

Factors Limiting the Developing Speed of Color Paper

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Abstract

The effects of yellow couplers on the developing speed of silver chloride were studied, and couplers having hydrophilic ballasting groups were found to retard the initiation of development. Oil droplets containing such couplers absorbed more color developing agent than did couplers having more hydrophobic ballasting groups. Results suggested that an initial lack of color developing agent in the aqueous gelatin phase of an emulsion caused this retarded initiation of development.

Introduction

The rapid development of color paper has long been desirable, yet many obstacles remain to higher developing speeds. Tomotake et al. studied the relationship between the structures of yellow couplers and their reactivities. They suggested that couplers with ballasting groups that included a sulfonyl group yielded higher final densities¹. However, such couplers brought about slower developing speed in the initial development stage. Later, Tomotake reported that the higher the hydrophilicity of yellow coupler was, the more retarded silver development was². Our study examined such effects, with the distribution of color developing agents of particular interest.

Experimental

To analyze silver development, test strips were fabricated, exposed, processed, and measured through x-ray fluorescence. Coupler emulsions were prepared using an ultrasonic homogenizer to homogenize the oil and aqueous phases of emulsions. Their oil phases contained di-*n*-butyl phthalate along with various couplers, while their aqueous phases were composed of gelatin, surfactants, and distilled water. These coupler emulsions were then mixed with gelatin and blue sensitized silver chloride microcrystals averaging 0.87 μ m in size. The mixture was coated on resin-coated paper, resulting in a coupler coverage of approximately 1.1mmol/m², a silver chloride coverage of approximately 2.9mmol/m², and a gelatin coverage of 1.5g/m². Finally, a protective layer of gelatin and a hardener was overcoated on the emulsion layer. Following this fabrication, the resulting test strips were exposed and then developed with color developer (K-20P1, Konica Corporation). The pH of the developing solution was adjusted to pH 10.1 at 25°C, while processing was carried out at 35°C. After

development, the test strips were dipped in a stopping solution (3% acetic acid) and a fixing solution, and then washed with water.

To analyze the diffusion of a color developing agent into the oil phase, buffered emulsion solutions were prepared for voltammetric measurement. The buffered emulsion solutions were composed of 10ml of coupler emulsion, 10ml of carbonate buffer (109.4g K₂CO₃/liter, 63.2g KHCO₃/liter), and 2ml of 10mM CD (4-amino-3-methyl-*N*-ethyl-*N*-(β -methylsulfonamidoethyl)aniline). A reference solution without di-*n*-butyl phthalate or couplers was also prepared. The method of voltammetric measurement was similar to that of Matsubara and Texter³, but cyclic voltammetry was employed instead of rotating disk voltammetry. A BAS100B/W electrochemical analyzer was used. The working electrode consisted of a gold disc (1.6mm in diameter), polished with alumina powder before each measurement, while the counter electrode consisted of platinum wire and the reference electrode of Ag/AgCl. Temperature during measurement was adjusted to 40°C.

Results and Discussion

We measured the silver development profiles of a number of test strip coatings containing various yellow couplers. Typical of our results were those obtained with couplers Y-1 and Y-2, seen in Figure 1. Note that the ballasting group in Y-1 contains a sulfonyl substituted alkyl group, while that in Y-2 contains a normal alkyl group. As a reference, the silver development of a test strip coating with no oil component was also measured. Figure 2 presents silver development profiles for all three.

In the early development stage (i.e. within the first 10 seconds), silver development in emulsions with Y-1 was much slower than in emulsions with Y-2 or no oil component. Note that the Y-1 coupler is more hydrophilic than the Y-2 coupler. When we tested coatings containing analogues of Y-1 that had larger alkylsulfonyl ballasting groups (e.g. -SO₂C₁₈H₃₇), and were thus less hydrophilic, this retardation of silver development decreased. Together, these observations suggested that coupler hydrophilicity effects the initiation of silver development.

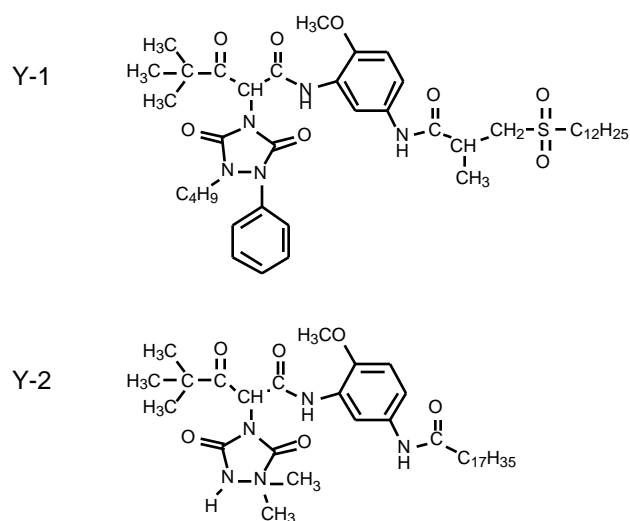


Figure 1. Yellow coupler structures

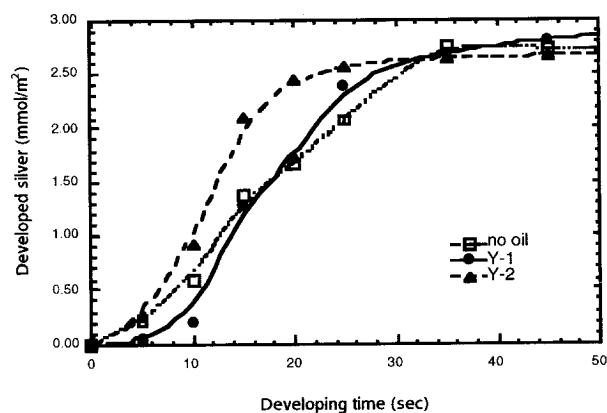


Figure 2. Silver development retarded and accelerated by couplers

The measurements in Figure 2 show that after a small amount of silver (approximately 0.2 mmol/m^2) was developed, the speed of silver development accelerated in both coupler emulsions. From this point onward, the developing speeds of the two coupler emulsions were approximately the same, though, because of the retarded initial development in the Y-1 emulsion, development in the Y-1 emulsion lagged behind that of the Y-2 emulsion by about 5 seconds. Because the chromogenic reaction in color paper that follows such redox reaction is faster than the redox reaction, the initial delay in development observed in the Y-1 emulsion is a serious obstacle to rapid processing.

The mechanism of this initial delay in development can be explained by interpreting cyclic voltammograms of CD in buffered emulsion solutions, as seen in Figure 3. Note that the oxidation peak current of CD decreased with the addition of coupler emulsions. It can be assumed that only those CD molecules dissolving in the aqueous phase were able to be oxidized. Since no substantial change of diffusion coefficient or of viscosity due to the addition of couplers would be likely under our experimental conditions, the decrease of the oxidation peak current was assumed to result from a decrease in the CD concentration in the aqueous

phase due to the diffusion of CD into the oil phase. Under this interpretation, Figure 3 indicates that the Y-1 oil phase contained a greater amount of CD than did the Y-2 oil phase.

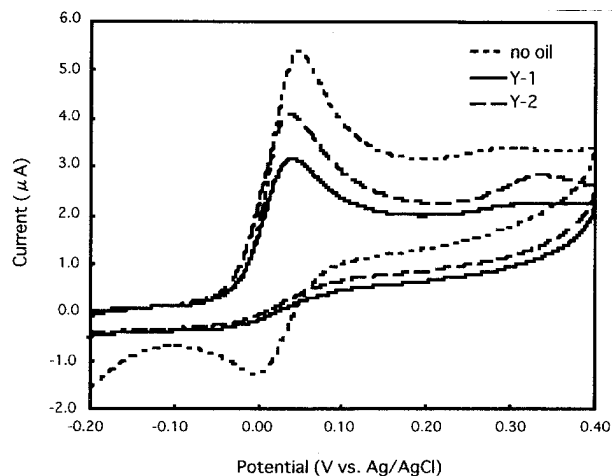


Figure 3. Cyclic voltammograms of CD in buffered emulsion solutions

Table 1. Voltammetric data and distribution coefficients of CD in buffered emulsions

Coupler	Cyclic voltammogram peak current (μA)	Distribution coefficient
no oil	5.03	0
Y-1	2.87	23.0
Y-2	3.95	10.7

We calculated the CD concentrations in the aqueous and oil phases, based on the volume of the oil phase being about 3%. We found, as Table 1 indicates by way of the distribution coefficients between the oil and aqueous phases, that large amounts of CD were diffused into the oil droplets. Texter et al. reported that the distribution coefficient of CD between di-*n*-butyl phthalate and the aqueous gelatin phase was about 9.0⁴. Our own results indicated that larger amounts were diffused into the oil phase when couplers were added.

This suggests the following mechanism. In the initial stage of development, CD diffuses from the developing solution into the aqueous gelatin layer. Based on the measured diffusion coefficient of CD in a gelatin layer being approximately $1 \times 10^{-6} \text{ cm}^2/\text{sec}$, we calculated that it takes 5-10 seconds to reach equilibrium concentration in gelatin layers of the thickness of our test strips. During this initial period of development, developing speed is determined by the concentration of CD in the aqueous gelatin phase. That concentration, in turn, is affected by the amount of CD that must be diffused into the oil droplets; the greater the amount that must be diffused into the oil droplets, the longer it takes for the concentration of CD in the aqueous phase to reach equilibrium, and the greater the retardation of silver development. Since the Y-1 oil droplets absorbed more CD

than did the Y-2 oil droplets, the former emulsion experienced a longer delay in silver development.

Approximately 5-10 seconds after the initiation of development, the concentration of CD reaches equilibrium both between the developing solution and the emulsion layer and between the aqueous and oil phases. Developing speed now depends on the electrochemical potential around the AgCl microcrystals. The couplers remove the oxidized CD from around the AgCl microcrystals, which increases the negative electrochemical potential around the AgCl microcrystals. This is why, in our experiments with test strips, silver developing speed accelerated by couplers after the first small amount of silver (approximately 0.2mmol/m²) was developed.

Since emulsions with oil phases whose yellow couplers have hydrophobic ballasting groups such as Y-2 absorb less CD into the oil droplets, but still efficiently remove oxidized CD, they complete silver development more rapidly than emulsions with oil phases whose yellow couplers have hydrophilic ballasting groups or emulsions that do not incorporate couplers.

Summary

The volume of CD diffusion into the oil phase of test emulsions proved to depend on the structures of the couplers they contained. The oil phases containing a yellow coupler with a sulfonyl substituted alkyl ballasting group absorbed more CD than that of a yellow coupler with a normal alkyl

ballasting group. The diffusion of a large amount of CD into the oil phase retarded silver development in the initial stage of development. In the next stage, development was accelerated by the efficient removal of oxidized CD from around the silver chloride microcrystals. This suggests that a yellow coupler with a less hydrophilic ballasting group shows greater promise in achieving the more rapid development of color paper.

Acknowledgments

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References

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