3 percent iodide) emulsion with an average grain size of 40 nm was prepared. Spectral sensitization was conducted with the same dye at a dye surface coverage of 60 percent. The absorption spectrum for the dye is shown in Fig. 6, as obtained from the difference between absorption spectra of the sample with and without the dye.

In this way the spectra could be compared in a better way for the systems consisting of AgX alone, AgX and silver behenate and as a reference only silver behenate.

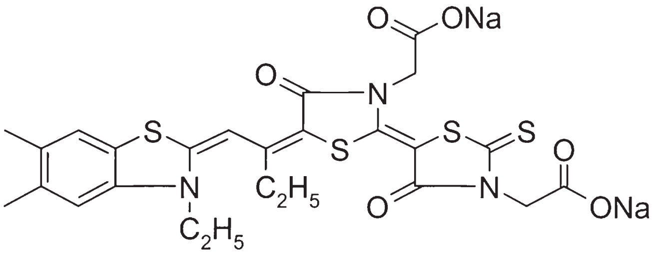


Figure 4. Chemical structure of the spectral sensitizing dye CASRN 137788-83-1.

A similar hypsochromic shift was observed for the 40 nm silver halide when the silver behenate was present in the dispersion. In absence of silver halide, a low flat absorption was observed in the range 560 to 640 nm, more or less resembling the absorption spectrum of the dye in solution. These results have been interpreted as showing that the latent image formation is controlled by a positively charged AgX surface.

TBMS During Thermal Development

As mentioned earlier, TBMS is believed to create a "window for imagewise development". It was decided to examine the concentration of TBMS in different infrared sensitive photothermographic samples, which were exposed to different exposure levels and wavelengths and which were then thermally processed. The infrared sensitive samples consisted of 2 samples prepared on the lab scale, similar to the formulation described in US Patent 6,376,159, and two commercial materials (the medical films, Kodak DryView™ and Konica DryPro™). The UV exposure was conducted with an Agfa Printon DL1000 set to 10 exposure units and using a greyfilter with optical density 1.5 in combination with a step tablet of 0.15 cm^{-1}. For the infrared exposure a lightbox containing lightbulbs for a total of 750 W, operated at 220V in combination with a step tablet of 0.15 cm^{-1} and a cut off filter of 775 nm. Chemical analysis of these film samples was performed by ultrasonic extraction with methanol followed by HPLC to determine quantitatively the amount of TBMS present in the material. The HPLC was equipped with an Alltima C18 5 µm column from Alltech and used an eluant consisting of a 40/60 mixture of water acetonitrile containing 0.02 M KH_2PO_4 at pH 2.5.

It was found that in photothermographic materials exposed to UV light and processed the concentration of TBMS decreased with optical density as illustrated by Table I. Very similar results were obtained when the materials were exposed to infrared light instead of UV light. This excludes a possible direct destruction of the TBMS by UV.

It was decided to examine one of the samples in more detail in order to obtain more data. The results were then plotted as the percentage of consumed TBMS as a function of exposure. It is remarkable to see how well the data can be fitted onto the sensitometric curve in Fig. 7.

Furthermore it was also found that unprocessed samples which were exposed to different levels of UV or infrared radiation all contained the same amount of TBMS as the unexposed, unprocessed sample. From this it can be concluded that the decrease of TBMS takes place during thermal development and not during the exposure process.

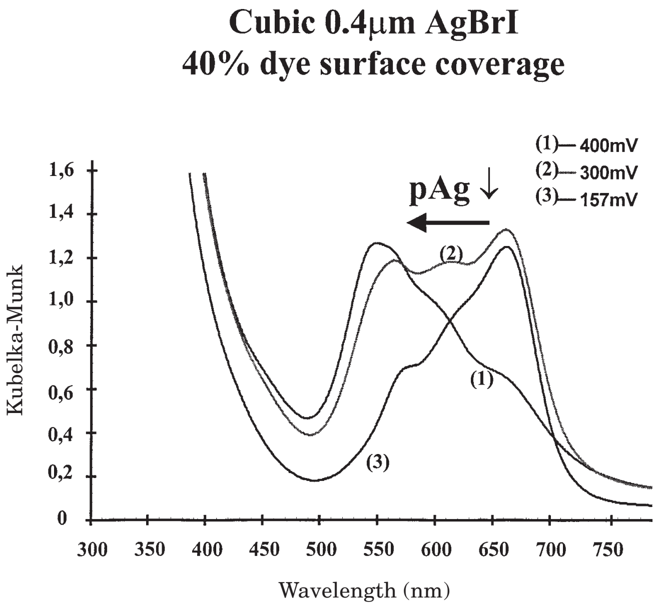


Figure 5. Spectral shift to shorter wavelengths by lowering pAg on an 0.4 µm AgBrI crystal.

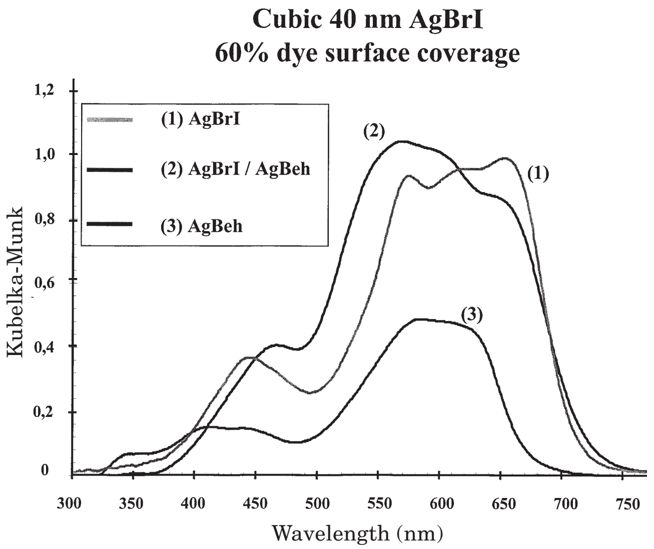


Figure 6. Spectral shift to shorter wavelengths by adding silver behenate to 40 nm AgBrI.

It is known that TBMS reacts with metallic silver and that as a result silver bromide is formed. Therefore it was decided to determine the concentration of silver bromide during thermal development using High Temperature X-Ray Diffraction (HT-XRD). In these experiments different compositions of silver halide-silver carboxylate (*ex situ* AgBr added during the preparation of silver behenate) were composed with a sterically hindered phenol (2,2'-(2-methylpropylidene)bis[4,6-xylenol], CASRN 33145-10-7) as reducing agent (RED), 4-methylphthalic acid (MPA) and phthalazine (PTZ) either in the presence or absence of the TBMS-compound tribromomethylphenylsulfone (BMPS). The compositions had been exposed to daylight. The intensity of the silver bromide peaks was followed with HT-XRD using heating steps of 10°C in 10 seconds and performing a scan every 10°C (duration 2 min). The total peak integrated surface is compared to a standard reference. In

TABLE I. Remaining Amount (%) of TBMS (100% = Original Concentration)

		Lab sample 1		Lab sample 2		Commercial film 1	Commercial film 2
Light Exposure	Thermal Processing	UV-exposure	IR-exposure	UV-exposure	IR-exposure	IR-exposure	IR-exposure
Unexposed	No	100%	100%	100%	100%	100%	100%
Unexposed	Yes	98%	96%	100%	95%	91%	91%
Density = 1	Yes	92%	78%	97%	81%	67%	61%
Density = D_{max}	Yes	72%	58%	29%	40%	12%	17%

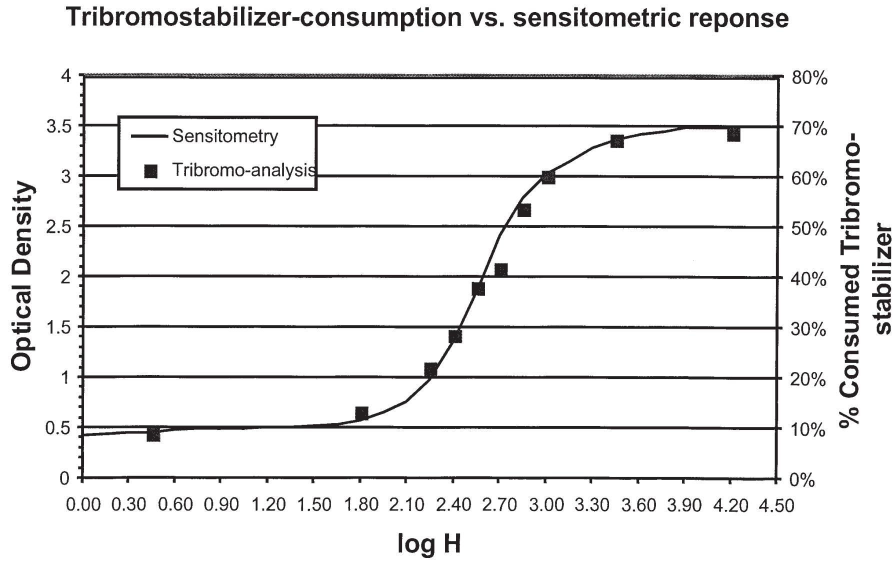


Figure 7. Comparison of the percent consumed tribromomethyl-stabilizer with the sensitometric curve.

the absence of TBMS, an unexpected decrease in AgBr-intensity was observed (Fig. 8). It has already been mentioned in the introduction that reduction proceeds with silver ions from the silver carboxylate and not from the silver halide itself.[1,2] If this statement is true, there is no explanation for the decrease of the silver bromide intensity in HT-XRD.

When TBMS is present in the composition, the amount of silver bromide clearly increased as shown in Fig. 9, thus confirming again the decrease of TBMS during thermal development.

Arrested Development

Finally, an arrested development study was conducted by TEM on a coated photothermographic material, which was exposed to UV-light to obtain an optical density of 3.2 after standard processing conditions of 15 seconds at 122°C. Images were taken of samples processed at 122°C that were quenched to temperatures below 100°C after 3, 7, 11 and 15 seconds of heating.

Various phases could be observed during thermal development. In the images after 3 seconds, which was called the initiation phase, the latent image had grown into a small filament. In the continuation phase these filaments grew larger and larger. In the termination phase also small silver spheroids were also formed on the filament and finally a silver structure resembling "broccoli" was obtained. Similar pictures of "broccoli" type of developed silver have been also reported by other authors.[13] All available silver carboxylate in the neighborhood of the silver halide appeared to be reduced.

A Novel Theory for Thermal Development

A novel mechanism for the image formation in photothermographic silver imaging media is proposed in which the TBMS plays an active role. It can be noted that the destruction of TBMS has an opposite effect ($\mathrm{Ag}^{\circ} \rightarrow \mathrm{Ag}^{+}$) to the reduction reaction ($\mathrm{Ag}^{+} \rightarrow \mathrm{Ag}^{\circ}$). It is assumed that the first Ag° on which the TBMS acts is in fact the latent image itself. Depletion of TBMS in this latent image area allows the reduction reaction to take place. This first slow reduction of silver ions in the neighborhood of the latent image results in the formation of a compact silver filament and a fatty acid melt. At the same time silver is extracted by phthalic acid[9] from the silver carboxylate with the simultaneous formation of more fatty acid melt, in which reducible silver complexes are formed with the aid of phthalazine.[14] These reducible silver complexes migrate over short distances towards the silver filament (which grows away from the latent image) where they are reduced by the reducing agent. As the destruction reaction proceeds with further depletion of TBMS, the reduction reaction accelerates and finally spherical silver particles (likely to be stabilized by fatty acid molecules) are formed which can migrate over very short distances in the fatty acid melt towards the silver filament resulting in a "broccoli" type of developed silver. In this last phase it is believed that the reduction reaction is catalyzed so vigorously by the increased mobility in the fatty acid melt of the reducing agent and the different silver complexes, that the reduction takes place even in the absence of any metallic silver in the immediate neighborhood. This phenomenon

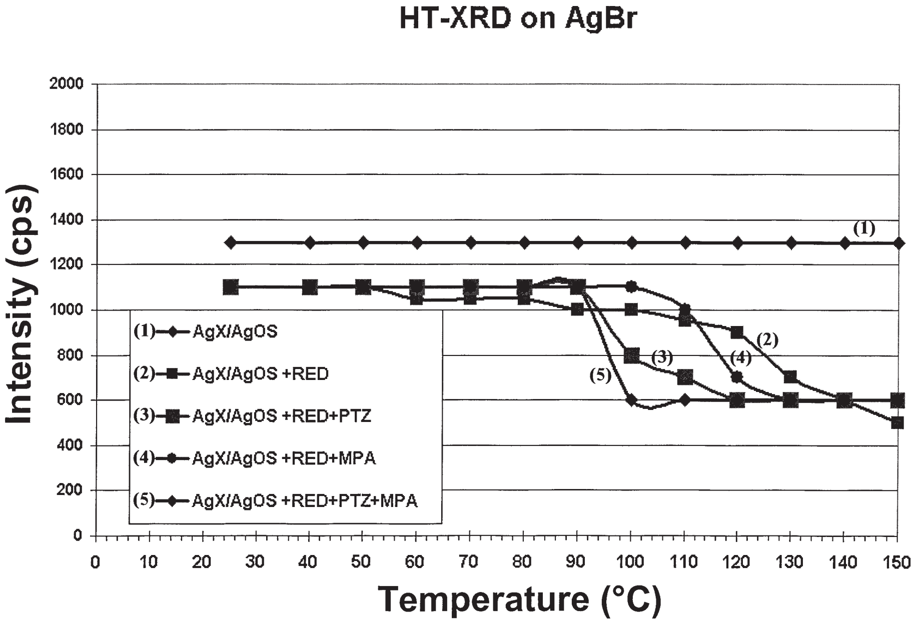


Figure 8. HT-XRD results of silver bromide in AgX/AgOS-compositions with a TBMS absent.

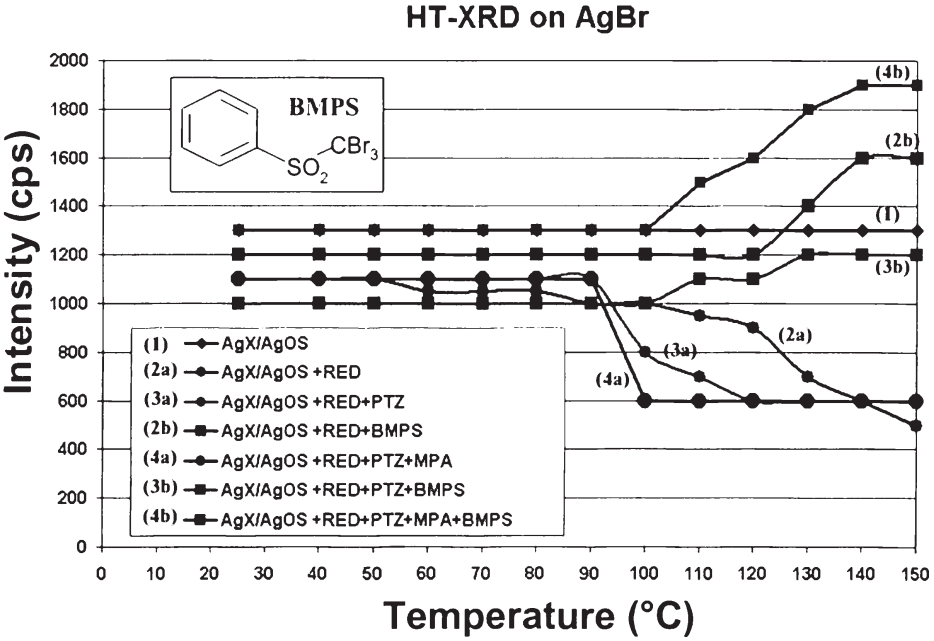


Figure 9. HT-XRD results of silver bromide in AgX/AgOS-compositions with a TBMS present.

of "secondary nucleation" was also reported by Hill, Mizen, Sahyun and Usanov[10] in their TEM study of the intermediate stages of development. The depletion of TBMS can be looked at as a concentration gradient where the reduction reaction slows down as the distance from the latent image increases. The "Sphere of Influence" as defined by Klosterboer and Rutledge[2] is consistent with this novel concept.

Conclusions

The following statements summarize our research:

- There is no epitaxial interface between an *in situ* silver halide and the silver organic salt.
- Latent image formation is not controlled by a photochemically reactive interface.
- It is believed the positively charged silver halide surface controls the latent image formation.
- TBMS creates a "window for imagewise development".
- The destruction of TBMS and the reduction reaction work in opposite direction; depletion of TBMS allows the reduction reaction to take place.
- An arrested development study illustrates the different stages in the formation of the'broccoli'-shaped silver.

The purpose of this study is to contribute to reaching a general consensus on the actual mechanisms. From

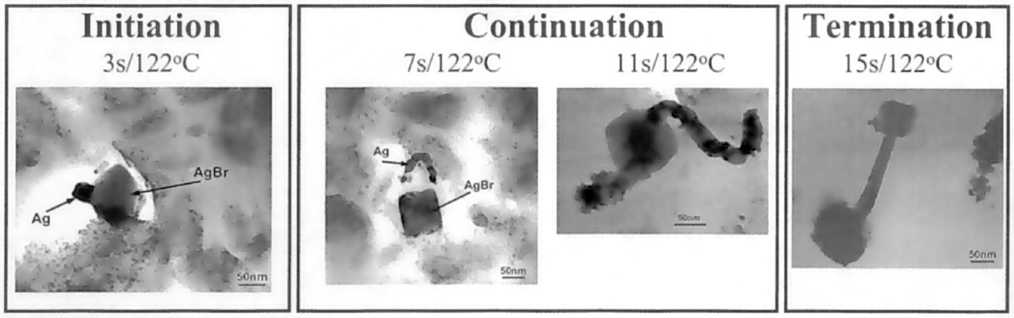


Figure 10. TEM pictures of an arrested development study

the many experiments, novel mechanisms were deduced for both the latent image formation and the actual image formation by thermal development. It is clear that more research on this issue will result in adjustments and corrections of the proposed mechanisms, and maybe even by complete new proposals for the mechanisms. After all wasn't it Albert Einstein[15] who once said: "If we knew what it was we were doing, it would not be called research, would it?"

Acknowledgment. This research was supported by the IWT, Institute for the Promotion of Innovation by Science and Technology in Flanders, and Agfa-Gevaert N.V. I also wish to thank my colleagues at Agfa, Dr. I. Geuens, Dr. C. Van Roost, Dr. J. Loccufier and Dr. J. Van Luppen and at the University of Antwerp, Dr. O. Richard and Dr. P. Potapov, for the interesting discussions and their contributions to the experimental work.

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