# Effect of Pre-Exposure Heating on Thermally Developed Dry Silver Type Imaging Materials

**Yu. E. Usanov*, T. B. Kolesova, and I. M. Gulikova**
*State Optical Institute S. I. Vavilov, St. Petersburg, Russia*

**L. P. Burleva**
*Institute of Solid State Chemistry, Novosibirsk, Russia*

**M. R. V. Sahyun▲**
*Department of Chemistry, University of Wisconsin, Eau Claire, Wisconsin*

**D. R. Whitcomb▲**
*Eastman Kodak Company, Oakdale, Minnesota*

The sensitometric effects of pre-exposure heating in TDPM of the Dry Silver type were investigated. Loss of developable density with increasing time of pre-exposure heating was shown to involve the toners which are essential to selective, image-wise TDPM development. Pre-exposure heating was found not to affect the latent image forming system (silver halide-silver carboxylate interface) in TDPM. Our observations support previously proposed interpretations of the mechanism of TDPM development. Pre-exposure heating may thus lead to either (a) loss of toner, e.g., by volatilization or air oxidation, and/or (b) side reactions between toner and silver carboxylate leading to formation of less reactive species. From a practical point of view these results provide mechanisms for both the storage instability of the TDPM sensitometric responses, as well as for inefficiency in latent image amplification.

Journal of Imaging Science and Technology 43: 545–549 (1999)

## Introduction

Photographic materials based on admixtures of silver carboxylates and silver halides of the so-called dry silver type are characterized by their light sensitivity from the UV to the IR region of the spectrum, short thermal development times, and high quality images. These properties of thermally developed photographic materials (TDPM) make them attractive for various technological applications, especially micrographics, medical imaging, and graphic arts. The light sensitivity of TDPM remains, however, inferior to that of traditional silver halide photographic materials which are wet processed. This difference has been attributed both to the low concentration of the silver halide in the TDPM photosensitive layer[1] and to inefficiencies in the thermal development process. It is the objective of the present work to investigate this latter problem.

TDPM are known not only for their practical applications, but also for their use as model systems to study the physico-chemical processes of development center formation and visualization. Some published observations, however, argue against the complete analogy between photochemical processes occurring in traditional silver halide films and those in materials of the Dry Silver type.[2–4] For example, heating can lead to selective reduction of silver in silver carboxylate particles not having direct contact with AgBr,[4,5] even though the silver halide-silver carboxylate interface is prerequisite to image-wise development.

The strategy employed in this work is to investigate TDPM development reactivity in Dry Silver type materials subjected to pre-exposure heating. We started from the supposition that pre-exposure heating should reveal processes that may occur in the initial stages of thermal development. The studies were carried out with both commercial TDPM as well as with model films. In these latter films we left the toners, such as phthalimide and succinimide, and developers out of the photographic

Original manuscript received December 15, 1998

▲ IS&T Member

* Author to whom correspondence may be addressed

layer. They were mixed into a separate layer (developing layer) in order to investigate the effect of pre-exposure heating of the photographic layer in their absence. The role of the toners in the latent image center amplification reaction is only partly understood. The mechanism and consequences of pre-exposure heating are also of practical significance insofar as they may model processes occurring during storage and aging in commercially significant TDPM.

## Experimental

**Experiments on Commercial TDPM.** Experiments were carried out on thermally developed photographic films from Imation Corp., type 7858, which have a high fog stability in the development process owing to the presence of antifoggants. The presence of these agents allows these films to be subjected to pre-exposure heating at 115°C for up to 30 s without significant increase in the optical density due to fog ($D_o$).

These film samples were subjected to pre-exposure heating with the backside of the substrate on a thermally controlled metallic surface at 115°C. Contact time was from 0 to 60 s, then samples were exposed in a UKEP-1 spectrometer for 5 s or on an FSR-41 sensitometer for 30 s and developed at 115°C for various times. Optical density ($D$) of image areas was measured on a model DP-1 densitometer.

### Model Films with Toner

TDPM which incorporated toner and developers were prepared as previously described.[6] Accordingly, we prepared three samples of TDPM which differed in the silver halide component and the method of its preparation. The first sample contained silver bromide, obtained by adding LiBr to silver stearate (AgSt), and the second comprised a mixture of silver bromide and silver chloride, obtained by adding a mixture of LiBr/LiCl to an aqueous dispersion of AgSt. The third sample contained silver bromide, freshly prepared by the double jet emulsification method, was added to an aqueous solution of sodium stearate prior to the addition of silver nitrate. That is, formation of the silver stearate was carried out in the presence of the AgBr. Thermally developed formulations were made from these three components, and additionally contained polyvinylbutyral (PVB, dissolved in isopropanol) as the binder, excess stearic acid (HSt), lithium stearate (in equivalent concentration to silver stearate), chemical ripeners, toners (phthalimide and succinimide), and an optical sensitizer (merocyanine dye). These films were coated on a polyester substrate and dried at room temperature giving 2-3 μm thick layers.

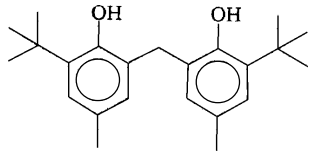
The samples thus obtained were heated for various times at 115°C, then the surface of the imaging layer was overcoated with a 2.5 wt % solution of PVB containing bis-alcophen (see below) as the developer. The TDPM so obtained was exposed in the sensitometer and developed at 115°C for 5, 10, and 20 s. The optical densities of all the developed films were measured on a DP-1 densitometer.

### Model Films without Toner

Other films were prepared as follows, based on the method of Ref. 6. In a stainless steel reactor 240 mL of distilled water and 0.02 mol of stearic acid were added and heated to 82°C. Then, sequentially, 30 mL each of aqueous 0.475 M NaOH and 0.7495 M $AgNO_3$ were added dropwise with stirring over a 5 min interval. The resulting suspension of silver stearate was cooled to 28°C. With intensive mixing, an additional 3.0 mL of LiBr (1.0 M) was then added under safelight.[2] The subsequent ripening time was 30 min. The precipitate was then filtered at room temperature through a Büchner funnel and washed until the silver ion test was negative in the filtrate. The resulting silver soap precipitate was dried with isopropanol and then placed in a ball mill containing 50 mL of 7.5% polyvinylbutyral (PVB) in isopropanol. The toners (phthalimide and succinimide) and developer (bis-alcophen) were not added at this point. The ball milling process was carried out for 3 h at room temperature.

The preparation of the TDPM was then carried out by adding a merocyanine dye to 10 mL of the silver soap suspension in PVB for 5 min. The full composition was coated on polyester film and dried. The dry photolayer was 8-10 μm thick, and corresponds to a silver coating weight of about 1.5 g Ag/m$^2$.

The developing layer was prepared from a 2.5% solution of PVB in isopropanol containing 15.0 mL of a 12.0% solution of the developing agent, bis-alcophen, without and with toners, as required.



bis-alcophen

After pre-exposure heating and sensitometric exposure of the photographic films, each was subsequently attached to a roller and overcoated with one of four topcoat solutions (based on a 2.5 wt % PVB solution). Three of them contained the toners phthalimide and/or succinimide.

1. Imaging layer and PVB with *bis*-alcophen.
2. Imaging layer and PVB with *bis*-alcophen and phthalimide (2.0 g/100 mL of 2.5% PVB solution)
3. Imaging layer and PVB with *bis*-alcophen and succinimide (12.0 mL of a 5% solution in acetone added to 100 mL of 2.5% PVB solution)
4. Imaging layer and PVB with *bis*-alcophen and phthalimide and succinimide (concentrations as in layers 2 and 3).

After drying at room temperature these films were developed in the same manner as the other commercial and model films.

## Results

**Commercial Films.** In Fig. 1 the kinetic curves are shown for the development of type 7858 samples. Samples were subjected to pre-exposure heating for 0, 10 or 30 s at 115°C. All were then exposed 5 s in the sensitometer and developed for various times at 115°C. For samples without pre-exposure heating and developed for 10 s, exposures required to obtain $D$ = 1.0 and 2.0 above $D_o$ were determined, $H_1$ and $H_2$, respectively. The optical density of all 12 samples with pre-exposure heating were then measured at $H_1$ and $H_2$ and plotted in Fig. 1. From the curves it can be seen that pre-exposure heating induces a decrease in developed density which is more significant at the lower level of light exposure and for longer times of pre-exposure heating.

It might be suggested that one of the variables responsible for the observed decrease in density is the overall time interval from the start of pre-exposure heating through the development of the exposed film. That

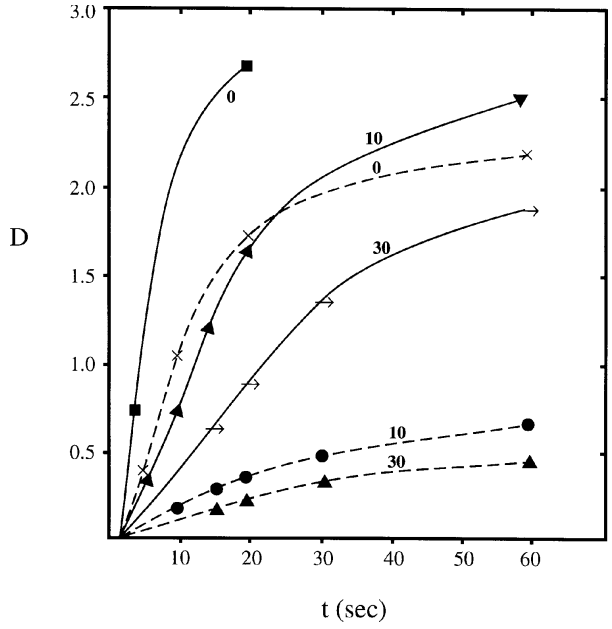



**Figure 1.** Development kinetics for type 7858 TDPM samples: density versus time of development (seconds at 115°C) for samples heated to 115°C for 0, 10, and 30 s prior to exposure. Plotted densities are obtained at the exposures $H_1$ and $H_2$ as described in the text.

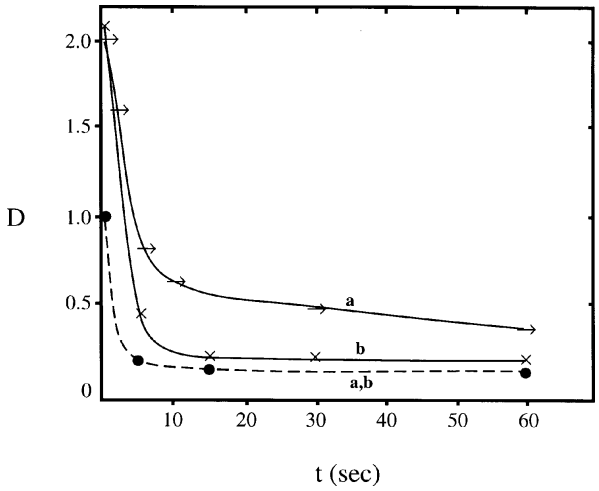



**Figure 2.** Effect of heating duration (115°C) prior to exposure on the optical density for sections of the step wedges exposed onto type 7858 film and developed at 115°C for 10 s, corresponding to $D$ = 2.0 (solid lines) and $D$ = 1.0 (dashed lines) without pre-exposure heating: (a) flash lamp exposure; (b) sensitometer exposure.

is, over the course of the time during which the photographic film was heated and cooled, physical and chemical processes could occur which could further influence the kinetics of development.

In order to exclude this possibility, a flash lamp was used for the exposure of the 7858 film while it was in contact with the heated substrate. The duration of the flash lamp exposure of the sample on the heated surface was 1/300 of a sec. A sensitometric wedge, prepared on a flexible substrate, was applied to the photographic film, which was then placed into contact with the heated surface. Time of heating prior to exposure is the pre-exposure heating time, $t_{PEH}$, and the time after exposure is the development time. Based on optical densities

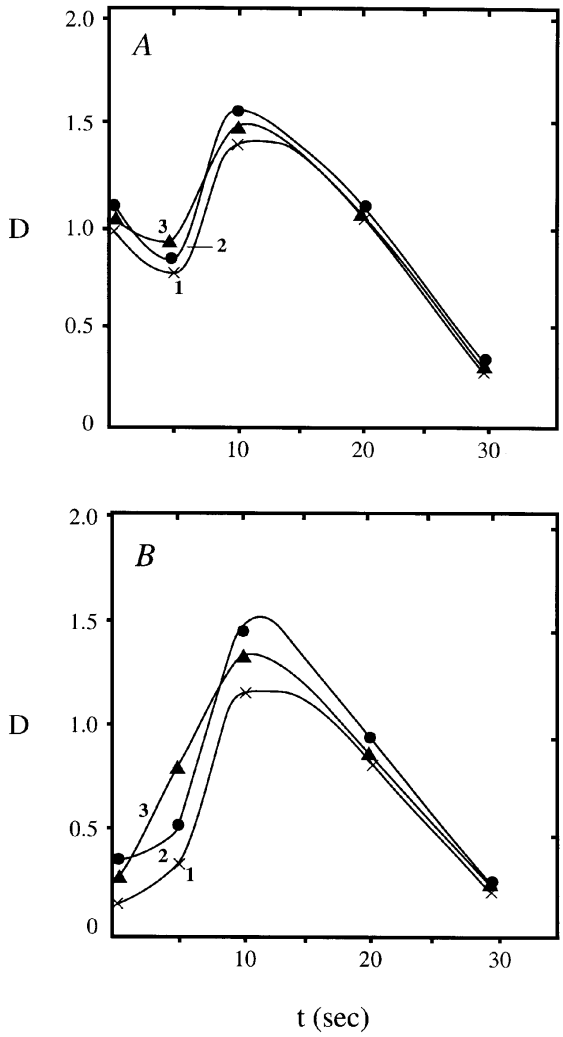



**Figure 3.** Dependence of optical density of (a) image and (b) fog on duration of pre-exposure heating (115°C). Development time was 10 s at 115°C. Curve 1: AgBr from LiBr and AgSt. Curve 2: AgBr(Cl) from LiBr and LiCl and AgSt. Curve 3: AgBr from double jet precipitation added to sodium stearate prior to $AgNO_3$ addition.

of the images obtained on development at 115°C for 10 s, density differences between pre-exposure heated and unheated samples, for exposures corresponding to $H_1$ and $H_2$ were obtained (Fig. 2). It can be seen that the shapes of the various curves for $D = f(t_{PEH})$ obtained by the two procedures are comparable. Decrease in optical density of the developed image is most clearly evident with no more than 5 s pre-exposure heating.

### Model Films With Toner

The 7858 photographic film has a complicated composition and structure, so in order to control the effects of these factors, the investigation was extended to model thermally developed photographic films formulated with the three different silver halide preparations. All of these TDPM incorporated toners. From sensitometric measurements the relationship $D = f(t_{PEH})$ was constructed for the regions of the step wedge where (a) $D$ = 1.0 in the absence of pre-exposure heating, and (b) fog, as shown in Fig. 3.

From Fig. 3 it can be seen that for samples having pre-exposure heating times less than 5 s there is a decrease

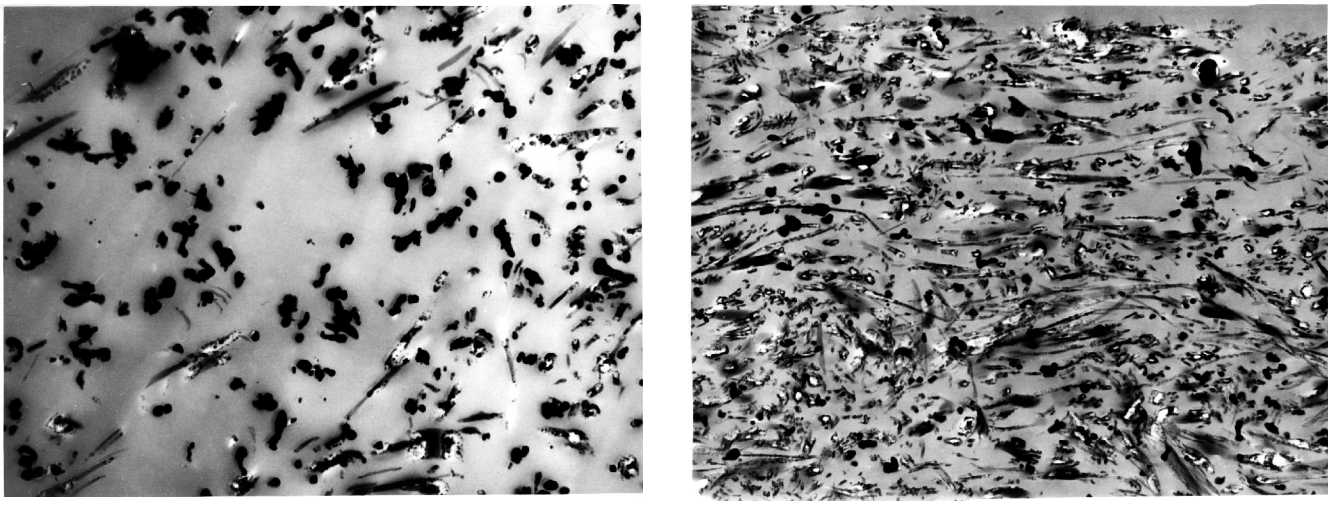


**Figure 4**. Transmission electron micrographs of sample corresponding to curve 1 in Fig. 3. with (left) and without (right) pre-exposure heating (10 s at 115°C), after development for 10 s at 115°C (60,000X).

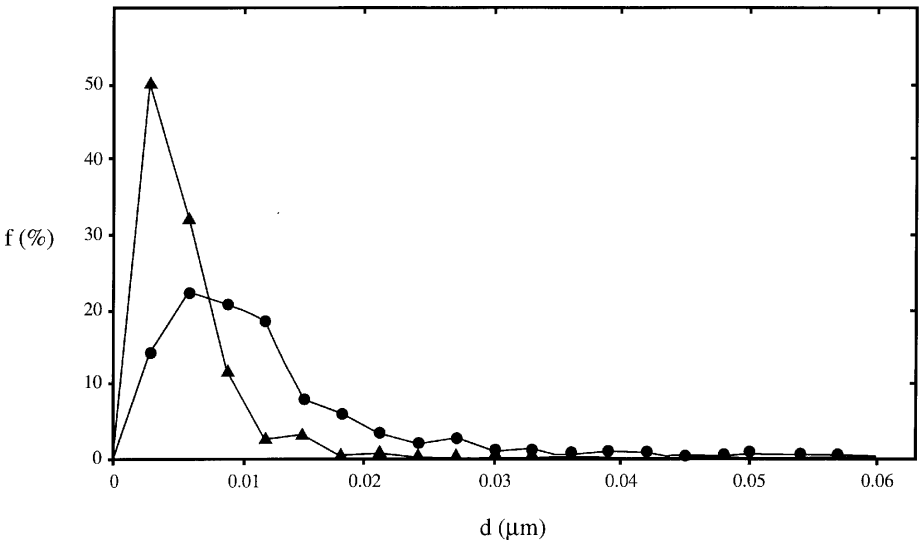



**Figure 5.** Histogram of developed silver particles shown in Fig. 4: unheated (circles) and heated (triangles) prior to exposure at 115°C for 10 s.

in the density ($D$) of the image as described earlier for the 7858 samples. For long development times there are essentially no differences among the films. The densities for the exposed portions of the film and the fog both increase. Pre-exposure heating exceeding 15 s decreases the ability of the AgSt to be reduced. For the samples subjected to pre-exposure heating more than 30 s, development does not occur at all, even if the films are heated for a long time. Thus, despite the various compositions of the light sensitive phases and the processes for obtaining them, the effect of pre-exposure heating on developability is the same. That is, TDPM pre-exposure heating does not necessarily appear to influence the silver halide component itself or the process of latent image formation, which is thought to depend on the morphology of the silver halide-silver carboxylate interface.[3,7]

Transmission electron micrographs (TEM) were obtained for two samples of the film halidized in situ with LiBr. One sample was subjected to pre-exposure heating for 10 s at 115°C. Both samples were exposed at the same level of the step wedge, and developed at 115°C. The TEM images are shown in Fig. 4. From these data, the number and sizes, taken as the diameter, $d$, of the smallest circle incorporating an otherwise irregularly shaped particle, of the developed particles were estimated. The resulting histograms are shown in Fig. 5. We conclude from the histograms that the number of developed silver particles remains essentially unaffected by the influence of pre-exposure heating, but the average size of these silver particles decreases substantially. This result confirms that the observed decrease in optical density in image areas of pre-exposure heated TDPM is a consequence of a decrease in the silver carboxylate reduction reactivity, not a consequence of any effect of pre-exposure heating on latent image formation.

## Model Films without Toner

The investigation was then extended to model films which did not incorporate toners at the time of pre-heating in order to establish whether or not these reagents played a role in the sensitometric consequences of pre-exposure heating. The increase in optical density with development time was followed. The data are presented in Table I. Values for $D$ (image) are taken from the fifth step on the step wedge.

It can be seen that when only developing agent, i.e., no toner, is present in the developing layer the process

**TABLE I. Development of model TDPM subjected to pre-exposure heating; optical density as a function of development time.**

| | Pre-exposure heating time (seconds): | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | | 2 | | | 5 | | | 10 | | |
| | Development time (seconds): | | | | | | | | | | | |
| **Top-coat** | 5 | 10 | 20 | 5 | 10 | 20 | 5 | 10 | 20 | 5 | 10 | 20 |
| | (a) Image (step 5) | | | | | | | | | | | |
| 1 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| 2 | 0.42 | 0.72 | 1.40 | 0.30 | 0.52 | 1.18 | 0.34 | 0.51 | 1.14 | 0.35 | 0.42 | 0.97 |
| 3 | 0.37 | 0.85 | 1.33 | 0.53 | 1.07 | 1.42 | 0.48 | 1.15 | 1.68 | 0.55 | 1.22 | 1.76 |
| 4 | 0.50 | 1.67 | 1.80 | 0.59 | 1.91 | 2.08 | 1.02 | 1.88 | 2.06 | 1.42 | 1.97 | 2.03 |
| | (b) Fog ($D_o$) | | | | | | | | | | | |
| 1 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| 2 | 0.15 | 0.16 | 0.21 | 0.15 | 0.15 | 0.27 | 0.15 | 0.21 | 0.27 | 0.17 | 0.21 | 0.27 |
| 3 | 0.08 | 0.09 | 0.17 | 0.17 | 0.23 | 0.29 | 0.28 | 0.32 | 0.42 | 0.48 | 0.92 | 1.50 |
| 4 | 0.12 | 0.60 | 1.43 | 0.17 | 0.80 | 1.44 | 0.37 | 1.04 | 2.03 | 0.87 | 1.60 | 2.13 |
| | (c) [D(image) - $D_o$] | | | | | | | | | | | |
| 2 | 0.27 | 0.56 | 1.19 | 0.15 | 0.37 | 0.91 | 0.19 | 0.30 | 0.87 | 0.18 | 0.21 | 0.70 |
| 3 | 0.29 | 0.76 | 1.16 | 0.36 | 0.84 | 1.13 | 0.20 | 0.83 | 1.26 | 0.07 | 0.30 | 0.26 |
| 4 | 0.38 | 1.07 | 0.37 | 0.42 | 1.11 | 0.64 | 0.65 | 0.84 | 0.03 | 0.55 | 0.37 | $\leq 0$ |

of latent image amplification is not initiated. Addition of phthalimide or succinimide toner to the developing layer results in selective development in the film. The toner is thus critical to the development process, as has been previously proposed.[1] The results are consistent with the concept that the toners convert the silver ion from silver carboxylate to complexes which are the reactive intermediates in the development reaction.[8,9] Layers containing only phthalimide (top-coat 2) have lower contrast and fog than those containing succinimide (top-coats 3 and 4).

Generally, increasing the duration of pre-exposure heating leads to an increase in fog density, which in the presence of succinimide also leads to an overall density increase measurable in the image area. The presence of the combined toners in the developing layer leads to an acceleration of development and decreases, even in the control sample, the selectivity of the development process, as [$D$(image) - $D_o$].

## Discussion

These results show that pre-exposure heating introduces significant changes in the kinetics of the development process only if the toners are present during this heat treatment. In all cases, however, pre-exposure heating can lead to fog formation. Thus, pre-exposure heating must affect development kinetics by a process involving toner, such as (a) loss of toner by volatilization or air oxidation, and/or (b) side reactions between toner and silver carboxylate, leading to the formation of less reactive species.

The latter possibility is of particular concern from a technological point of view. The same processes may operate during storage or aging of unexposed TDPM, leading to alteration of the sensitometric properties with aging of the film. The processes resulting in the loss in reactivity of the development chemistry in TDPM on pre-exposure heating may also function concurrently with development. This competition would lead to inefficient image development in these films and degradation in sensitometric response from that expected on the basis of simple models.[4]

We have proposed the following scheme for the development of TDPM.[7] Toners react on latent image or fog centers during development to form silver complexes[8,9] which can be reduced by the developers at lower reduction potentials than required for the reduction of silver carboxylate. This process is more active when larger numbers of latent image or fog centers are present, e.g., at higher exposure.[4] The resulting family of complexes may include highly dispersed silver with an extremely reactive surface.[6] The onset of the reduction reaction is accompanied by the release of a large amount of heat. We actually observe active continuation of the development process after removal of the photolayer from the heating surface. This observation is critical to the engineering of equipment for the processing of TDPM.

## Conclusions

The sensitometric effects of pre-exposure heating on TDPM of the Dry Silver type were investigated. Loss of developable density with increasing pre-exposure heating time was shown to involve the toners, which are essential to selective, image-wise development of the TDPM. Pre-exposure heating was found not to affect the latent image forming system (silver halide-silver carboxylate interface) in TDPM. Our observations support previously proposed interpretations of the mechanism of TDPM development.

Pre-exposure heating may thus lead to either (a) loss of toner, e.g., by volatilization or air oxidation, and/or (b) side reactions between toner and silver carboxylate leading to formation of less reactive species. From a practical point of view these results provide mechanisms for both the storage instability of TDPM sensitometric response, as well as for the inefficiency of latent image amplification.

## References


1. D. H. Klosterboer, in *Imaging Materials and Processes*, 8th ed., J. M. Sturge, V. Walworth, and A. Shepp, Eds., Van Nostrand-Reinhold, New York, 1989, Chapter 9.
2. D. H. Klosterboer and R. L. Rutledge*, Preprints of Paper Summaries, 33rd Annual Conf. SPSE*, SPSE, Washington, DC, 1980, paper N74.
3. C. Zou, M. R. V. Sahyun, B. Levy, and N. Serpone, *J. Imaging. Sci. Technol.* **40,** 94 (1996).
4. S. E. Hill, M. B. Mizen, M. R. V. Sahyun, and Yu. E. Usanov, *J. Imaging Sci. Technol.* **40,** 568 (1996).
5. W. J. Miller and R. W. Baxendale, US Patent 3,761,273 (1973).
6. Yu. E. Usanov and T. B. Kolesova, *J. Imag. Sci. Technol.* **40,** 104 (1996).
7. M. R. V. Sahyun, *J. Imag. Sci. Technol.* **42,** 23 (1998).
8. D. R. Whitcomb and R. D. Rogers, *Polyhedron* **16,** 863 (1997).
9. D. R. Whitcomb and R. D. Rogers, *J. Chem. Cryst.* **25,** 137 (1995).