

Separating Developer and Amplifier Baths: Achieving Process Stability and Superior Image Quality in a Low Silver System

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Abstract

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 to surmount the difficulties of solution stability and image degradation. The system provides excellent color balance, granularity, and whiteness while providing robust environmental protection, and delivering high-speed processing.

Introduction

The redox amplification process for low silver systems has been studied for some time[1-3]. 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 environment has grown up.

With redox amplification, this is the chemistry of the color formation:

$$CD + AgCl \longrightarrow CD_{ox} + Ag^0 + Cl^- \qquad (1)$$

$$CD + H_2O_2 \xrightarrow{Ag^0} CD_{ox} + H_2O \qquad (2)$$

$$CD_{ox} + \text{Coupler} \longrightarrow \text{Dye} \qquad (3)$$

Conventional development consists of reactions (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 reaction (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 could be developed, this 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. Evans et al. and Wildman et al. discussed the low silver system of color paper in ICPS 1998 [4,5]. They and their colleagues have made many efforts on the progress of this technical field, and improved the stability of redox amplifier process[6]. From work such as this, 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. Wildman et al. chose the single bath system because the replenishment rate could be lowered. So, their study was focused on the improvement of the solution stability.

In our own work, we took the converse approach. We believed that the mixing of a developing agent and an oxidizing agent was inherently unstable. Rather, we believed that a separate developer and amplifier bath system could not only overcome solution instability, but could also present ways to improve image quality.

Separating Developer and Amplifier Baths

We developed a redox amplification color paper/processing system whose color paper contained a low quantity of AgCl (about 20% of that found in conventional color paper) and whose process employed separate developer and amplifier baths. With this system, AgCl microcrystals carrying latent images are developed in the developer bath. But 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 is absorbed 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 color developer subsequently reacts with the couplers in the emulsion layers to generate appropriate amounts of dyes. Again, the silver nuclei created in the developer bath serve to catalyze the color forming reaction in the amplifier bath.

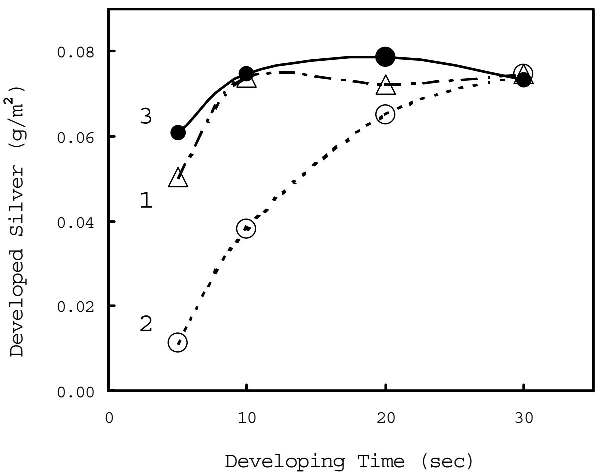

Figure 1. Effects of ascorbic acid on development speed.

Curve 1: pH 10, Curve2: pH 7

Curve3: pH 7 with ascorbic acid

Obviously, a sufficient amount of color developer 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 process. To solve this, we examined the possibility of raising the color developer concentration in the developer bath. The conventional color developing agent, p-phenylendiamine (PPD) dissolves more readily at lower pH. However, the lower the solution pH is, the weaker the developing activity of PPD. This might cause long processing time. We examined the acceleration of the silver development at low pH, and got the result that adding black-and-white developing agents were effective[7]. Figure 1 indicates the change of silver developing speed with pH and containing ascorbic acid. The silver development was almost finished within 10 seconds even in pH 7 solution.

In this process, the desired functions of the developer bath and amplifier bath are clearly divided. That of developer bath should be limited only to generate silver nuclei which acted as catalysts in the amplifier bath. While the color paper in the developer bath, PPD diffuses uniformly throughout all emulsion layers. The yellow color forming layer, with its characteristically larger AgCl grain, is usually located in the bottom. The developing speed of this layer is relatively slow, which causes uneven color forming speed. The single developer/amplifier bath process increases the imbalance of each color forming speed, and makes it difficult to control the Dmax/Dmin balance. But in the separate baths process, 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 PPD has been already diffused. This makes it easy to control Dmax/Dmin balance. We adopted 0.09% of H_2O_2 solution for amplifier, and found it took 10 seconds to obtain the adequate density for each color.

Improving Image Quality

Poor granularity due to the low volume of silver is 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. To compensate for this, smaller microcrystals can be used while simultaneously increasing the number of development centers, a technique that allowed us to bring the edge length of the AgCl microcrystals up to about 60% before granularity noticeably diverged from that of conventional color paper. In addition, we found that optimization of the chloride ion concentrations in the developer and amplifier baths, and of the H_2O_2 concentration and pH in the amplifier bath, could be manipulated to significantly improve granularity.

Although a redox amplification system makes exceptionally low silver coverage possible, 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 tried to employ H_2O_2 as a bleaching agent, which seemed to be an ecologically preferable compound. 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 PPD carried from the developer bath, and was considerable in the case of employing single developer/amplifier bath. But by using separate developer and amplifier baths, the amount of PPD carried to the amplifier bath was limited and most of it was disappeared before it reached the bleach bath. In the amplifier bath, PPD in Dmax area was reacted with the couplers, and PPD in Dmin area diffused to the bulk of the solution. As seen in Table 1, this kept fog generation in the bleach bath low, and whiteness after processing was fairly improved.

Table 1. Lower fog generation using separate developer and amplifier baths

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

Providing Processing Speed and Protecting the Environment

We chose the separate bleach and fix baths containing ecologically preferable compounds though the number of baths was increased. As mentioned above, we employed H_2O_2 as the bleaching agent instead of the ferric complexes of aminopolycarboxylic acids, as well as employed sodium sulfite (Na_2SO_3) as the fixing agent instead of thiosulfate compounds[8]. As indicated in Figure 2, the bleaching speed depended on the pH and the concentration of sodium chloride. Therefore we worked with these factors, adopting a 1.5% H_2O_2 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. In addition, using 0.20 mol/l of sodium sulfite, the system's color paper was fixed in less than 5 seconds. The biochemical oxygen demand levels of H_2O_2 and Na_2SO_3 are fairly low. In addition, if the bleaching solution and fixing solution is mixed before ejection, sulfate ion is generated and the total biochemical oxygen demand level can be more decreased.

We propose the new rapid processing system for color paper. The redox amplification process with separate developer and amplifier baths, which was combined with H_2O_2 bleaching and Na_2SO_3 fixing, was employed. In fact, this low silver processing system provides quite rapid overall processing, taking less than 20 seconds for development, 10 seconds for amplifying, under 10 seconds for bleaching, under 5 seconds for fixing, and approximately 15 seconds for stabilizing. Total processing before drying takes less than a minute.

Conclusion

We were able to design a redox amplification process with separate developer and amplifier baths that surmounted the difficulties of solution stability and image degradation to provide fine image quality, robust environmental protection, and high-speed processing in a low silver system.

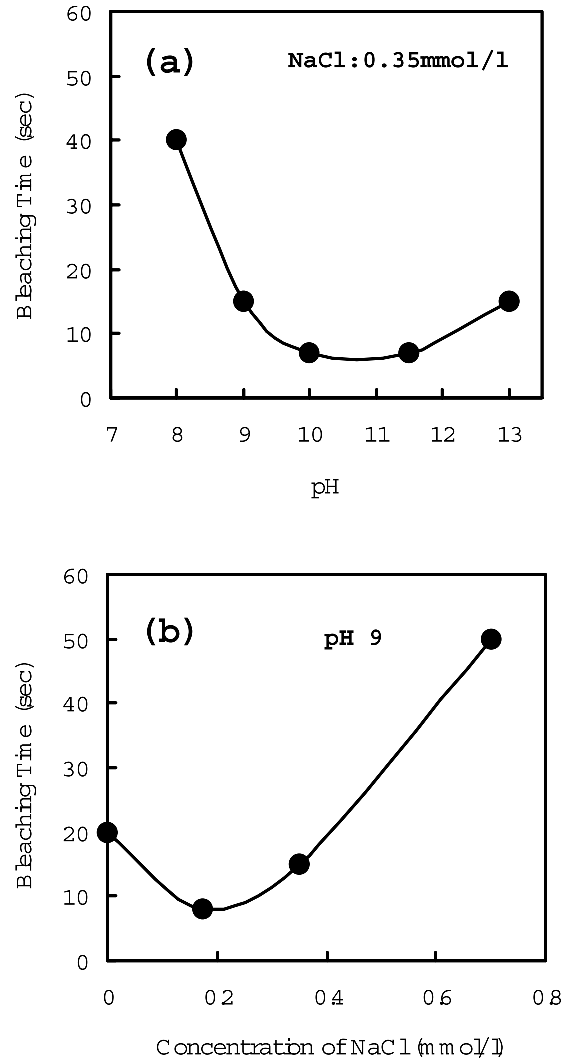

Figure 2. Effects of pH (a) and NaCl concentration (b) on bleaching speed.

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Biography

Kazuhiro Miyazawa received his master degree in organic chemistry from the Niigata University in 1988. He joined Konica Corporation the same year, and, since then, has been engaged in the research and development of color photographic materials.