Study of Image Contrast in a One Sheet Diffusion Transfer Reversal System Influenced by Several Inhibitors

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Effects of several inhibitors on contrast of physical developed silver in one-sheet DTR (diffusion transfer reverse) system were studied in this article. In this DTR system, the general measured reflection density could not be directly adopted because it was a comprehensive value of physically developed silver on the surface and chemically developed silver in the emulsion. For this reason, a one-dimensional CCD instrument was applied to monitor the reflected light intensity during development. The light intensity was accepted to describe the amount of physically developed silver of each exposed step on plate, then the contrast coefficient could be calculated out from the curve of light intensity versus logE. It was found that some inhibitors could improve the contrast of physically developed silver image accompanied with an improvement on sensitivity in this one-sheet DTR system.

Journal of Imaging Science and Technology 46: 123–128 (2002)

Introduction

The silver halide diffusion transfer reversal system (DTR) has been widely used in offset materials, stencil printing systems and instant photography.[1] In recent years, Computer-to-Plate (CTP) printing plates based on the one-sheet DTR system have attracted much interest since it became one of the most popular CTP processes after Drupa 1995.[2,3] When a strip of this type of plate is developed, silver halide grains in the fully exposed area are chemically developed into silver in the emulsion, meanwhile the grains in unexposed area are physically developed to silver and deposited on surface of the plate. In the moderately exposed area, there is both chemically developed silver in the emulsion and physically developed silver on the surface. Usually, the characteristic curve (D – Log E) is applied to describe the relationship of optical densities D of developed silver to exposures, where D is either reflection or transmission density.[4] When we try to determine the characteristic curve of the one-sheet DTR plate in the usual manner, numerous difficulties are encountered.

The theoretical characteristic curves of physically developed silver and chemically developed silver are respectively shown as Curve A and B with dashed lines in Fig. 1,[5] and the measured characteristic curve (reflection density versus Log E) on the developed plate is shown as Curve C. Obviously, the measured characteristic curve C is a result of superposition of Curve A and B, i.e., the measured reflection density is a comprehensive value with physically developed silver on the surface and chemically developed silver in the gelatin layer. So it is impossible to distinguish how much of the measured reflection density should be attributed to the former or the latter. For this reason, conventional reflection densitometry is not suitable for describing the characteristic curve of developed silver in such a one-sheet DTR system, and some kind of new approach is required.

Because the charge coupled device (CCD) has many advantages, it has been widely used in many scientific fields, such as astronomy,[6] microscopy,[7] spectroscopy,[8–10] etc. In our earlier research,[11,12] a one-dimensional CCD instrument was successfully established to monitor the kinetics of physical development *in situ* in real time. In this article, we attempt to apply it to determine the characteristic curve of physically developed silver on the one-sheet DTR plate.

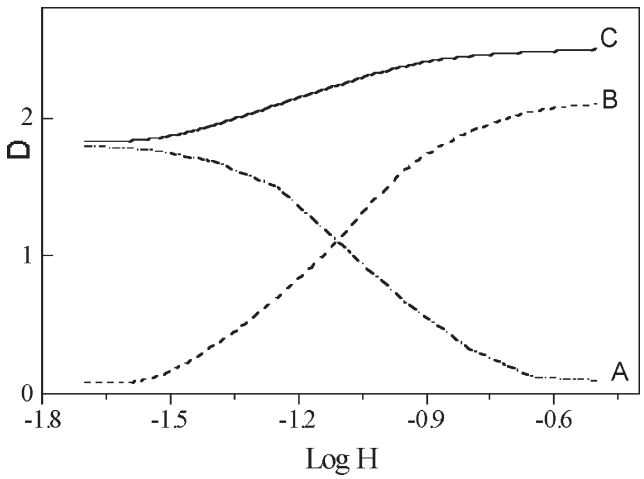

Figure 1. The theoretical characteristic curves for physical developed silver and chemical developed silver and the measured characteristic curve. A: physically developed silver; B: chemically developed silver; C: measured reflection density (D) – Log E.

Original manuscript received May 19, 2000

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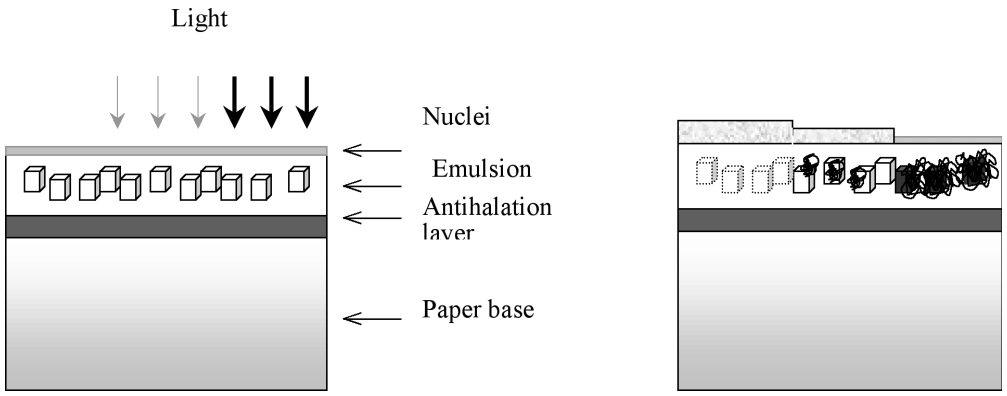


Figure 2. Cross sections of the experimental plate. a: Exposing; b: After development.

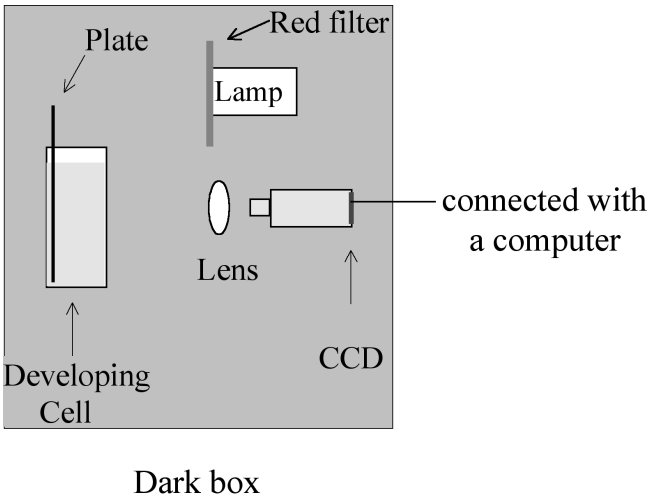


Figure 3. CCD instrument monitoring the developing process.

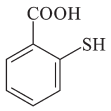
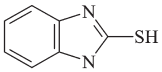
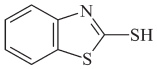
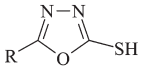
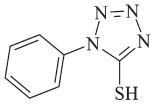
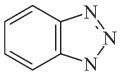
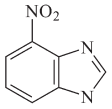
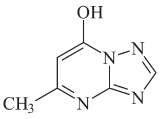
As known, many properties of a plate can be obtained from its characteristic curve, such as sensitivity, silver density, fog density, and contrast. Above all, the image contrast is the most important characteristic for a printing plate in order to obtain a good halftone image. Several approaches have been proposed to obtain high contrast in chemical development, including lith development,[13] hydrazine[14] and iodide anion infectious development.[15] Inhibitors also can be used to improve the contrast. Sahyun[16,17] claimed that **NBM** (6-nitrobenzimidazole) greatly improved the contrast in chemical development when it was synergistic with iodide anions. He also found that the effect of Benzotriazole (**BTA**) on contrast was negligible although it could suppress fog and improve the development selectivity of the latent image. In addition, the effects of some other inhibitors on contrast were examined by many researchers.[18–20] Concerning influence on contrast in physical development, however, there are few results to be found in the literature. In this article, the effects of several inhibitors on contrast of physical development in the one-sheet DTR system have been studied with our established CCD instrument.

Experiments

Experimental Plate

The experimental plate was prepared as described in our previous article.[21] The cross sections of plate before and after development are shown in Fig. 2 (left). An antihalation layer containing hydroquinone and Metol was first coated on a plastic coated paper and then a silver chloride emulsion layer sensitized to green light was coated on the dried anti-halation layer. After these two layers were hardened, colloidal metal sulfide was coated on the surface of emulsion layer to serve as nuclei of physical development. After the plate was exposed and developed, filamentary silver was formed in the emulsion layer whereas physically developed silver was deposited on the nucleation layer, as shown in Fig. 2.

TABLE I. Molecular Stuctures of Inhibitors

Molecular structure	Name	Abbreviation
	2-mercaptobenzoic acid	MBA
	2-mercaptobenzimidazole	MBM
	2-mercaptobenzithiazole	MBT
	2-mercapto-5-heptyl-oxidiazole	MHO
	1-phinyl-5-mercapto-tetrazole	PMT
	Benzotriazole	BTA
	6-nitrobenzimidazole	NBM
	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	TAI
KBr	Potassium bromide	KBr

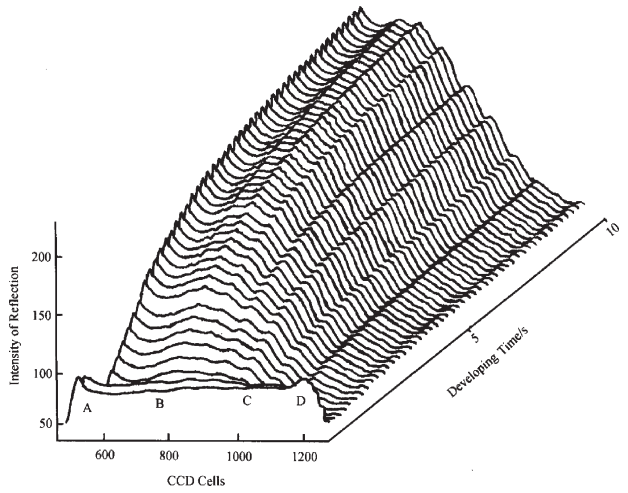


Figure 4. The three-dimension plot monitored by CCD—changes of reflection intensities with time and exposures. AB: weakly exposed steps; BC: moderately exposed steps; CD: strongly exposed steps.

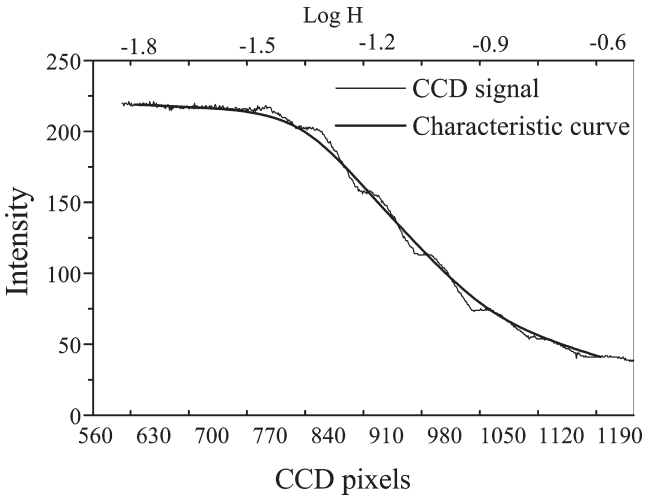


Figure 5. Relation between reflected light intensity of physically developed silver and CCD pixels (corresponding to exposure step) at development end.

Developer Solution

The general composition of the development activator solution was:

Potassium hydroxide	5.0g
Sodium sulfite	50.0g
Sodium carbonate	5.0g
Sodium thiosulfate	5.0g
Diethanolamine	80.0g
Add water to	1 liter

Inhibitors were added optionally to the development activator solution. Nine inhibitors were used in the experiments. Among them, there were five inhibitors with mercapto groups and three (excluding those with both mercapto groups and amino groups) with the amino groups. Their molecular structures are listed in Table I.

CCD Instrument

The schematic for the CCD instrument is shown in Fig. 3. A tungsten iodide lamp with a red filter was fixed on the upper side of a developing solution cell in which a strip of plate was developed. The illumination was 12.9 lux and the incident angle was 45 degree to the plate surface. A one-dimensional CCD (TCD102C type, 2048 pixels) was installed to collect the reflected light every 200 ms for 20 sec from the normal direction to the plate. The whole instrument was put in a dark box, and the CCD was interfaced with a computer.

Results and Discussion

Characteristic Curve Monitored by the CCD Instrument

When a strip of plate was developed in the developing cell, the reflected light from the physically developed silver on each step was collected by the pixels of CCD and transferred to the computer. A three-dimensional plot indicating the change of reflected light intensity with CCD pixel number and time was recorded as shown in Fig. 4. The x-axis indicated CCD pixel number, every 70 of which represented a step on the wedge as shown in Fig. 5. As reported in our earlier experiment,[12] the reflected light intensity was approximately

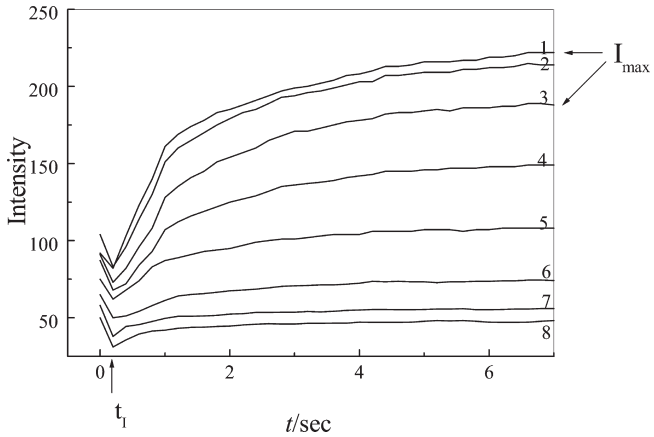


Figure 6. Developing process for each step on strip. I_{max}: maximum intensity when development end; t_I: induction period.

proportional to the amount of the physically developed silver per unit area (g/m^2), and had little correlation with chemically developed silver in the gelatin layer. Therefore, the reflected light intensity could be adopted to indicate the amount of physically developed silver for a certain exposure level. The resulting curve in Fig. 5 was similar to a conventional reversal characteristic curve. Then the contrast could be obtained from Eq. 1, in which ΔI was the change of reflected light intensity over a segment of the linear portion of the curve.

$$\gamma = -\Delta I/\Delta \log H \quad (1)$$

There is no equation available to calculate the sensitivity for a one-sheet DTR system, especially under these conditions using reflected light. So here we arbitrarily define sensitivity as the reciprocal of the exposure where the reflected light intensity reaches $I = I_0 + 20$.

The development process of each step on the strip can be seen clearly in Fig. 6. In this figure, the exposure of these steps increases sequentially from curve 1 to curve 8 where curve 1 corresponds to the step of the wedge at CCD pixel No. 630 and curve 8 corresponds to the step

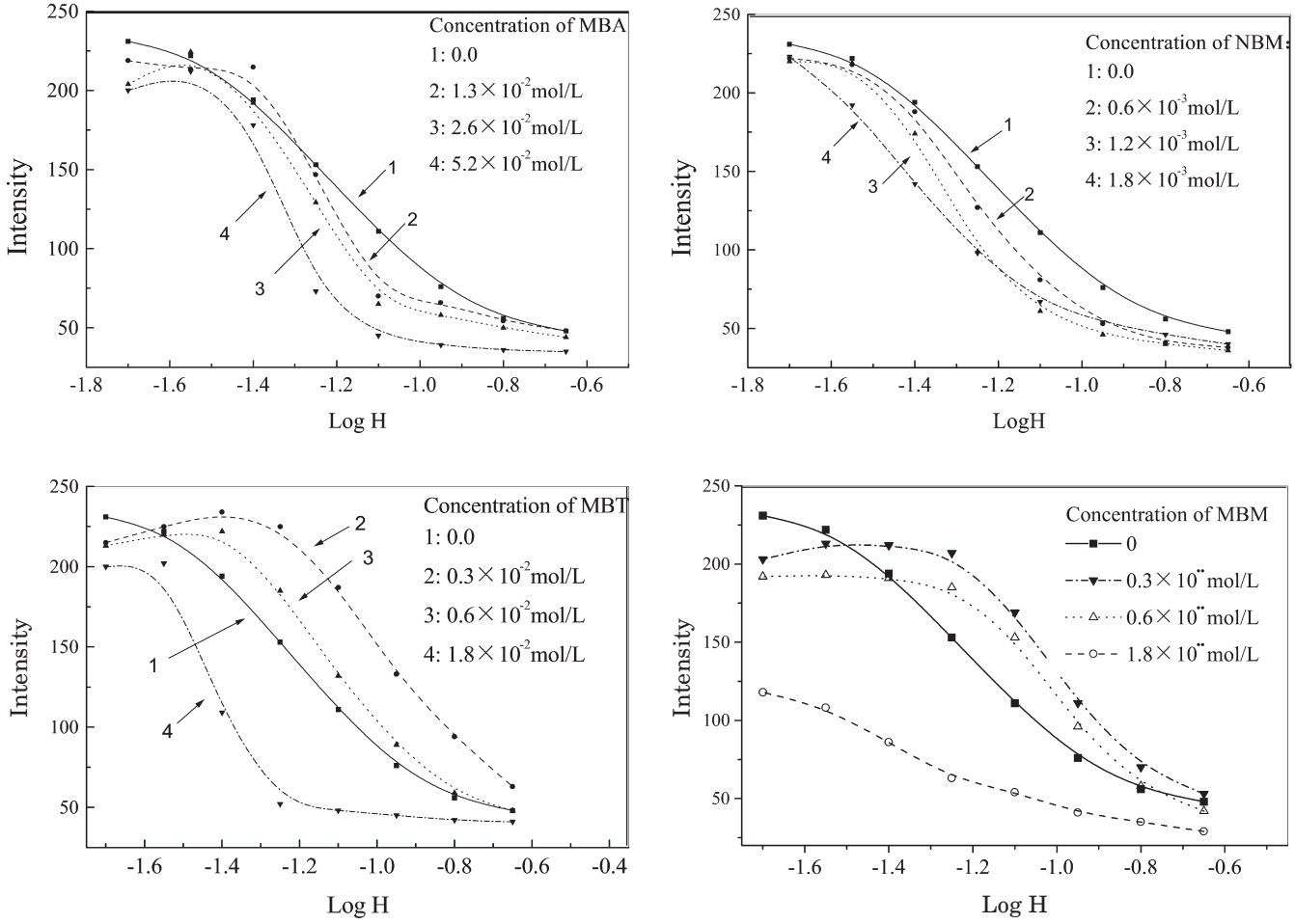


Figure 7. Effects of different inhibitors on characteristic curves.

of the wedge at CCD pixel No. 1190; t_I is the induction period of physical development; I_{max} is the maximum reflected light intensity at the end of development. The t_I estimates may differ from each other for each of these 8 steps, as did their I_{max}, showing different dynamics of the developing process at different steps.

Effects of Inhibitors on Characteristic Curve

The inhibitors were added into development activator solution, and the resulting characteristic curves at different concentrations are shown in Fig. 7. It was shown in Fig. 7-1 that MBA greatly inhibits the physical developed silver on strongly and moderately exposed steps with the increase of its concentration. Meanwhile the weakly exposed steps were only slightly influenced. As a result, the characteristic curve, e.g., curve 4, became sharper compared with curve 1 (no inhibitor), indicating that the contrast of the physically developed image was improved. A similar result was obtained when NBM was used instead of MBA, which was shown in Fig. 7-2 as curve 2 and curve 3. However, if the concentration became higher, the contrast again decreased due to inhibition both in strongly exposed steps and weakly exposed steps.

From Figs. 7-3 and 7-4, it could be seen that the contrast could be improved in another way. For the inhibitor MBT, the physical development, both in the strong exposed steps and in moderately exposed steps, seemed to be enhanced when the concentration of MBT was 0.3×10^{-2} mol/L (see curve 2) and 0.6×10^{-2} mol/L (see curve 3). The slope of curve also slightly improved. When the concentration increased to 1.8×10^{-2} mol/L, the physically developed image in the strongly exposed steps was reduced to a very low level. On the contrary, the influence on the weakly exposed steps changed only slightly. As a result, the image contrast again was improved. The behavior of MBM was similar to MBT: at its lower concentration, it enhanced the physical development in strongly exposed steps, accompanied with a slight improvement in contrast; when its concentration became higher, physical development in all steps wes strongly inhibited.

If we take the contrast coefficient of a developed plate without any inhibitor in the developing solution as 1.00, then the relative contrast coefficients with inhibitors may be calculated. The results are illustrated in Fig. 8. The inhibitors,[16,17,19,20] which were expected to improve the contrast, did improve, more or less, the contrast of physically developed silver in the DTR system. Considering that the total amount of silver is constant, inhibitors should be also effective in improving the contrast if they functioned in chemical development. Of course, this is not a problem of simple arithmetic, because the diffusion of the silver complex into solution also varies with exposure.[17] Furthermore, exposition of internal latent image on dissolution of silver halide caused by

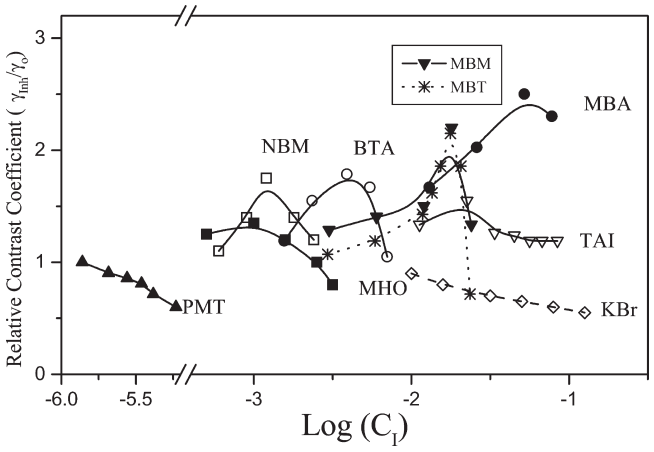


Figure 8. Effects of inhibitors on relative contrast coefficients at different concentrations C_I: concentration of inhibitor (mol/L).

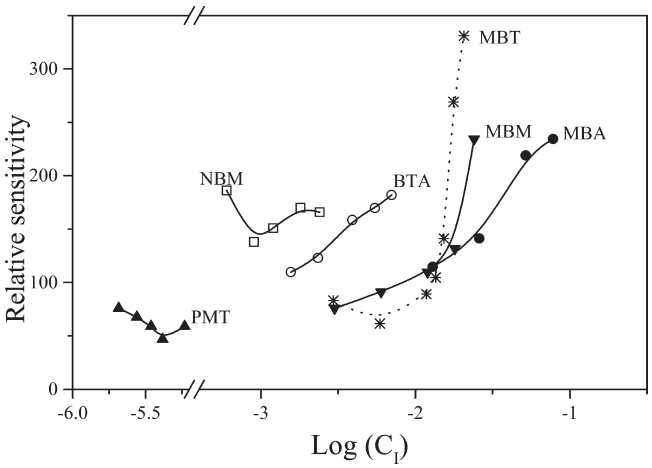


Figure 9. Relative sensitivities affected by inhibitors under different concentration.

fixer may also effect the contrast improvement, as pointed out by Sahyun.[18] This effect might be explained as a result of different behavior of an inhibitor in physical development and chemical development. The details however, require further evidence and will not be discussed in this article.

The effects of inhibitors on the contrast coefficient are shown in Fig. 8. Generally, the contrast increases with concentration of inhibitor, reaches a maximum, and then goes down except for PMT and KBr. It also may be seen that the concentration ranges and the extent of improvement of contrast for the various inhibitors are quite different. For instance, PMT is a strong inhibitor, it suppresses the image contrast; on the contrary, KBr, which also suppresses the contrast, is only a weak inhibitor. Furthermore, MBA improves the contrast greatly although its inhibition ability is similar to that of KBr. So it could be inferred that the effect of an inhibitor on contrast is of little relationship to its development inhibition ability.

The relative sensitivities (taking sensitivity without inhibitor as 100) affected by these inhibitors are shown in Fig. 9. For MBA and BTA, the sensitivity increased with the increase of inhibitor's concentration. This seemed contrary to our general knowledge. However, it would be tenable when we consider the competition between chemical development in the emulsion layer and physical development in the nucleus layer. When a plate was put into the development activator solution, the inhibitor preferred to react with the surface metal nuclei to inhibit the physical development, and reduce the amount or rate of inhibitor diffusing into the emulsion layer. As a result, the chemical development was less inhibited than physical development. The exposure to obtain a given intensity of physically developed image thus became lower than without inhibitor. In other words, selective inhibition on the nuclei improved the sensitivity of the physically developed image.

For the inhibitors MBT and MBM, the sensitivity went down below 100 at first and then rose as their concentration increased. This result implied that the chemical development was inhibited more than physical development when the concentration was low. As we know, the size of the nuclei is of the order of several nanometers, far larger than the size of latent image on the silver halide crystal. When we take into consideration their different sizes, it might be understandable that the relative sensitivity of these two kinds of centers varied with the change of the inhibitor's concentration. At lower concentration of inhibitor, the chemical development, due the small size of the latent image, was more sensitive to the inhibition effect than the nuclei. Thus, physical development took precedence over chemical development, resulting in a decrease of sensitivity. When the concentration of the inhibitor became higher, the physical development would preferentially be inhibited compared to chemical development, because of the difference in inhibitor's concentration owing to diffusion.

Effects of Inhibitors on Developing Process

Physical development processes affected by some inhibitors were monitored with the CCD as shown in Fig. 10. Compared with the dynamic curves without inhibitor seen in Fig. 6, it appeared that the induction periods of physical development were prolonged more or less for all steps. The induction period in weakly exposed steps (curves 1~3) reached 2.8 sec when MBA was used as inhibitor (Fig. 10-1), compared with no longer than 0.2 s when no inhibitor was used (see Fig. 6). The intensities recorded for the physically developed image in curves 1~3 were above 200 when the development finished, indicating that the physical development was only slightly inhibited. In the strongly exposed steps, e.g., curves 6~8, the physical development was strongly inhibited or did not occur at all.

After examining the other figures, we found that the differences among induction periods for different steps was enhanced. The greater the exposure, the longer the induction period would be. For example, the induction period of curve 4 was longer than for curve 3 in Fig. 10-1; the induction period of curve 3 was longer than that of curve 2 in Fig. 10-4. Furthermore, the physical development rate would obviously slow down for strongly exposed steps or even be totally inhibited, e.g., curves 6~8 in Fig. 10. On the contrary, the physical development in the weakly exposed steps was little influenced in rate although the induction periods were prolonged. The difference of inhibition effect in different exposure steps resulted in an improvement in the image contrast.

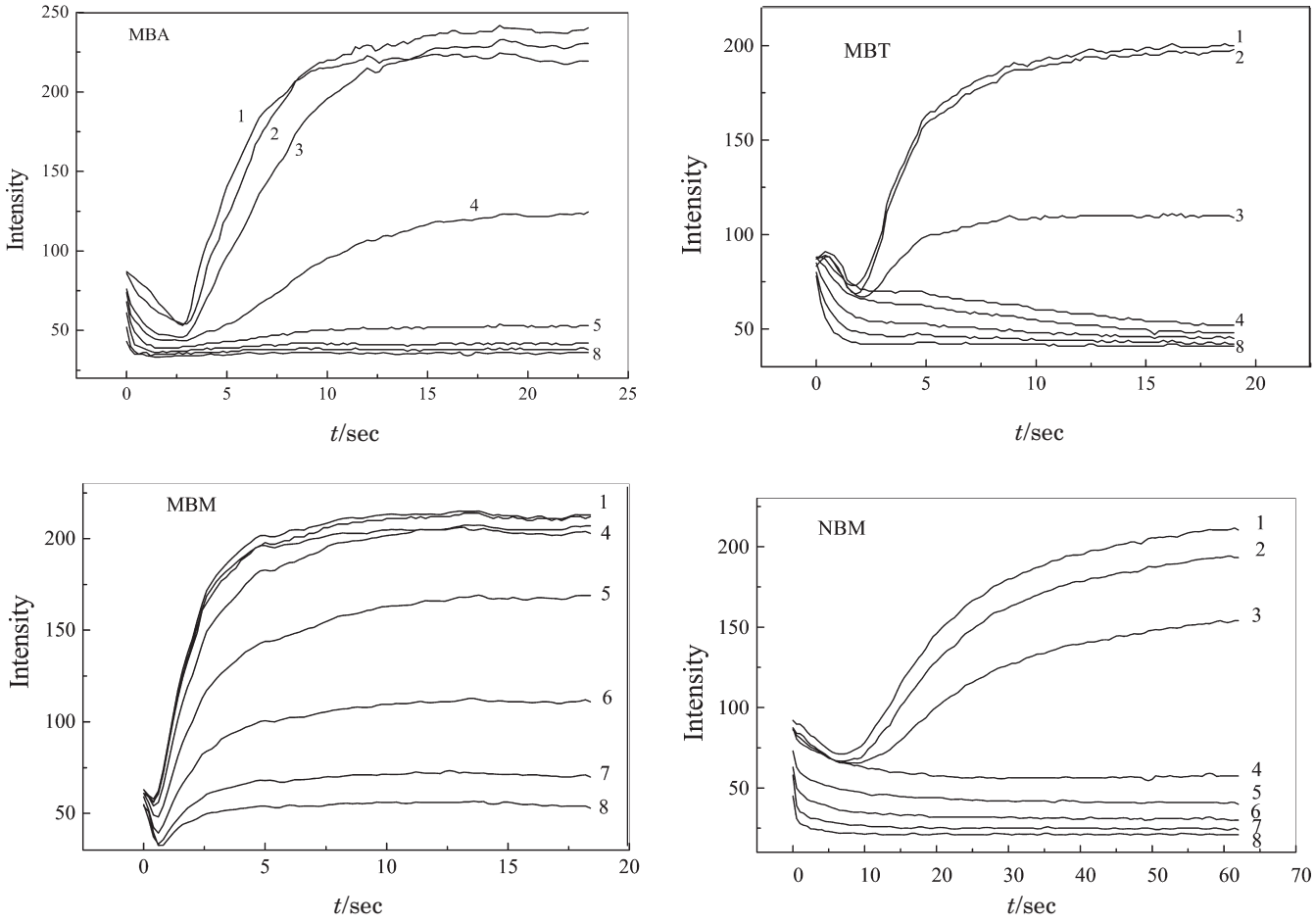


Figure 10. The dynamic curves of physical development for each step. The concentrations of MBA, MBT, MBM and NBM were 5.2×10^{-2} mol/L, 0.3×10^{-2} mol/L, 1.8×10^{-2} mol/L and 1.2×10^{-3} mol/L, respectively.

Conclusion

The CCD technique was applied to study the characteristic curve of a one-sheet DTR system and to examine the effects of several inhibitors on contrast of physically developed silver. The results showed that some inhibitors were effective in improving the contrast in physical development accompanied with an increase of sensitivity. The difference in prolongation of the physical development induction period and a slowing down of development rate in variously exposed steps appeared to be factors interacting to improve the contrast.

Acknowledgment. The authors are in debt to Professor Peijie Xia for his kind suggestions to the experiments. And thanks should be given to the editors and referees of this Journal for their constructive comments to this article. This work was supported financially by the National Science Foundation of China (Grant No. 69848002) and by the Eastman Kodak Company.

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