

Peculiarities in the Kinetics of Thermally Developed, "Dry Silver" Type Photographic Materials

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Abstract

Experiments carried out with thermally developed "Dry Silver" (DS) photographic materials showed that preheating at temperatures higher than 100ºC prior to exposure results in decreased speed during development. Consequently, a decrease in the sensitivity was observed. Analogous results were also obtained if the films were exposed during the preheating process. The higher the pre-heating temperature above 100ºC and the longer the time of preheating, the lower the film sensitivity. It was determined that this phenomenon depends neither on the composition of the silver halides nor on the method of incorporating them into the thermally developable composition.

Based on electron microscopy data and histograms of the developed films, which were either preheated or not preheated before exposure, we concluded that the lower light sensitivity of DS materials, compared to conventional silver halide materials, is due to the peculiarities of the development kinetics in DS. The development centers receiving low light exposure have a longer induction period compared to those receiving high exposure. Therefore, these development centers either catalyze the reduction of silver carboxylates very slowly or they do not catalyze the reduction at all. One reason for this behavior is related to the change in the structure of the silver carboxylate in the initial stages of the thermal development process.

Introduction

Photographic materials based on carboxylate and halide silver salts of the "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 the thermally developed photographic materials (TDPM) make them attractive for various scientific applications, non-impact printing, and professional and amateur photography. The light sensitivity of TDPM (having microcrystals of silver halide as the light sensitive component) is inferior to that of traditional silver halide photographic materials which are wet processed. The difference in the light sensitivity is related to the low concentration of the silver halide in the TDPM photosensitive layer[1] and the inefficient thermal development process. It is the objective of this work to investigate this latter problem.

Previously, potentiometric methods showed that the stearic acid melt in water can react with silver nitrate to bond with the ionic silver.[2] On this basis it can be proposed that this reaction also occurs in the TDPM imaging layer at the initial stages of thermal development when the process of catalytic reduction of the silver carboxylate has not yet started and the carboxylic acid has already melted.

The objective of this work is the investigation of the TDPM development kinetics for "Dry Silver" type materials subjected to pre-exposure heating (PEH). We started from the supposition that the PEH enables the processes which occur at the initial stages of thermal development to be revealed, that is, before the start of the reduction processes.

Results and Discussion

Experiments were carried out on thermally developed photographic films from 3M, type 7858, which have a high fog stability in the development process allowing them to be subjected to PEH at 115°C for up to 30 seconds without a significant increase in the optical density of fog (D_o).

Film samples were subjected to PEH with the backside of the substrate on a thermally controlled metallic surface at 115°C. Contact time was from 0 to 60 seconds, then the samples were exposed in a UKEP-1 spectrometer for 5 seconds and developed at 115°C for various times. The optical density (D) of image sections was measured on a DP-1 densitometer.

In Figure 1 the kinetic curves for the development of 7858 type samples are shown which were subjected to PEH for 0, 10 and 30 seconds at 115°C. All samples were exposed 5 seconds, developed for 5, 10, 15, 20, 30, 60 seconds (at 115°C), then for the non-PEH sample (developed for 10 seconds) the exposure required to obtain D = 1.0 and 2.0 was determined, H_1 and H_2. The optical density of all 12 PEH samples were then measured at H_1 and H_2 and are plotted in Figure 1. From the curves it can be seen that PEH induces a decrease in D of the developed image which is more significant for lower amounts of light exposure of the photographic film and for longer times of PEH.

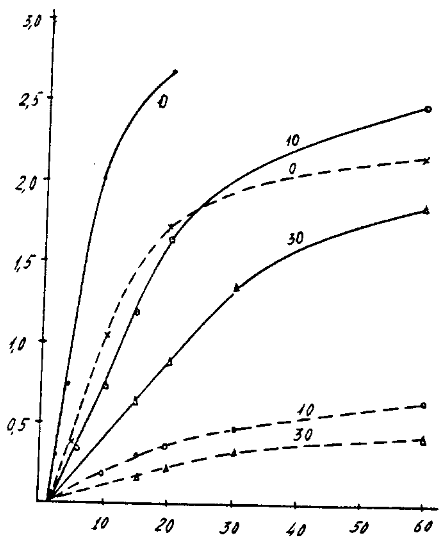

Figure 1. Development kinetics for TDPM samples (type 7858), density versus time of development (seconds, 115°C), heated to 115°C prior to exposure for 0, 10 and 30 seconds. Plotted densities are from the 0, 10 and 30 second PEH samples at the exposure required to achieve D = 2.0 (solid lines) and D = 1.0 (dashed lines).

It can be proposed that one of the reasons for the observed decrease in D is the time interval from the moment of the start of the PEH to the development of the exposed film. That is, over the course of the time during which the photographic film was heated and cooled, physical and chemical processes can occur which can further influence the kinetics of its development.

In order to exclude this possibility, a flash lamp was used for the exposure of the 7858 film. A sensitometric wedge, prepared on a flexible substrate, was applied to the photographic film, which was then placed into contact with the heated surface. The time for the flash lamp exposure of the sample on the heated surface was 1/300 of a second. The time of heating prior to exposure is the PEH time and the time after exposure is the development time. Based on the optical densities of the developed images the relationship between D and the duration of the PEH after development at 115°C for 10 seconds, for D equal to 1.0 and 2.0 for the portions of the step wedge of the unheated samples with exposure in the sensitometer or flash lamp (Figure 2), was constructed. From this figure it can be seen that the decrease in optical density of the developed image resulting from PEH is most clearly evident at the initial stages of development for at less than 5 seconds PEH.

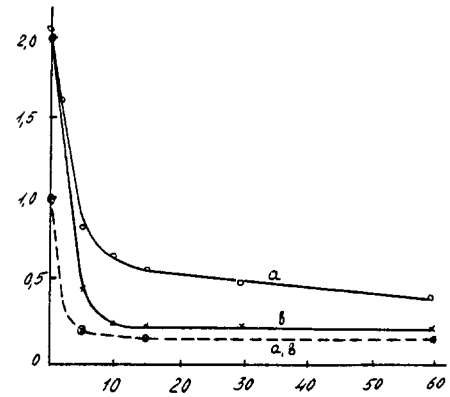

Figure 2. Effect of the duration of heating at 115°C, prior to exposure, on the optical density for the sections of the step wedges at D = 2.0 (solid lines) and at D = 1.0 (dashed lines) obtained for unheated samples (type 7858) developed at 115°C for 10 seconds. a = flash lamp exposure; b = sensitometer exposure.

In combination with this is the fact that the 7858 photographic film has a complicated composition and structure, so we continued the investigation on a model thermally developed photographic film.

According to the procedure described previously,[2] we prepared three samples of a TDPM which were different in the silver halide component and the method for obtaining it. The first sample contained silver bromide (obtained by adding LiBr to AgSt) and the second had a mixture of silver bromide and silver chloride (obtained by adding a mixture of LiBr/LiCl to an aqueous dispersion of silver stearate, AgSt). The third sample contained silver bromide (freshly prepared by the double jet emulsification method) which was added to an aqueous solution of sodium stearate prior to the addition of silver nitrate. That is, the formation of the silver stearate was carried out in the presence of the AgBr. Thermally developed formulations (TDF) were made from these components, which additionally contained polyvinylbutyral as the binder (dissolved in isopropanol), excess stearic acid (HSt), lithium stearate, equivalent silver stearate, chemical ripeners, toners (phthalimide and succinimide) and an optical sensitizer (dye). The TDF was coated on a polyester substrate and dried. The samples obtained were heated for various times at 115°C, then the surface of the imaging layer was coated with a solution of PVB containing bis-alcofen as the developer. The TDPM so obtained was exposed in the sensitometer heated to 115°C. From the measurements of the optical densities the relationship D = f(t_{PEH}) was constructed for the regions of the step wedge where D = 1.0 (a) and fog (b) which are shown in Figure 3.

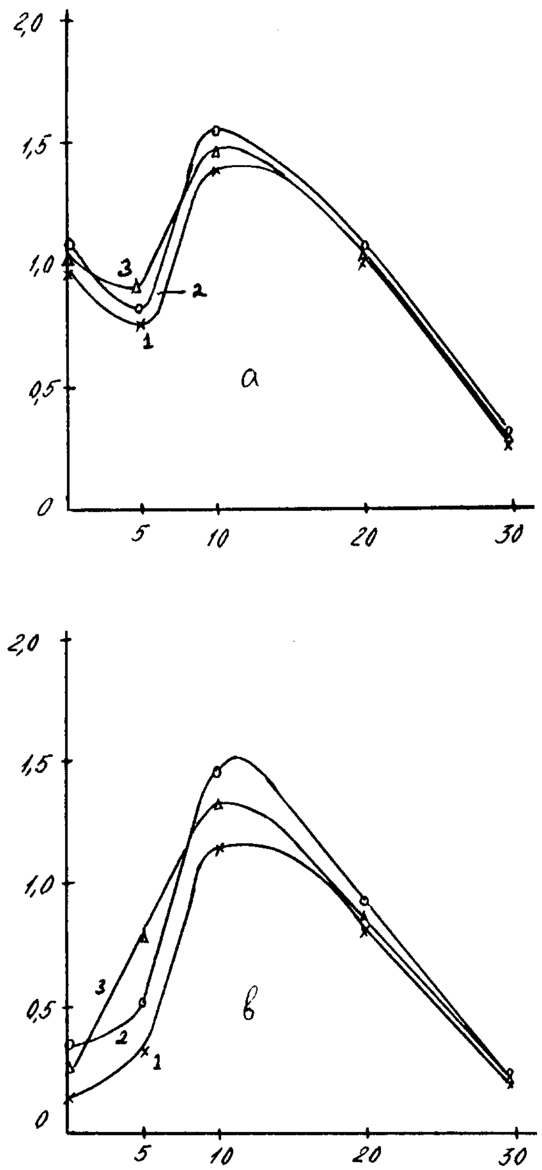

Figure 3. Relationship of the optical density of the image (a) and fog (b) on the duration of PEH (115°C). The development time was 10 seconds at 115°C. 1 = AgBr from LiBr and AgSt, 2 = AgBr/Cl from LiBr/LiCl and AgSt, 3 = AgBr from double jet precipitation and added to sodium stearate prior to $AgNO_3$ addition.

From Figure 3 it can be seen that for samples having PEH less than 5 seconds there is a decrease in the D of the image as described earlier for the 7858 samples. For long development times there are essentially no differences between the densities achieved in the exposed (images) and unexposed (fog) portions of the film. PEH exceeding 15 seconds induces a decrease in the ability of the AgSt to be reduced. For the samples subjected to PEH more than 30 seconds, darkening does not occur, even if heated for a long time. Based on these results, shown in Figure 3, it can be seen that despite the various compositions of the light sensitive phases and the conditions of obtaining them, changing the kinetics of development the effect of the PEH is the same for all of them. That is, short time PEH does not appear to influence the silver halide and the process of latent image formation in it.

The transmission electron micrographs obtained for sample 1 at the same exposure level of the step wedge, one subjected to PEH and one not, exposed for 10 seconds at 115°C and developed at 115°C, are shown in Figure 5. From these data, the number and size of the developed particles were calculated and the resulting histogram is shown in Figure 4. We can conclude from the histogram that the number of developed silver particles essentially remains unaffected by the influence of the PEH. But the average size of the particles decreases substantially. In addition, these results suggest that the observed decrease in the optical density in the image for the PEH TDPM may be a consequence of the PEH induced decrease of the silver carboxylate reduction reaction rate or in the reaction rate of the carboxylic acid with the silver salts.

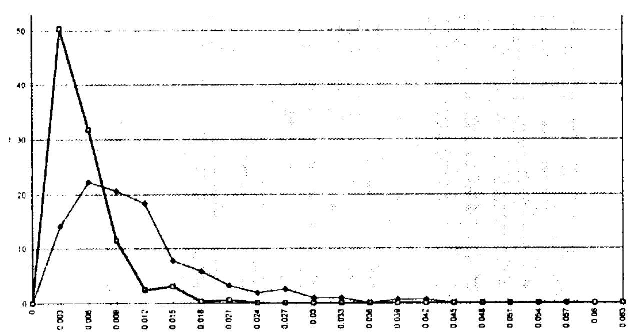

Figure 4. Histogram of sample 1 (Figure 3), unheated (squares) and heated (diamonds) prior to exposure at 115°C for 10 seconds.

Conclusions

Using the method of pre-exposure heating of thermally developed photographic materials of the "Dry Silver" type we were able to show that the initial stages of the thermal process of development in the imaging layer processes proceed in such a manner as to restrain the catalytic reduction of the silver carboxylate salts at the development centers. The result of this is the decrease in the photographic sensitometric parameters such as the magnitude of the optical densities and light sensitivity.

References

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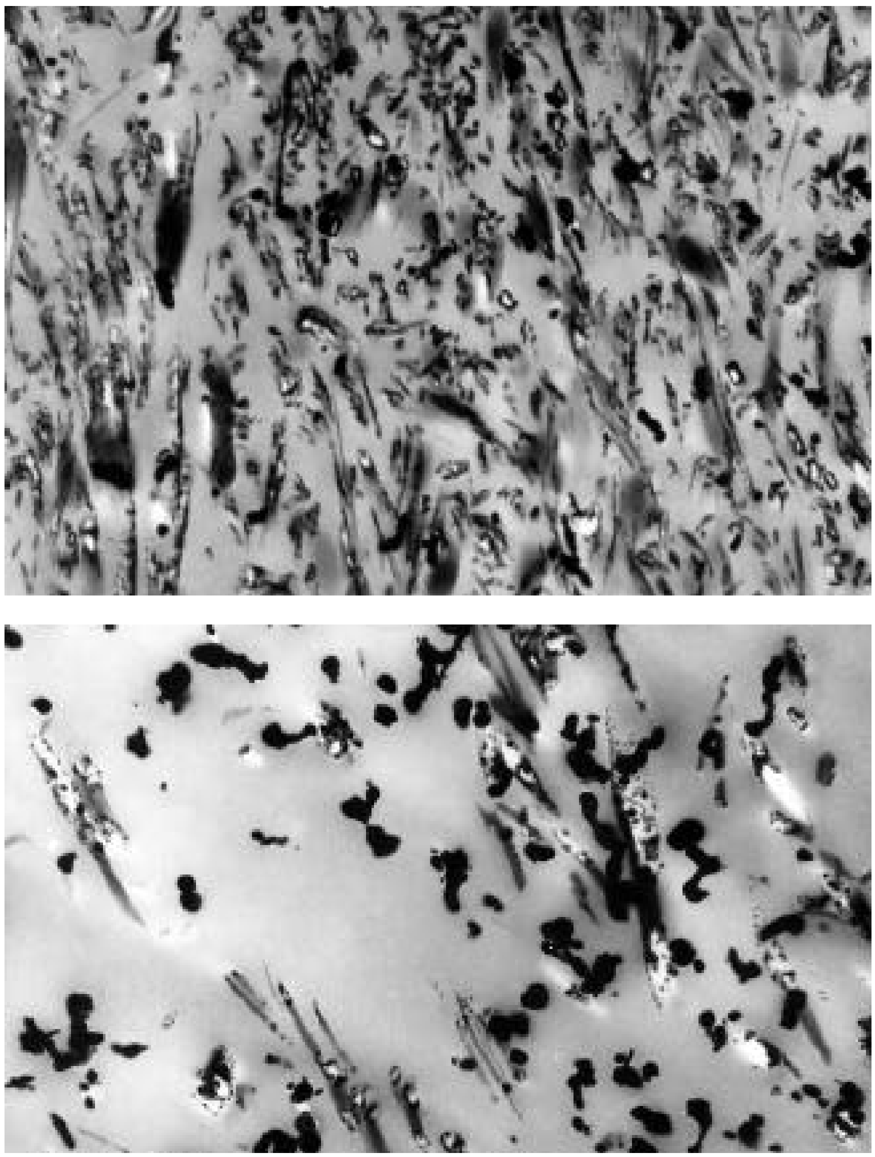

Figure 5. Transmission electron micrographs of sample 1 (Figure 3), with (top) and without (bottom) PEH (10 seconds at 115°C), developed 10 seconds at 115°C (60,000X).