Sensitometric Consequences of Pre-Exposure Heating on Thermally Developed Photographic Materials (TDPM)

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

B. B. Bokhonov
Solid State Chemistry Institute, Russian Academy of Sciences, Siberian Branch, Russia

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

Reduction of sensitometric image parameters of two-layer thermally developed photographic materials, subjected to pre-exposure heating, is connected with the presence of toners in the photolayer. It is shown that incorporating the developing agent in the photolayer and the toners in the protective layer improves sensitometric image parameters of such materials. Mechanisms for the effects are discussed.

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Introduction

Thermally developed photographic materials (TDPM), based on admixtures of silver halides and silver carboxylates, make up a complex system, aimed at optical image recording and visualization through a development process. But regardless of the similarity of their functions to those of classic silver halide photolayers, they have some distinctive peculiarities,[1] influencing the processes of latent image formation and development. Unlike classical photographic materials, in which the photosensitivity of the photolayer[2] is raised by heating to 100° for up to 20 min., the TDPM already begins to lose its development selectivity on 2 sec of pre-exposure heating (PH) at 115°. We have proposed[3] that such TDPM behavior is connected with the toners in a photolayer, which either lose their activity or somehow influence the development centers while being subjected to PH. Our results, however, appear to be contrary to those reported by Leenders and co-workers[4] who claim that sensitivity of TDPM can be increased if exposure is simultaneous with heating.

The aim of this article is to elucidate PH action on sensitometric parameters of two-layer TDPM samples. These constructions, which are well-known in the art of TDPM,[5] comprise a photo- (lower) and a protective (topcoat) layer, in which toners and a developing agent are introduced in different combinations.

Experimental

A photolayer, prepared by a published method,[6] comprised silver stearate (AgSt), silver bromide (AgBr), stearic acid, and optical sensitizing dye, all dispersed in polyvinylbutyral (PVB) resin. Halidization was effected by the in situ process, using LiBr. After the photolayer had dried in air, a protective layer was then coated from 2.5 wt. % PVB solution in isopropyl alcohol. In the formulation of these layers, the following components were introduced from 100 ml. stock solution: the developing agent, *bis*-alcophen (BA, 15 ml. of 12% alcohol solution), and toners, phthalimide (PI, 2 g.) and succinimide (SI, 12 ml. of 5% solution in acetone). Structures and origin of the dye, developing agent, and toners used in these formulations are as previously reported.[3,6] The thickness of the dried photolayer was 8 μm, and of the protective layer was 2 μm, coated on polyester film base.

Pre-heating and sensitometric experiments were carried out in the manner previously described.[3] The samples were subjected to PH of different durations, exposed in an FSR-41 sensitometer and developed. The temperature of PH and of development was 115°. Development was for 20 s for the data reported below; other development times were also employed, but results obtained under these conditions essentially paralleled those obtained at 20 s. Optical step tablet densities were measured with a DP-1M densitometer; image densities reported below correspond to step 5 of the wedge.

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▲ IS&T Member

* Author to whom correspondence may be addressed at: usanov39@mail.admiral.ru

TABLE I. Sensitometric Consequences of Location of Toners in Bilayer TDPM with Developer in Top Coat, With and Without 20 sec PH

PI	SI	PH	D	D_o	$(D - D_o)$
+	–	–	1.82	0.22	1.60
–	+	–	1.27	0.25	1.02
+	+	–	1.81	0.34	1.47
–	–	–	1.02	0.28	0.74
+	–	+	0.90	0.35	0.55
–	+	+	0.77	0.42	0.35
+	+	+	1.02	0.87	0.15
–	–	+	0.94	0.31	0.63
Contrasts for effect of:	PI in photolayer		+ 0.19	+ 0.065	+ 0.13
	SI in photolayer		+ 0.024	+ 0.09	– 0.065
	PH		– 0.28	+ 0.108	– 0.39
	Interaction of PH with PI in photolayer :		– 0.14	+ 0.06	– 0.20
	Confidence limits:		+ 0.04	+ 0.08	+ 0.067

Results

In the first statistically designed experiment we compared the effects of locating the toners, phthalimide and succinimide, in the top coat and in the photolayer, for bilayer films in which the developing agent was always in the top coat. The design of the experiment, sensitometric responses and contrasts for effect,[7] i.e., variable-dependent differences in responses, are reported in Table I. In Table I, (+) designates that a reagent is in the photolayer; (–) designates that it is in the top coat. The sensitometric responses are image density at step 5 (D), fog density (D_o), and development selectivity ($D - D_o$). Contrasts for effect are calculated in the usual manner for designed experiments. Statistically significant results are underlined in the Table. Duration of preheating was 0 (–) or 20 sec (+). These notations follow the usual practice in statistical design of experiments.[7] Intermediate PH times yielded similar, but less dramatic, effects.

We find that phthalimide in the photolayer activates the development process (higher D at a given time of development) and improves selectivity of development. But it also sensitizes the TDPM to the effects of PH, namely image density losses and fog increases. The location at which SI is introduced appears to have little sensitometric consequence.

In the second designed experiment, carried out on bilayer films with toners in the top coat, we looked at the effect of putting the developing agent in the photolayer, versus the top coat. The plan of the experiment and results are shown in Table II, following the same notation and with the same confidence limits as used in Table I. In this case, all reported contrasts for effect are statistically significant. From these results we infer that when all major reactive components of the film are in the top coat, PH is essentially without effect; this result had already been apparent in the data of Table I. When the developing agent is in the photolayer, however, the most reactive construction results, as evidenced by the large values of D and of ($D - D_o$). Both sensitometric consequences, i.e., density losses and fog increases, of PH furthermore require developing agent in the photolayer.

To clarify the role of the toners in PH a further experiment was carried out, in which the developing agent was included in the photolayer, and toners were again in the top coat. One construction (a) was subjected to PH after coating the photolayer but before application of the top coat; the second construction (b) was fully

TABLE II. Sensitometric Consequences of Location of Developing Agent in Bilayer TDPM with Toners in Top Coat, With and Without 20 sec PH

BA	PH	D	D_o	$(D - D_o)$
–	–	1.02	0.28	0.74
+	–	3.67	0.60	3.07
–	+	0.94	0.31	0.63
+	+	1.25	1.05	0.20
Contrasts for effect of:	BA in photolayer	+ 0.74	+ 0.265	+ 0.48
	PH	– 0.625	+ 0.12	– 0.745
Interaction of PH with BA in photolayer:		– 0.585	+ 0.105	– 0.69

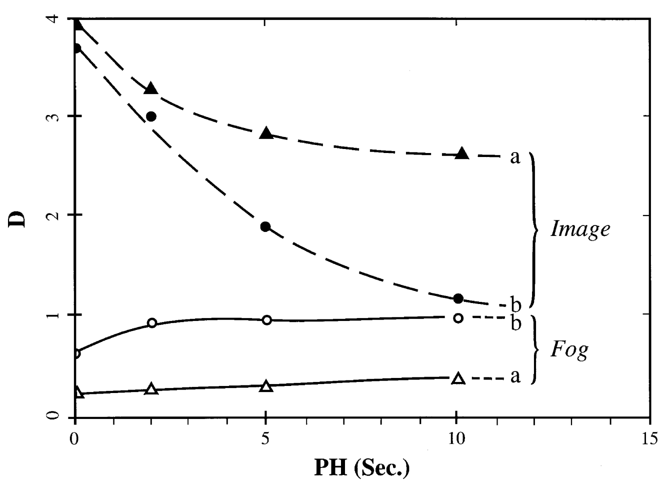

Figure 1. Changes in image density (D, dashed lines) and fog density (D_o, solid lines) with time of PH for films in which toner containing top coat is applied after (a) and before (b) PH. Lines are solely for the purpose of guiding the eye.

assembled before being subjected to PH. In this experiment, PH times from 0–10 s were employed. Changes in D and in D_o with time of PH are shown in Fig. 1. While both constructions exhibit loss in D with PH time, the effect is much more pronounced in film (b) in which the toners are present in the top coat during PH. Interestingly, however, almost no growth in D_o occurs during PH in the absence of toner. It should be understood here that, because PH occurs above the T_g of PVB, species from the top coat may diffuse into the photolayer. This diffusion may be enhanced as a result of plasticization of PVB by stearic acid,[8] which is present as the free acid in the photolayer of these constructions. Thus we infer that toner, as well as developing agent, is required for the sensitometric effects of PH. The hypothesis[3] that loss in image density may involve loss of reagents during PH are likewise excluded.

Discussion

We interpret the results reported in Tables I and II and in Fig. 1 in terms of a series of hypotheses. These, in turn, derive from the demonstrated significance of the role of the AgBr–AgSt epitaxial interface[9] both to latent image formation according to the photocatalytic mechanism,[1,10] and to the mechanism of the development process in TDPM.[11] The relevance of the AgBr–AgSt interface to the phenomenology of TDPM has recently been called into question,[12] albeit on exclusively negative evidence. We also assume that reaction between toner and AgSt, through formation of silver(I)-toner complexes, is prerequisite to the further reaction of silver ion with the developing agent, as demonstrated by Whitcomb and Rogers,[13] and more recently confirmed by Maekawa.[14]

1. During PH (or development) toners react with AgSt to form silver complexes preferentially at the AgBr–AgSt interfacial zones. This reaction structurally disrupts the interfacial zone.
2. The disrupted interfacial zone is less effective for photocatalytic latent image formation. Hence D falls with PH.
3. Toner complexes formed during pH react with developing agent to form fog centers. Hence D_o increases with PH time.
4. The fog centers may develop to produce silver with lower covering power than that formed from latent image in intact interfacial zones. This last proposal follows directly from the results reported by Bokhonov.[11]

To the extent that toner complex formation may be driven by the catalytic reduction of the complexes during development, this proposal also accounts for the apparent “secondary nucleation” occurring during continued image development of TDPM.[15]

Disruption of the interfacial zone may also be a consequence of disorder in the packing of the hydrocarbon chains in the silver carboxylate phase, which has been shown to occur at temperatures close to those of the PH.[16] Such structural disorder may also affect the ability of the silver carboxylate to function as a two-dimensional semiconductor, as demonstrated at room temperature[17] and as assumed in the photocatalytic mechanism.[10]

Conclusions

Degradation of sensitometric response under the influence of pre-exposure heating is determined by the toners’ presence in the photolayer of bilayer TDPM. Sensitometric parameters of TDPM, and, by inference, their shelf-stability, are considerably increased by toner exclusion from the photolayer and their introduction in the protective top coat. Exclusion of developer from the photolayer further mitigates the effects of PH but at the price of reduction in image developability. These results are interpreted in terms of a series of mechanistic hypotheses, which emphasize the importance of the epitaxial AgBr–AgSt interface to TDPM function.

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