Silver Halide Emulsion Technologies for Digital Minilab Systems

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Abstract

The digital minilab system with silver halide color paper at retailers is playing the leading role among digital print systems at the present when number of prints from digital cameras is increasing. In order to evolve the digital minilab systems further, performances required for color paper are enhanced digital image quality and rapid processing suitability that leads to increased prints productivity. The subjects imposed on silver halide emulsion for color paper so as to meet these requirements are to make contrast moderately high for laser-scanning high-intensity exposure, to sensitize smaller emulsion grains effectively and for grains to adsorb hydrophilic sensitizing dyes tightly. However, silver chloride emulsions used for color paper have the problems, which are peculiar to it and deteriorate the performances required for color paper.

A silver chloride emulsion is inclined to suffer from severe high intensity reciprocity law failure (HIRF) as compared with a silver bromide emulsion. Doping technologies play important roles to improve the HIRF of the silver chloride emulsion. The function of dopants is classified according to its electron-releasing time (ERT). The development of dopants, whose ERT is less than 1 sec, are especially important in order to solve this problem.

Increase in sensitivity on high intensity exposure causes fog formation due to the natural background radiation. In order to solve this radiation fog problem and to increase the rate of development further, it is effective to decrease the size of emulsion grains. However, the decrease in the grain size makes it necessary to increase the amount of spectral sensitizing dyes. Such an increase in the amount of sensitizing dyes bring about a new problems, giving stains with remaining dyes in a color paper after washing processes. Although hydrophilic sensitizing dyes are usually effective for reducing the stains, it is necessary to develop the technologies to achieve tight adsorption of hydrophilic sensitizing dyes to silver chloride emulsions for color papers. We propose that the modification of surface structure of silver chloride emulsion grains with iodide ions is effective for both increase in the sensitivity of the emulsion and tight adsorption of hydrophilic sensitizing dyes to the grains.

Introduction

The digital minilab systems with silver halide color paper have the features of excellent image quality, high print productivity, exceptional image stability and low running cost. Although the excellent image quality is the feature of silver halide color paper, it should be improved further to meet the requirement for digital exposure. Among many kinds of digital exposure systems, the laser scanning exposure system is especially eminent to get high image quality. Therefore, it is important to make further improvement of silver halide color paper to meet the laser scanning exposure.

The need for improvement in rapid processing suitability of silver halide color paper is still strong in the photofinishing market. In order to provide users with an acceptable service, for instance, it has been required that color paper should be developed and returned to the users within several tens minutes after acceptance of a digital media. In addition, rapid processing cycle permits excellent print productivity for a digital minilab, featuring the strong point of color paper among competing print systems. Thus, the rapid processing is of ever-increasing necessity.

In this paper, we report the recent progresses in the silver halide emulsion technologies to meet the requirement for the digital minilab systems.

Characteristics of the Emulsion Required for Color Paper

It is known that the quality of digital images is dependent not only on the hue of the developed dye, but also on contrast, density and resolution [1]. Enhanced contrast is especially desirable in order to improve text quality and image sharpness within limits by which uniformity of exposure is permitted. High-intensity exposure for about 10^{-7} second per pixel is carried out in the laser scanning exposure of digital minilab systems. Under such short time exposure, silver halide emulsions are inclined to exhibit high intensity reciprocity law failure (HIRF), owing to which the sensitivity and contrast of the emulsions should be remarkably deteriorated. Therefore, it is essentially important to improve HIRF of silver halide emulsion in order to get high quality digital image.

Silver halide grains in color papers suffer from gradual fog formation owing to their exposure to natural background radiation, and are thus inclined to cause the deterioration of whiteness on their prolonged preservation [2,3]. It turns out that the rate of fog formation due to the natural background radiation correlates strongly with the light sensitivity on high intensity exposure in such a manner that the improvement of HIRF should be accompanied by the increase in the radiation fog. However, the radiation fog decreases with decreasing the average volume of the grains. In order to reduce the radiation fog of the emulsions for digital exposure, it is therefore effective to reduce the volume of the grains without deteriorating their sensitivity.

The processing steps of color paper consist of color developing, bleach-fixing, washing and drying processes. Although the shortening of each process is important for the rapid processing, developing and washing processes mainly relate to silver halide emulsion technologies. It is known that the rate of development increases with decreasing the average size of silver halide grains in color papers, since the development of each grain proceeds in parallel with nearly the same rate in terms of the amount of developed silver per unit time. However, sensitivity usually decreases with decreasing the average size of the grains. It is therefore necessary to increase the efficiency of latent image formation in order to reduce radiation fog and to increase the rate of development by decreasing the average size of the grains without deterioration of sensitivity.

Since the total surface area of silver halide grains is inversely proportional to the size of the grains, the amount of spectral sensitizing dyes used for color paper should be inversely proportional to the size of the grains. However, it is also known that such an increase in the amount of sensitizing dyes used for color paper poses new problems. In particular, the color stain due to spectral sensitizing dyes remaining in a color paper after washing processes (the so-called residual color) constitutes an obstacle to the rapid processing. Therefore, it is also necessary to use the spectral sensitizing dyes that can be washed out rapidly during the processing.

Problems Peculiar to a Silver Chloride Emulsion

A silver chloride emulsion has been used for color paper, because it has the highest rate of development among other silver halide emulsions. However, a silver chloride emulsion has the problems, which are peculiar to it and deteriorate the performances required for a color paper.

The silver chloride emulsion exhibits severe HIRF as compared with silver bromide emulsions even without any chemical sensitization treatment. The optimum exposure time to achieve the highest sensitivity is about 0.1 second for the un-sensitized emulsion, and about 1 second for the gold-plus-sulfur-sensitized emulsion. The severe HIRF of silver chloride emulsion grains could be attributed to their restricted ionic conductivity. The severe inefficiency in latent image formation on high intensity exposure causes, not only sensitivity loss, but also gradation loss. In order to solve this problem, many kinds of dopants, which act as temporary or permanent traps for electrons, were introduced into silver halide grains with high chloride content.

It is known that silver halide emulsions with high chloride content are less sensitive in terms of the quantum sensitivity than a silver iodobromide emulsion for color negative film. In order to solve the problem of the radiation fog and to increase the rate of development further, it is necessary to develop sensitization technologies for a silver chloride emulsion, that enable to reduce the grain volume without deteriorating sensitivity.

It is indicated that the washout rate of spectral sensitizing dyes during color paper processing depends on its octanol/water partition coefficient (logP) value. Namely, the lower logP value is, the faster is the washout rate. It is therefore effective to use hydrophilic sensitizing dyes for improving the residual color problem. However, the dyes with low logP can not be adsorbed tightly to silver halide emulsions with high chloride content. Therefore, It is also necessary to develop the spectral sensitization technologies for sensitizing dyes with low logP to be tightly adsorbed to silver halide grains with high chloride content.

Doping Technologies

Doping technologies play important roles to improve severe HIRF of silver chloride emulsion. 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 and is then released from it. These processes are repeated many times. The ERT is defined as the time until an electron comes out of these trapping and de-trapping cycle.

A Class 1 dopant, whose ERT is less than about 10^{-4} second, increases sensitivity, and is called a shallow electron-trapping (SET) dopant. The number of doped centers is usually about 10^5 centers/grain. The typical examples of Class 1 dopants are hexa-cyano coordination complexes, such as $[Fe(CN)_6]^{-4}$ [4] and $[Ru(CN)_6]^{-4}$ [5]. Its HOMO is filled and LUMO is situated above the bottom of the conduction band of silver chloride. Then, it traps an electron by Coulombic attractive force of its net positive charge, and the effective mass approximation would be applicable. It is believed that a Class 1 dopant traps an electron immediately after the exposure to light, and then prevent it from recombining with a trapped hole within a short period of time [4]. A Class 1 dopant increases sensitivity especially on high intensity exposure.

A Class 2 dopant, whose ERT ranges from 10^{-4} to 1 second, make substantial generation time of photoelectrons longer than that for latent-image formation in un-doped silver chloride emulsion, converting the photographic response on high intensity exposure into that on lower intensity exposure on appearance. The number of doped centers is usually about 10^3 centers/grain. Since the above-stated processes prolong the process of latent-image formation, they bring about the growth of image centers during the time interval from exposure to processing. 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 Ir complexes. Since ERT of $[IrCl_6]^{-3}$ doped in silver chloride emulsion grains ranges from about 0.1 to 100 second with broad distribution, it is difficult to make improvement of HIRF of silver chloride grains without deteriorating the latent-image stability with $[IrCl_6]^{-3}$ dopant. Since ERT of $[IrCl_6]^{-3}$ strongly depends on the halogen composition in the region where it is doped and decreases with increasing its bromide content, localized doping of $[IrCl_6]^{-3}$ into the region having high bromide content in the grains with high chloride content had been proposed [6]. Recently some dopants with suitable ERT, which is less than 1 second in silver chloride emulsion, had also been proposed. One of them is such a complex with organic ligands as $[IrCl_5(thiazole)]^{-2}$ [7], and another is a complex with inorganic ligands such as $[IrCl_5(H_2O)]^{-2}$ [8]. Especially, $[IrCl_5(H_2O)]^{-2}$ dopant is effective to make the improvement of HIRF without deteriorating the latent-image stability during the time interval of several seconds from exposure to processing.

A Class 3 dopant, whose ERT range from 10^5 to 10^6 second, are substantially permanent electron traps and increase contrast with slight decrease in sensitivity. The number of doped centers is usually about 10 centers/grain. A dopant, whose ERT is less than 10^5 second, causes the latent-image stability problem taking place for a few days. On the contrary, a dopant, whose ERT is sufficiently longer than 10^6 second, may cause raw stock problem. It is believed that thermal electrons coming from the decomposition of silver clusters pre-existing before exposure in the emulsion grains fill the traps during raw stock. If ERT of a dopant is shorter than the time for the generation of thermal electrons, a trapped electron is released from the center and the dopant can regain the ability to capture an electron once more. On the other hands, if ERT of the dopant is longer than the time for the generation of thermal electrons, the center can not regain the ability to capture an electron once more. Typical examples are $[RhX_{(6-n)}(H_2O)_n]^{-(3-n)}$, where X=Cl or Br and n=0,1 or 2, and $[OsCl_5(NO)]^{-2}$ [9,10].

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

Sensitization Technologies

It is necessary to emphasize that the sensitization for color paper emulsion should not be accompanied by fog formation and gradation loss. In order to improve silver halide emulsion grains with high chloride content, various sensitization technologies have been proposed.

It is known that silver chloride emulsion grains having the regions with high bromide content near their corners provide the emulsion with high sensitivity and gradation [11]. 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, and therefore leads to the delay of the development step. Since a developer gradually dissolves the grains with latent image centers in the interior, it develops the grains when it reaches the centers, and thus gradually increases the number of developed grains as the development proceeds.

It is also well known that a small amount of silver iodide in the grains with high chloride content increases their sensitivity [12]. It is thought that one of the origins for the sensitivity increase by iodide ions is the remarkable increase in the ionic conductivity of the grains by the iodide ions. 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 sub-surface [13] or surface [14,15] of the grains with high chloride content.

The surface structure with iodide ions also plays an important role in spectral sensitization. Adsorption isotherms clearly show the effect of surface iodide ions on spectral sensitization. The lower the logP of sensitizing dyes is, the more quickly they are washed out during the color paper processing. However, they are not tightly adsorbed on the surface of silver chloride grains. On the contrary, they can be strongly adsorbed to the surface of the grains with high chloride content, which contain a small amount of silver iodide on the surface [14].

Conclusions

1. It still meets the demand of the times to improve digital image quality and to increase prints productivity of digital minilab systems furthermore. The performances required for the color paper of digital minilab systems are moderately higher contrast for laser scanning high intensity exposure and rapid processing suitability.
2. Doping and sensitization technologies are the keys for color paper emulsions that fulfill these demands.
3. Dopants, whose electron releasing time is not longer than 1 second, are especially important to make improvement of HIRF without deteriorating the latent image stability. One of such dopants is $[IrCl_5(H_2O)]^{-2}$.
4. Surface structure with iodide ions is effective for (1) the achievement of sensitivity increase, which make it possible both to reduce the radiation fog and to increase the rate of development by reducing the grain volume, and (2) the enhancement of the adsorption of hydrophilic sensitizing dyes to the grains, which promotes the washout rate of the dyes.

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Biography

Naoto Ohshima was graduated from the Waseda University in 1979, and from the graduated school of science and engineering in the same university, receiving masters degree in electrical engineering in March of 1981. His specialty is the physics of semiconductor. From April of 1981, he was employed by Fuji Photo Film Co., Ltd. at its Ashigara Research Laboratories, and was engaged in research regarding silver halide emulsions. From July of 1986 to date, he has been engaged in research of color papers, at the Ashigara Research Laboratories and Digital & Photo Imaging Materials Research Laboratories. He is a member of IS&T, SPSTJ and The Physical Society of Japan.