Development of New Direct Laser Printing System

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Abstract

A new photo- and heat-sensitive printing system has been developed. Full-colored and high-quality images can be printed quickly and easily by using this system. Images are printed by dry process using only one sheet of sensitive paper. No other materials are needed thus resulting in no waste. The noteworthy features of the newly developed sensitive paper are the chromogenic development using heat-sensitive microcapsules, the spectral sensitization by unique sensitizing dyes and borates, the photopolymerization of monomers functioning as color developers, and the bleaching of sensitizing dyes during fixing process. By laser irradiation, developers polymerized and lose ability to move into the capsules. In the unexposed area, however, developers are able to move into the capsules and change the precursors to dyes.

Introduction

Recently, a variety of digital imaging materials have been designed and developed in photo finishing field. They are, for example, silver photo system, ink jet, and electrophotography system. In this time, we developed a new digital printing system with unique characteristics.

Our new system is non-silver photographic system, and is based on photo- and heat-sensitive principles. The characteristics of this system are mono-sheeted and full-colored, and the photography-like images can be printed immediately by dry process. No other materials are needed such as ink, toner, or ribbon, thus resulting in no waste. So it is clean, easy to operate, and environment-friendly. The printer is quite simple, composed of three types of laser sources for recording, the heat source for developing, and white light sources for fixing. The images are recorded by laser irradiation in non-contact process, and developed and fixed succeedingly. Therefore full-colored and high-quality images can be printed quickly.

This new printing system of photo- and heat-sensitive type is composed of several unique techniques. They are; the photopolymerization technique using dye and borate as initiator and color developers functioning as monomers, the spectral sensitization technique, and the chromogenic development technique using heat-sensitive microcapsules, the multi-layer coating technique with a fair degree of precision, and the laser exposure technique using our original solid-state laser.

Principle of Image Formation

Our printing material is constructed of three color developing layers. Each layer develops yellow, magenta and cyan color. One of the photo- and heat-sensitive layers is shown in Fig. 1.

The photo- and heat-sensitive layer consists of heat-sensitive microcapsules, oil droplets and binder. The heat-sensitive microcapsule contains dye precursors. The oil droplet contains color developers functioning as monomers, sensitizing dyes and borates functioning as photopolymerization initiators, and other reagents which promote the polymerization.

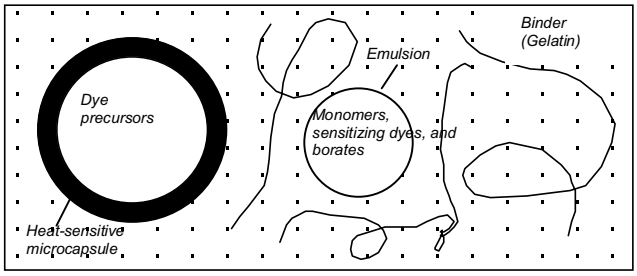

Figure 1. The structure of a photo- and heat-sensitive layer

The initiators are sensitive to visible light. By irradiation of visible laser, the initiators polymerize monomers. If the laser is not irradiated, the color developers remain as monomers. Therefore the degree of exposure determines the degree of polymerization and forms the latent images. And then, after the latent image formation, by heating the whole area, monomers diffuse to the microcapsules in unexposed area and develop the precursors to dyes by the acid-base reaction. On the other hand, in the

exposed area, the color developers can not move into the capsules, so the dyes can not be formed. Finally, the white light is irradiated. By this fixing process, monomers which remain in the unexposed area polymerize and the colored sensitizing dyes are bleached. The imaging process of this system is shown in Fig. 2.

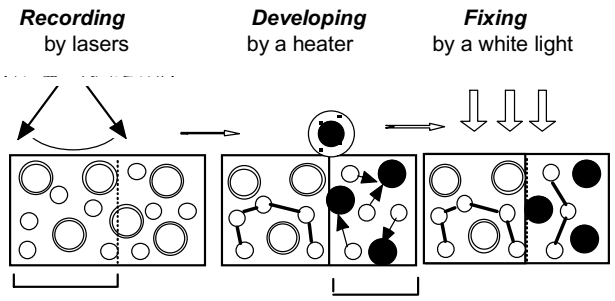

Figure 2. The imaging process of this system

The above mentioned process only describes on light sensitive layer. However, by using the same principle, we developed yellow, magenta, and cyan layer respectively using different spectral sensitization. Thus, full-colored images can be printed by the process similar to that of monolayer, that is, the exposure, the developing and the fixing. The model of the full-colored image formation is shown in Fig. 3.

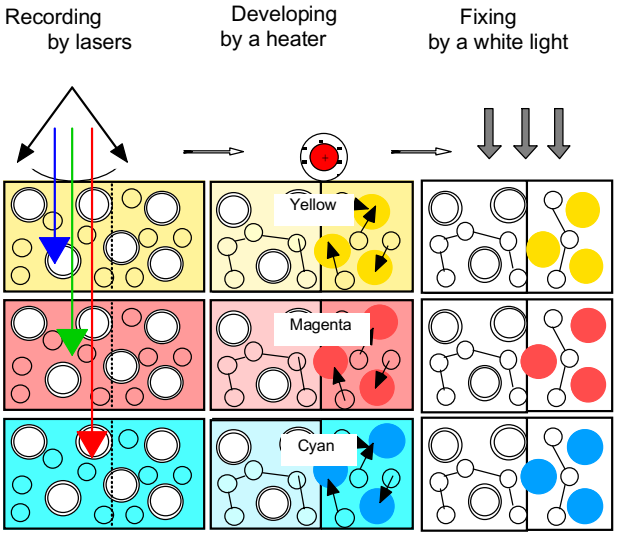

Figure 3. The imaging process of the full-color paper

To develop this new printing system, several techniques are developed such as monomer functioning as color developer, the photo- polymerization initiators with high sensitivity for visible lights, the bleaching of sensitizing dyes, the light sources of laser and so on.

Techniques of Image Formation

Developing of the Monomer

In these photo- and heat-sensitive materials, we selected the leuco dyes as the dye precursors enclosed in the microcapsules because they can change to bright colors. To develop the leuco dye, the electron donating compounds such as phenol derivatives are used. We synthesized the compound which has both of developing unit and the polymerizing unit and decided to use the compound which is shown in Fig. 4 for this paper.

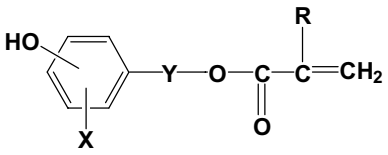

Figure 4. The structure of the monomer functioning as the color developer

Developing of the Initiators

We selected the following three types of compact lasers.
Blue Laser : 405 nm
Green Laser : 532 nm
Red Laser : 657nm

It is necessary to develop initiators having high sensitivity for the wavelength of the each laser. We paid attention to dye and borate as initiator. It is the ion complex consists of sensitizing dye and borate. The sensitizing dye is a cation, and the borate is an anion. The dye is excited by absorbing the light of laser, and then an electron transfer occurs to the borate (Fig. 5). As a result, a radical is created and it starts polymerization of monomers.[1~3]

$$Dye^{+} + R_3B^{-}R \longrightarrow Dye\cdot + R_3B + R\cdot$$

Figure 5. The formation of the radical for polymerization

To make the rapid printing, it is important to create the initiator which is high sensitivity. We developed some new compounds, sensitizing dyes, borates, and other reagents which promote the reaction.

These compounds are selected and are shown in Fig. 6. The sensitizing dye for the red light is shown in Fig. 6 (a), for the green light, in Fig. 6 (b), and for the blue light, in Fig. 6 (c). The borates which make complexes with dyes are investigated newly and widely, and the compound shown in Fig. 6 (d) was decided to use for our system.

Because of the high intensity of the laser irradiation in this system, we noticed that the high intensity reciprocity

law failure is somewhat noticeable. Therefore, to reduce the problem, we studied several kinds of reagents, and employed them in our system, for example, azide, thiourea, mercapto compound, are used for it.

By combining these compounds, the photosensitive recording layers respectively sensitive to light of different wavelengths, and the photosensitive paper has the highest sensitivity in the materials utilizing photopolymer. The sensitivity is 0.1~0.2mJ/cm^2.

Developing of the Bleaching Techniques

Our system is sensitive to the visible light, so the remaining stain of sensitizing dyes is annoying. We have to bleach the color of them. We developed the techniques to bleach the color of sensitizing dyes by applying the phenomena of bleaching reaction in cyanine dyes and borate compounds.

That is, by the electron transfer from excited dye to borate, radicals are created and can polymerize monomers.

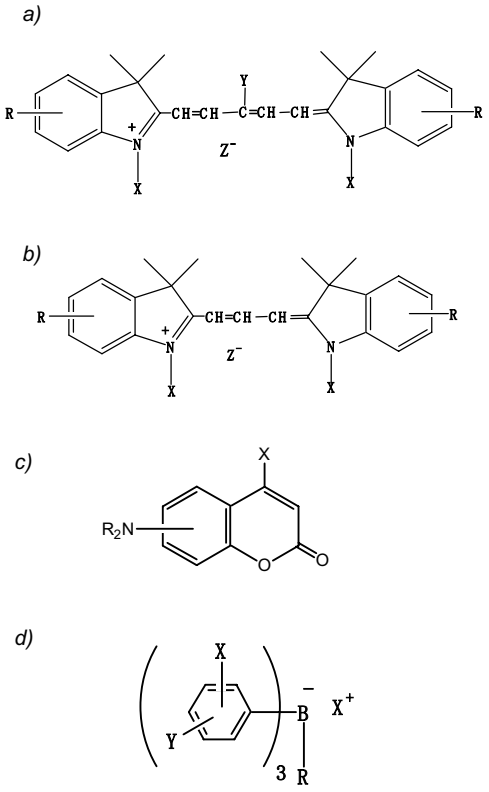

Figure 6. The structure of initiators

But these radicals react to the monomers to polymerize and also excited dyes to bleach.[4] The scheme of the reaction is shown in Fig. 7. It is one of the characteristics of our system that two reactions, polymerization and bleaching, are applied in the same material.

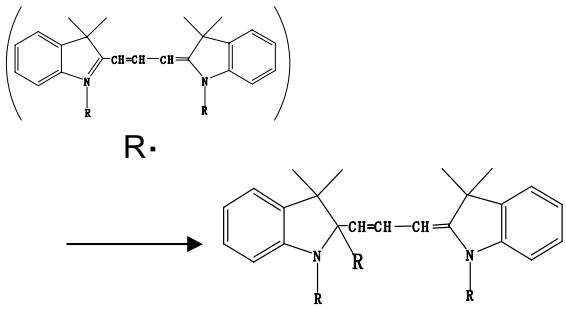

Figure 7. The scheme of the bleaching reaction

To print quickly, it is necessary to make the bleaching reaction fast enough. But there is a big problem for the fast printing. Because the speed of this bleaching reaction depends on the compounds used as initiator, but in general, the speed is very slow at room temperature, and the stain remains because the bleaching reaction dose not arrive at the necessary level.

We found that the bleaching reaction goes fast enough and no stains remain at high temperature. In this system, the last fixing process goes succeedingly after the developing process, so the remaining heat used for developing is applicable for accelerating the bleaching reaction.

These techniques make the bleaching reaction completed within a short time, so the stain is bleached completely below the level we can not recognize. The spectral absorbance of sensitizing dyes before and after bleaching is shown in Fig. 8.

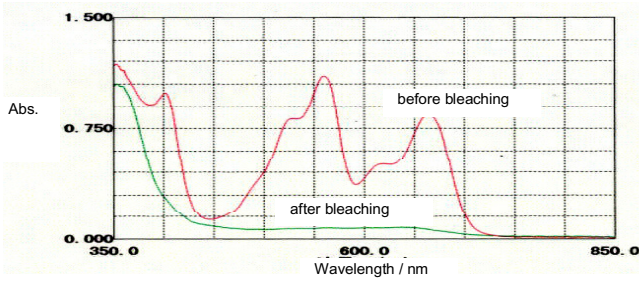

Figure 8. The spectra of sensitizing dye before and after bleaching

Any light sources are usable for bleaching if they illuminate at the wavelength where the sensitizing dyes absorb it. In this system, fluorescent lamps are employed in the printer.

Design of the Multi-Layered Paper

To make the paper glossy, protect the surface, and eliminate oxygen to keep good storability, the top layer is a protective layer made of polyvinylalcohol. And the intermediate layers are provided to prevent the diffusion between different color developing layers. Furthermore, the

intermediate layer containing the fluorescent whiting agents is provided to make papers whiter.

Using these techniques, full-colored images with high image quality and good storability can be achieved.

Design of the Printer

Three types of lasers were selected and used as described before. The green laser is an original solid SHG laser of Fuji Film Co., Ltd. The structure of the system is shown in Fig. 9.

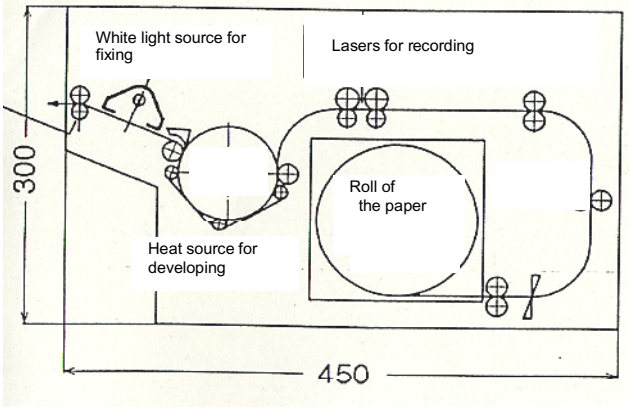

Figure 9. The structure of the printer of this system

As shown in Fig. 9, our printer is compact and has the light sources, the lasers for recording and the fluorescent lamps for fixing, and the heat source for developing. The rolled paper is set and is carried by roller. The sensitive paper is irradiated by three types of laser simultaneously to make the latent image, and developed and fixed succeedingly. It takes about 20 seconds for printing out an A4-size paper with easy operation.

Conclusion

We have developed the new full-color, high-image quality digital printing system. This system is completely dry, easy to operate, and applicable to many fields, not only photo-finishing field, but also to a wide variety fields, for example, the printing industry, the medical fields, and so on.

References

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Biography

Kyoko Senga graduated from the Department of Science in Nara Women's University in 1997, and received a Master of Science from Nara Women's University in 1999. Since 1999 she is with Fuji Photo Film Co., Ltd. Up to the present, she has mainly been studying heat-sensitive materials.

Her specialty is polymer science and photochemistry. She is a member of the Imaging Society of Japan, the Japan Photochemistry Association, and the Society of Polymer Science, Japan. E-mail address: kyouko_senga@fujifilm.co.jp