

# Rapid and Stable Processing for a Low Silver System

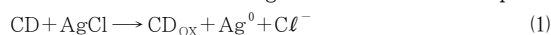
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Low silver color paper processing systems incorporating redox amplification are of two types, those with a combined developer/amplifier bath and those with separate developer and amplifier baths, and attempts to achieve a practical system with either have been fraught with difficulty. We were successful, however, in designing a system with separate developer and amplifier baths that employs the selection of processing solution additives and conditions to surmount the difficulties of solution stability and image degradation. In addition, the low silver system made it possible to employ hydrogen peroxide for bleaching agent and sodium sulfite for fixing agent. The system provides robust environmental protection, and delivering high-speed processing.

## 1 INTRODUCTION

The redox amplification process for low silver systems has been studied for some time.<sup>1-3</sup> When both the cost of silver and the volume of silver needed to make photographic materials were high, these studies were greatly motivated by economics. In recent years, however, the price of silver has been low and stable, while the volume of silver needed for photographic materials has dropped. In contrast, consciousness of environmental impact has grown.

With redox amplification, this is the chemistry of the color formation where CD designates the color developer:



Conventional development in color paper consists of Eqs. 1 and 3, so that the amount of developed silver is essentially equal to the amount of dye generated. The introduction of a redox amplifier Eq. 2 makes it possible to generate dye with a far smaller amount of silver developed, just 2% to 30% of the silver coated against conventional color paper. If a practical system were to be developed, this feature would naturally lower production cost, but the benefits would extend to the environment as well. There would be far less silver to be processed, and far gentler bleach and fix solutions could be used.

Efforts have been made to take advantage of this potential by tackling the problems inherent to redox amplification. From such work, two competing approaches have emerged: combining the developer and amplifier into a single bath and isolating the developer and amplifier from each other in two separate baths as shown in Figure 1.

The former process means that the reducing agent, that is, the color developer, and the oxidizing agent such as hydrogen peroxide are mixed together in the same

solution. Naturally, this makes the solution inherently unstable. In the latter process the reducing agent and the oxidizing agent are isolated in separate baths. These solutions are inherently more stable than the solution in the combined developer/amplifier bath. In this separate bath system, the CD is absorbed into the emulsion layer of the color paper in the development bath. The paper then carries it into the amplifier bath, where amplification and dye generation take place.

Evans et al.<sup>4</sup> and Wildman et al.<sup>5</sup> discussed the low silver color paper system of color paper at ICPS 1998. They and their colleagues have made many efforts toward progress of this technical field, and improved the stability of redox amplifier process.<sup>6-8</sup> They reported that they chose a single bath system because it allowed the replenishment rate to be lowered. This choice meant that their major challenge was the improvement of solution stability in this combined development/amplification bath. In our work, however, we took the converse approach. We believed that the mixing of a developing agent and an oxidizing agent was inherently unstable. Furthermore, we believed separate developer and amplifier baths could not only overcome solution instability, but could also present ways to improve image quality.

In addition to separate developer and amplifier baths, we decided to use separate bleaching and fixing baths as well. This allowed us to use environmentally preferable chemicals. We used hydrogen peroxide as our bleaching agent instead of ferric complexes of aminopolycarboxylic acids. And we used sodium sulfite as our fixing agent instead of thiosulfate compounds. Although this caused the system's total number of baths to increase, this was no sacrifice of processing speed.

## 2 RESULTS AND DISCUSSION

### 2.1 Silver Development and CD Absorption

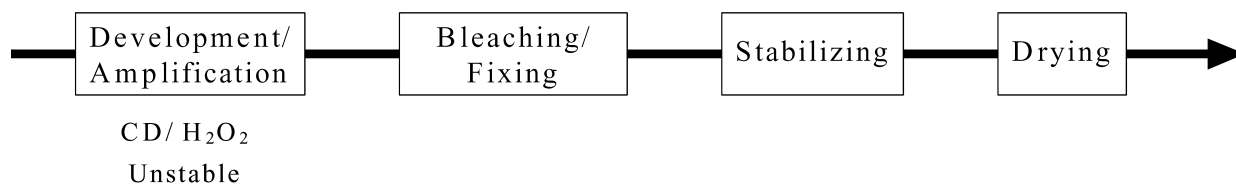
In the following experiments, a color paper containing AgCl about 20% of the level found in conventional ones was used. With this system, AgCl microcrystals carrying latent images are developed in the developer bath. Although the coupling reaction does occur, image dye generation is limited because the amount of oxidized color developer is small. At the same time, color developer (CD) is absorbed

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### (1) Combined developer/amplifier bath:



### (2) Separate developer and amplifier baths:

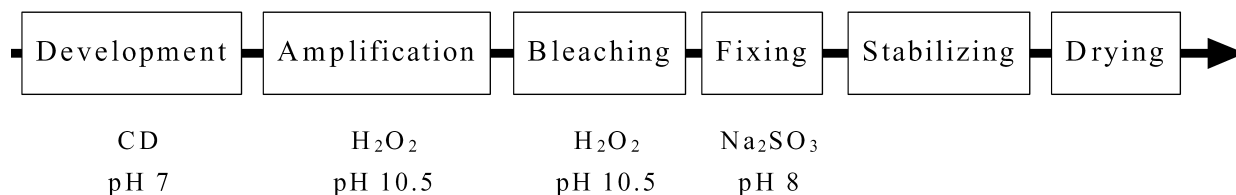


Figure 1. Two redox amplification processes. (1) Combined developer/amplifier bath, and (2) separate developer and amplifier baths. Bleaching and fixing baths can be divided in order to use gentler chemicals.

into the paper, where it diffuses evenly throughout all emulsion layers. When the paper reaches the amplifier bath, the absorbed developer is oxidized by the oxidizing agent, hydrogen peroxide ( $H_2O_2$ ), and the oxidized CD subsequently reacts with the couplers in the emulsion layers to generate appropriate amounts of dyes, insofar as the silver nuclei created in the developer bath serve to catalyze the color forming reaction in the amplifier bath.

Obviously, a sufficient amount of CD must be carried within the paper into the amplifier bath if adequate dye density is to be obtained. This is crucial to the use of separate developer and amplifier baths. To solve this problem, we examined the possibility of raising the CD concentration in the developer bath. The conventional color developing agent, *N*-[2-(4-amino-*N*-ethyl-*m*-toluidino)ethyl]-methanesulfonamide, dissolves more readily at lower pH. However, the lower the solution pH, the weaker the developing activity. As indicated in curve 2 of Figure 2, this might lead to long processing times. We examined the acceleration of the silver development at low pH, and found that adding black-and-white developing agents were effective.<sup>9</sup> Curve 3 of Figure 2 demonstrates the improvement in silver developing speed at pH 7 in the presence of ascorbic acid. The silver development was almost finished within 10 seconds even at this pH 7.

#### 2.2 Redox Amplification and Color Formation

When using a combined developer/amplifier bath, development, amplification and dye generation occur together. As indicated in Figure 3 (a), a longer processing time was taken to obtain adequate densities and color formation did not saturate, which might make the process unstable. Especially, the dye generation in yellow color forming layer which is usually located in the bottom of color paper and has characteristically larger AgCl grains, was relatively slow. This causes uneven color formation speed, and makes it difficult to control the color balance.

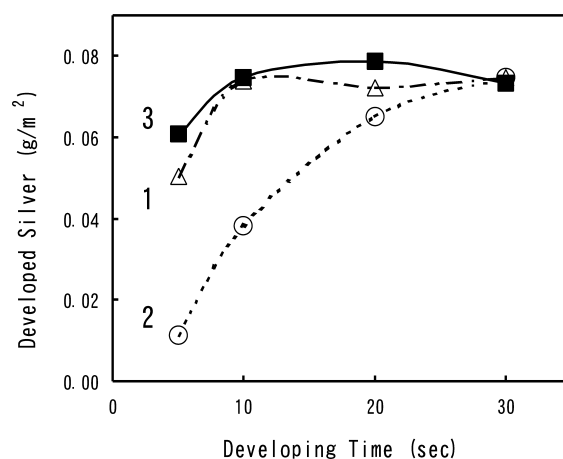


Figure 2. Effects of pH and ascorbic acid on development speed. Curve 1 ( $\Delta$ ); at pH 10, Curve 2 ( $\circ$ ); at pH 7, and Curve 3 ( $\blacksquare$ ); at pH 7 with 57mmol/l of ascorbic acid. The concentration of *N*-[2-(4-amino-*N*-ethyl-*m*-toluidino)ethyl]-methanesulfonamide (CD) was 19mmol/l at pH 10, and 43mmol/l at pH 7. In addition, 6.7mmol/l of NaCl and 8.4  $\mu$ mol/l of KBr were added to all the solutions.

In contrast, separating amplifier bath from developer bath led to rapid and stable color formation. While the color paper in the developer bath, CD diffuses uniformly throughout all emulsion layers. Each layer is in the same condition at the beginning of the amplifying process, that is, sufficient silver nuclei have been already produced and sufficient CD has already been introduced. Figure 3 (b) indicates that the color forming reaction in the separate development/amplification bath system is very rapid even in the yellow color forming layer. When using a redox amplifying solution whose  $H_2O_2$  concentration was 26 mmol/l at pH 10.5, maximum density reached saturation

within 10 seconds. This made it easy to control Dmax/Dmin balance. Although the high concentration of H<sub>2</sub>O<sub>2</sub> is not required, the high pH is necessary both for redox amplification and for dye generation.

This saturated density level is determined by the amount of color developing agent carried over from the developer bath. So, this process must be robust to the processing time and hydrogen peroxide concentration. The color developing agent carried from the developer bath decreased the hydrogen peroxide concentration in the amplifier bath, but we found that this small change of the H<sub>2</sub>O<sub>2</sub> concentration has little effect on color forming speed. And while some replenishment is necessary, process stability is maintained. To obtain more adequate density, balancing the oil components and the aqueous components of color paper would be necessary.

Poor granularity had been a problem commonly cited with redox amplification systems. Generally, the dye production at each development center of a redox amplification system is higher than in a conventional system, but there are fewer development centers, resulting in higher granularity and broader absorption spectra. The addition of the chloride ion to the developer and amplifier baths, and the adjustment of the H<sub>2</sub>O<sub>2</sub> concentration and pH in the amplifier bath, can be manipulated to improve granularity significantly. After these optimizations, the granularity reached to the level of conventional color paper when the number of AgCl grains in each system was equalized. We concluded that smaller microcrystals can be used while simultaneously increasing the number of development centers, which allowed us to use AgCl microcrystals with edge lengths up to about 60% of those conventionally used before granularity noticeably diverged from that of conventional color paper. It would also seem that this low silver system would best be matched not with a conventional analogue exposure system but with a digital exposure system with high power light source.

### 2.3 Bleaching and Fixing

Although a redox amplification process achieves exceptionally low silver coverage, obtaining the best color reproduction possible still requires removing silver from the developed paper, and this means that bleaching and fixing are indispensable. Nevertheless, the low silver system makes it possible to use gentler bleaching and fixing agents.

We chose the separate bleach and fix baths containing ecologically preferable compounds though the number of baths was increased. We employed H<sub>2</sub>O<sub>2</sub> as the bleaching agent instead of the ferric complexes of aminopolycarboxylic acids. The problem with this choice was that the bleaching speed of H<sub>2</sub>O<sub>2</sub> is quite a bit slower than that of the ferric complexes, making for long bleaching time. Of course, bleaching time depends directly on the amount of silver in the paper, so slow bleaching in a low silver system is not as serious as in a conventional system. Still, we did want to provide rapid processing, so, we tried to accelerate this H<sub>2</sub>O<sub>2</sub> bleaching.

As indicated in **Figure 4**, the bleaching speed depended on the pH and the concentration of sodium chloride. Therefore we worked with these factors, adopting a 0.44mol/ℓ H<sub>2</sub>O<sub>2</sub> bleaching solution adjusted to pH 10 and about 0.17 mol/ℓ of NaCl. This allowed the system's color paper to be bleached in under 10 seconds.

But, to get rapid bleaching speed the solution pH needed to be high, which increased Dmin because amplifying chromogenic reaction still continued in the bleach bath. This was caused by CD carried from the developer bath, which was considerable in the case of employing single developer/amplifier bath. But by using separate developer and amplifier baths, the amount of CD carried to the amplifier bath was limited and most of it was disappeared before it reached the bleach bath. As seen in Table 1, this kept fog generation in the bleach bath low, and whiteness after processing was greatly improved. This was the conclusive factor that let us decide to employ separate

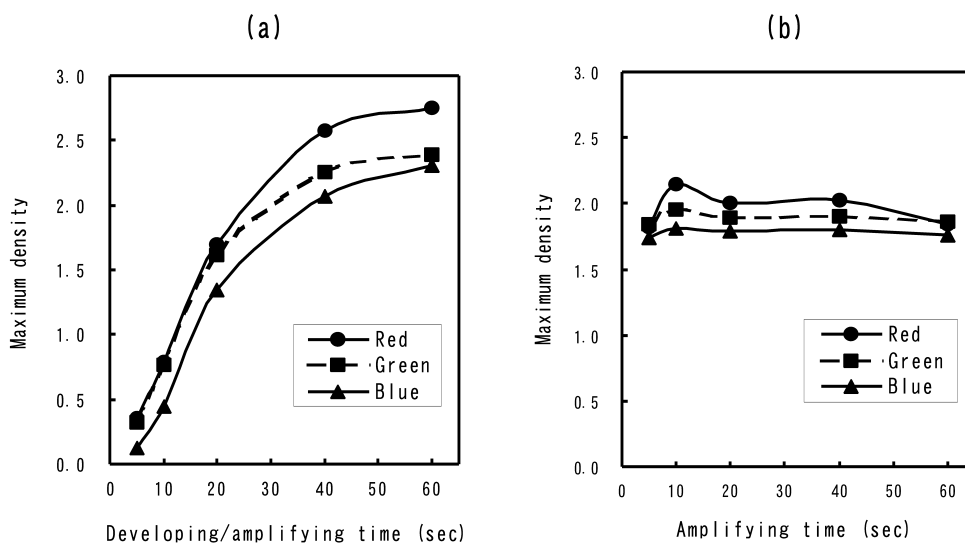


Figure 3. Color formation in combined developer/amplifier bath (a), and separate amplifier bath (b). In case (a), development, amplification and dye generation occurred together. A long processing time was taken to obtain adequate densities, and color formation did not saturate. In case (b), rapid amplification and dye generation occurred after separated silver development, then maximum density reached saturation within 10 seconds. A redox amplifying solution containing 26 mmol/ℓ of H<sub>2</sub>O<sub>2</sub> at pH 10.5 was used.

developer and amplifier baths.

Table 1. Lower fog generation in bleach bath using separate developer and amplifier baths process

	Increase of Dmin in bleach bath		
	Red	Green	Blue
Combined developer/ amplifier bath	0.028	0.020	0.051
Separate developer and amplifier baths	0.001	0.002	0.015

In the fixing bath, we decided to use sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) as our fixing agent instead of conventional thiosulfate compounds.<sup>10</sup> Sodium sulfite is a far more preferable ecologically. The biochemical oxygen demand level of it is fairly low, and, in addition, it has no strong, unpleasant odor, and it causes no sulfur deposits in the bath. In addition, if the bleaching and fixing solutions mix during disposal, sulfate ions are generated, and the total biochemical oxygen demand level is cut even further.

The only problem with sodium sulfite is that its fixing speed is relatively slow. Using 0.20 mol/l of sodium sulfite solution at pH 8, it took more than 30 seconds to fix conventional color paper. However, when it was used with low silver content paper, it took less than 10 seconds, which is much more acceptable.

After fixing, the color paper needs to be washed or stabilized. We estimated it took 15 seconds for the low silver paper to be stabilized. Shorter stabilizing should be possible because bleaching solution was not colored. This means total processing time before drying can be shorter than a minute.

### 3 CONCLUSIONS

We designed a new redox amplification process with separate developer and amplifier baths, which was

combined with hydrogen peroxide bleaching and sodium sulfite fixing. This process surmounted the difficulties of solution stability and image degradation to provide fine image quality. In addition, the system provided robust environmental protection and quite rapid overall processing. It took less than 15 seconds for development, 10 seconds for amplifying, under 10 seconds for bleaching, under 10 seconds for fixing, and approximately 15 seconds for stabilizing. Total processing before drying thus takes less than a minute.

### 4 ACKNOWLEDGMENT

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### 5 REFERENCES

1. R. Matejec, US Patent 3,674,490(1972)
2. V. L. Bissonette, US Patent 3,748,138(1973)
3. H. Hirai, K. Nakamura and H. Iwano, SPSTJ's Annual Conference, SPSTJ, Tokyo, 1984, pp.155-157
4. G. B. Evans, J. Kempster, J. A. Bee and D. Gibson, ICPS Proceedings, KVCV, Antwerp, 1998, pp.149-152
5. R. Wildman, P. J. Twist and J. R. Fyson, ICPS Proceedings, KVCV, Antwerp, 1998, pp.153-155
6. J. R. Fyson, WO 9311459(1993)
7. P. J. Twist, WO 9311460(1993), EP 654707(1995), EP 706085(1996)
8. P. J. Twist and C. J. Winscom, EP 713138(1996), EP 716340(1996)
9. K. Miyazawa, S. Tanaka, N. Kokeguchi, Y. Suda and J. Itoh, US Patent 5,972,573(1999)
10. K. Miyazawa and S. Tanaka, Japanese Patent Application No.10-246941(1998)

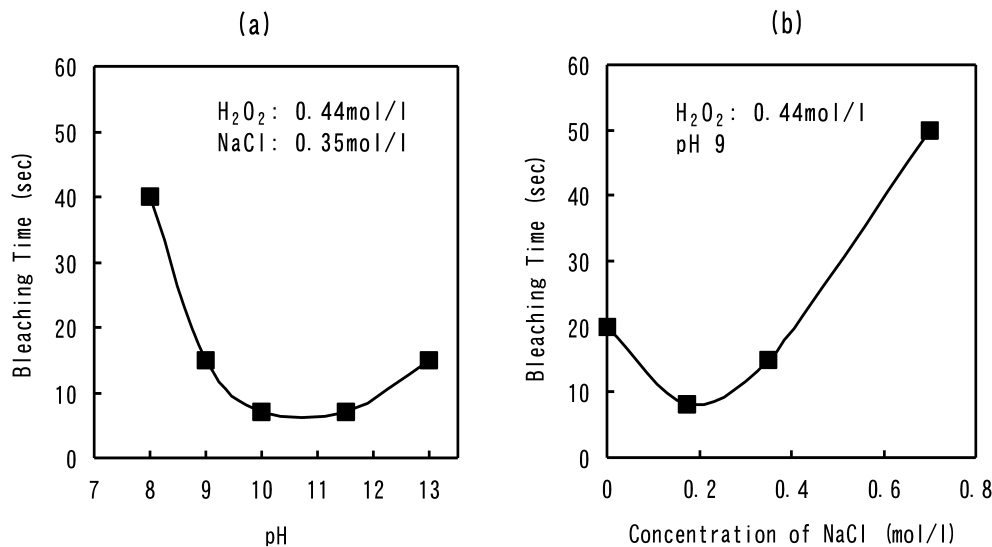


Figure 4. Effects of pH (a) and NaCl concentration (b) on bleaching speed. When using 0.44 mol/l of  $\text{H}_2\text{O}_2$  solution, bleaching was fastest at around pH 10-12, and with about 0.2 mol/l of NaCl, which allowed the system's color paper to be bleached within 10 seconds.