Rapid Process with New Fujicolor Paper

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Abstract

A rapid process is one of the essential requirements for photographic digital printer processors. Color paper technologies to achieve the rapid process have been developed. These technologies include a new yellow dye-forming coupler (1,1-dioxo-1,2,4-benzothiadiazine yellow coupler), a new cyan dye-forming coupler (1H-pyrrplo[1,2-b][1,2,4-]triazole cyan coupler) and fine silver halide crystals (sensitized with dopants, iodide ions, and hydrophilic sensitizing dyes). These technologies have been introduced into New Fujicolor Paper, "Crystal Archive Paper Type II" and enable high processing capacity in the "Frontier 570 Digital Lab System".

1. Introduction

Digital minilab systems which use silver halide color paper provide excellent image quality, high print productivity, exceptional image stability, and low running cost.

Although traditional colorprint papers have been acceptably used in digital minilab printer processors, there have been demands for improving rapid processing suitability of silver halide color paper in the photofinishing market. In terms of customer convenience, it is expected that a customer can pick up prints within several minutes after uploading image files from digital camera media. In addition, rapid processing significantly contributes to increased print productivity in the digital minilab systems which is a great advantage over both current conventional photographic processing and other printing systems like inkjet or dye sublimation. Therefore, rapid processing suitability is one of the key features for today's silver halide color paper.

In this paper, we report the recent progress in dye forming coupler technologies and silver halide emulsion technologies to meet the requirements for improved silver halide color paper.

2. Rapid Processing Suitability

The processing steps of silver halide color paper consist of color developing, bleach-fixing, washing, and drying. For achieving a rapid process, it is important to shorten each processing step. Table.1 shows the effects of some factors required to shorten each processing time.

2-1. Rapid Developing Process

Lowering the coated silver amount and/or reducing the average size of silver halide grains are known to be very effective to shorten the developing time. However, maximum density usually decreases with lowering the coated silver amount and sensitivity usually decreases with reducing the average grain size. It is therefore necessary to shorten the development time without sacrificing either the maximum density or the sensitivity.

Table.1
Effects of Factors Required to Shorten Each Processing Step

	Developing	De-silvering	washing
Coated Ag amount ↓	◎	◎	×
AgX grains size ↓	◎	○	×
Coating thickness ↓	○	◎	◎
Hydrophilic sensitizing dye	×	×	◎

New yellow coupler and cyan coupler technologies have been developed to achieve equivalent maximum density as the current couplers even if the coated silver amount is reduced. This achievable due to the fact that the new yellow coupler and new cyan coupler are able to produce dyes of higher molecular extinction coefficients than that of dyes from the current couplers.

In addition, two new sensitization technologies have been developed in order to reduce the average size of silver halide grains without loss of sensitivity. The first technology includes a dopant whose electron-releasing time is not longer than 1 second. The second technology enables the surface structure of the silver halide crystal to be modified and refined by using silver iodide.

2-2. Rapid De-silvering Process

Because these two new technologies make it possible to reduce not only the coated silver amount but also the coating thickness, achieving these reductions are very effective to shorten the de-silvering process and thereby providing a shorter bleach-fix time.

2-3. Rapid Washing Process

While smaller silver halide grains allow a reduction in both developer and bleach-fix processing time, it also leads to an increase in spectral sensitizing dye amount This is because the total surface area of silver halide grains, which contains the sensitizing dyes, is inversely proportional to the grain size. The resulting higher amount of spectral sensitizing dye poses a color stain problem on processed color paper due to residual spectral sensitizing dyes which is difficult to remove with the washing step. Typically, wash time has to be increased.

Therefore, new hydrophilic sensitizing dyes which can be washed out quickly, have been developed. At the same time new silver halide grains have been developed which have surface structure by using silver iodide to let the hydrophilic sensitizing dyes be absorbed firmly.

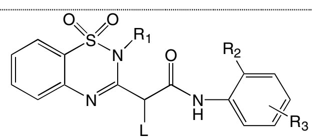
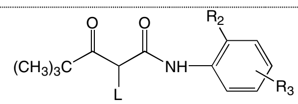
3. New Coupler Technologies

3-1. Yellow Coupler

A 2-pivaloyl-acetoanilide type yellow coupler has conventionally been used in Fujicolor paper. The molecular extinction coefficient of the azomethine dye from this coupler is lower than that of dyes from a magenta or cyan coupler. As a result, a blue sensitive layer requires a larger amount of a yellow coupler as well as silver halide than a green sensitive layer or a red sensitive layer.

As a coupler which has a high molecular extinction coefficient, we have found 1,1-dioxo-1,2,4-benzothiadiazine yellow couplers[1] (Table.2). The molecular extinction coefficient of the azomethine dye from the new coupler is 1.6 to 1.7 times higher than that of dyes from pivaloylacetoanilide-type couplers. We have studied this new structure in-depth and developed one yellow coupler optimized for silver halide color paper.

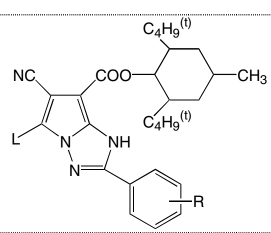
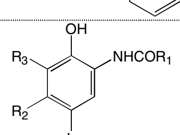
Table.2 Structure of Yellow Couplers

New type	
Current type	

3-2. Cyan Coupler

For the cyan coupler, a phenol-type has conventionally been used in Fujicolor paper. The molecular extinction coefficient of the dye from this coupler is lower than that of dyes from a magenta coupler. As a coupler which has a high molecular extinction coefficient, we have found 1*H*-pyrrolo [1, 2-b] [1, 2, 4]triazole[2] (Table.3). The molecular extinction coefficient of the azomethine dye from the new coupler is two or more times higher than that of dyes from conventional phenol-type couplers. We have also done further in depth studies on this new structure and developed one cyan coupler optimized for silver halide color paper.

Table.3 Structure of Cyan Couplers

New type	
Current type	

3-3. Enhanced Color Reproduction

The dyes from the new yellow coupler and the new cyan coupler not only have high molecular extinction coefficients but also vivid color reproduction.

Fig.1 compares the spectral density distributions of New Type Fuji Color Paper now being introduced with the new couplers. According to these properties, New Type Paper has enhanced color reproduction in the regions of violet, blue, and green compared with the current type paper.

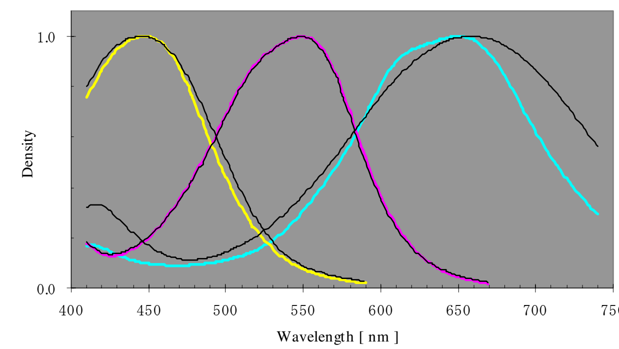


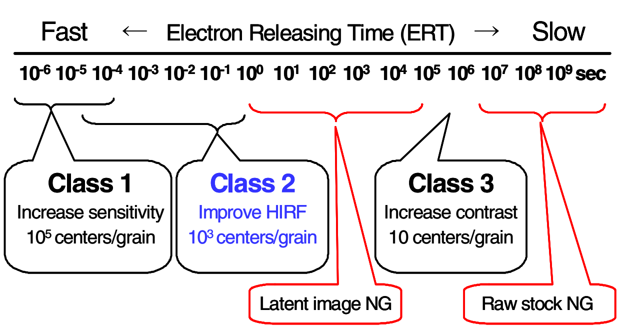
Figure1; Spectral density distributions of cyan, magenta and yellow Dye Colored Lines; New Type, Black Lines; Current Type

4. Doping Technologies

In digital minilab systems such as the rapid process photographic printer processor, high-intensity exposures of about 10^{-7} second per pixel are carried out in the laser scanning exposure step. Under such short time exposure conditions, the sensitivity of the emulsions will be significantly decreased due to high intensity reciprocity law failure (HIRF). Therefore, it is essential to improve HIRF of the silver halide emulsions used in digital minilabs in order to lower the coated silver amount and/or reduce the average size of silver halide grains to achieve an optimized rapid process.

Doping technologies play an important role to improve severe HIRF of silver chloride emulsions. To study the effects of different doping techniques, it is convenient to classify many kinds of electron-trapping dopants according to their electron-releasing time (ERT). A photoelectron stays at a trap center for a certain period of time and is then released from it. These processes are repeated many times. The ERT is defined as the time required for an electron to come out of a trapping and de-trapping cycle.

Table.4 Classification of Dopants



Class 1 dopants, whose ERT is less than about 10^{-4} second, increase sensitivity especially upon high intensity exposure. Typical examples of Class 1 dopants are hexa-cyano coordination complexes, such as $[Fe(CN)_6]^{-4}$ [3] and $[Ru(CN)_6]^{-4}$ [4]. It is believed that a Class 1 dopant traps an electron immediately after the exposure to light, and then prevents it from recombining with a trapped hole within a short period of time [3].

By using Class 2 dopants, whose ERT ranges from 10^{-4} to 1 second, the reciprocity failure caused by high intensity digital exposure can be overcome to produce the sensitivity effect of lower intensity exposures, especially those used in traditional minilab printers. The use of Class 2 dopant technology achieves this effect by allowing a substantially increased regeneration time of photoelectrons for latent image formation over the time for an un-doped emulsion. A dopant whose ERT is longer than about 1 second causes the problem of latent-image stability, which prevents the production of stable digital prints. Useful class 2 dopants are mostly iridium (Ir) complexes. Recently some dopants with suitable ERT, which are less than 1 second in silver chloride emulsions, have also been proposed. One of them is such a complex with organic ligands such as $[IrCl_5(\text{thiazole})]^{-2}$ [5]; another is a complex with inorganic ligands such as $[IrCl_5(H_2O)]^{-2}$ [6]. This latter complex, $[IrCl_5(H_2O)]^{-2}$ dopant, is especially effective to improve HIRF without causing deterioration of latent-image stability during the time interval of several seconds between exposure and processing.

A Class 3 dopant, whose ERT ranges from 10^5 to 10^6 second, are substantially permanent electron traps and provide increased contrast with only a slight decrease in sensitivity. A dopant, whose ERT is less than 10^5 second causes latent-image stability problems which takes place over a several day time period. On the other hand, a dopant, whose ERT is sufficiently longer than 10^6 second, may cause raw stock problem. It is believed that thermal electrons produced by the decomposition of silver clusters pre-existing before exposure in the emulsion grains fill the traps during raw stock manufacture. Typical examples of this class of dopants are $[RhX_{(6-n)}(H_2O)_n]^{-(3-n)}$, where X=Cl or Br and n=0,1 or 2, and $[OsCl_5(NO)]^{-2}$ [7,8].

Among these three classes of dopants, Class 2 dopants are especially important for color paper emulsions to be able to achieve the stable latent-image performance required for use with high-intensity laser exposure, even during the time interval of several seconds between exposure and processing.

5. Sensitization Technologies

As noted earlier, in order to reduce the average size of silver halide grains without loss of sensitivity, it is necessary to develop improved sensitization technologies for a silver chloride emulsion. Various sensitization technologies for silver halide emulsion grains with high chloride content have been proposed.

It is known that silver chloride emulsion grains which have regions of high bromide content near their corners provide emulsions with high sensitivity and gradation [9]. However, this sensitization method tends to form internal latent image centers at interfaces between the silver chloride host grain and the regions with high bromide content, therefore leading to a delay in the development step.

It is also well known that a small amount of silver iodide in the grains with high chloride content increases their sensitivity [10]. It is thought that one of the origins for the sensitivity increase by iodide ions is the significant increase in the ionic conductivity of the grains by the iodide ions. Also important is the fact that a small amount of silver iodide does not seem to cause the formation of internal latent images. The small amount of silver iodide is located at the sub-surface [11] or surface [12,13] of grains with high chloride content.

In addition, the surface structure using silver iodide plays an important role in spectral sensitization and processing time reduction in the washing step. Adsorption isotherms clearly show the effect of surface iodide ions on spectral sensitization. The lower the log P (octanol/water partition coefficient) of sensitizing dyes is, the more quickly they are washed out during color paper processing. While sensitizing dyes are not tightly adsorbed onto the surface of pure silver chloride grains, with the addition of a small amount of silver iodide to the crystals, they can now be adsorbed firmly [12].

6. Application of new technologies

These new technologies have been introduced into New Fujicolor Paper, "Crystal Archive Paper Type II ". By combining this with the rapid process CP-49E chemicals and the Frontier 570 processor, processing time has been drastically shortened (Dry to Dry: 3min45sec → 1min 22sec) while processing volume has been increased (4Rsize: 1450 prints/hrs→1800prints/hrs) and installation area has been decreased ($2.04m^2$ → $1.86m^2$) without any sacrifice in quality.

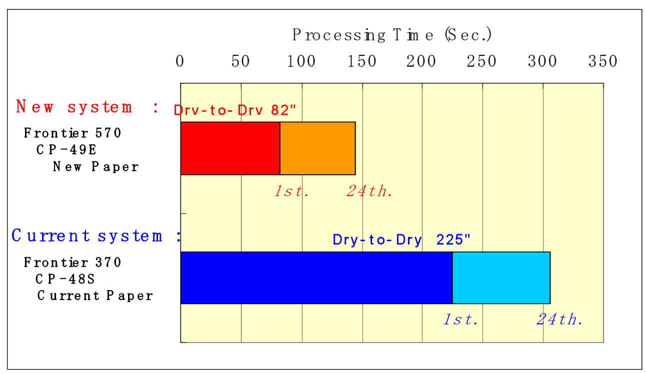


Figure 2; Comparison between current paper processor Frontier 370 and new paper processor Frontier 570

7. Conclusion

The following technologies have been developed and introduced into New Fujicolor Paper, "Crystal Archive Paper Type II " to achieve the high quality features expected by customers with rapid processing required for use in photographic digital printer processors.

New coupler technologies

A new yellow coupler and a new cyan coupler are capable of forming dyes having high molecular extinction coefficients, even with reduced silver coating weights.

Doping technologies

Dopants, whose electron releasing time is not longer than 1 second, are especially important to minimize the effects of HIRF which occurs with digital laser exposure.

Sensitization technologies

Silver halide grain size reduction is achieved by modifying the surface structure using silver iodide. This is effective for: (1) achieving a sensitivity increase; and, (2) enhancing the adsorption of hydrophilic sensitizing dyes to the grains, which can be more quickly washed out.

8. References

[1] K.Takeuchi, et al, Fuji, US Patent 6,727,053(2004)
[2] M.Suzuki, et al, Fuji, US Patent 5,256,526(1993)
[3] See for example K. Shiba, et al, Fuji, U.S. Patent 5,057,402 (1988)
[4] J. E. Keevert, et al, Kodak, U.S. Patent 4,945,035 (1988)
[5] M. T. Olm, et al, Kodak, U.S. Patent 5,360,712 (1993)
[6] T. Owaki, et al, Fuji, U.S. Patent 6,579,670B2 (2000)
[7] W. G. McDugle, et al, Kodak, U.S. Patent 4,933,272 (1988)
[8] R. S. Eachus, et al, Phys. Rev. B 59, 8560 (1999)
[9] K. Hasebe, et al, Fuji, U.S. Patent 4,820,624 (1986)
[10] See for example T. Ogawa, Fuji, U.S. Patent 5,496,689 (1989)
[11] B. T. Chen, et al, Kodak, U.S. Patent 5,726,005 (1994)
[12] S. Nakahira, et al, Fuji, U.S. Patent 6,017,690 (1998)
[13] S. Aiba, et al, Fuji, U.S. Patent 6,706,468B2 (2000)

9. Biography

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