Durability of Dyes in Thermal Dye Transfer Printing

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Abstract

Durability of dyes in thermal dye transfer printing images was improved by developing the Over Protect Layer(OP layer) and optimizing printing conditions. In this report, the relation between image durability and the condition of the transferred dyes in the dye receiving layer is studied. As for the thermal dye transfer printing image, the durability of the dye itself is important, even the interaction between the dyes and the dye receiving layer materials is important. The transferred dyes exist in the surface of the dye receiving layer in the dye receiving sheet. It is understood that dyes diffuse toward the depth of the dye receiving layer by thermal transferring the OP layer. It is conceivable that the dyes that exist in the molecule state in the dye receiving layer are strong in terms of durability. The UV(ultraviolet) rays absorbents that are included in the OP layer, have accomplished the role that prevents the dye deterioration.

Introduction

Recently, the scene that the image data on the digital still camera and on the Internet web are printed has increased rapidly. The printed matter with photograph quality can be obtained from various kinds of printers, because handled images have been turned high density data. As for the print of photograph picture quality, high speed printing and high durability of image have become necessary. In various kinds of print methods, thermal dye transfer printing can give high speed printing and high durability of images. Thermal dye transfer printing can give a A6 size print within 20 seconds. Thermal dye transfer printing has become a powerful candidacy as the printer for photograph quality. Also, thermal dye transfer printing has approached silver halide photograph real high durability levels by the improvement of print materials. The adoption of OP material is giving a remarkable effect to the light fading for dye images. In this report, the factor affecting the durability of dye image will be analyzed.

Experiment

Preparation of Print Materials

The ink ribbon was made from a polyethylene-terephthalate PET film 4.5μm thick, coated with a 1μm layer of dye and binder resin(polyvinilacetal). Pyrazoro-triazol dye was used for SIMS (Secondary Ion Mass Spectrometry) analysis and fluorescence dye (Kayaset Yellow SF-G) was used for fluorescence spectrum analysis.

OP ribbon with the Over Protect layer and only PET (OP-less ribbon) without the Over Protect layer were also prepared. Receiver paper that was mass-produced as a marketing article was used. Special receiving paper that dye was included in the dye receiving layer beforehand was prepared.

Thermal Dye Transfer Printing Conditions

The test printer that is able to reproduce conditions similar to the thermal dye transfer printer of marketing was prepared. The dyes were transferred from the ink ribbon to the receiver paper. The OP layer was transferred to the surface of the dye receiving layer. OP-less ribbon was used to heat the dye receiving layer that included the transferred dye.

Measurement of Transferred Dyes

Distribution of transferred dyes in the dye receiving layer was measured by SIMS(ATOMIKA,A-DIDA3000). SIMS detects the special atom that is only included in the dye receiving layer. In this report, the nitrogen atoms of Pyrazoro-triazol dye were detected. Materials of the dye receiving layer does not include any nitrogen atoms, the detected nitrogen atoms correspond to the distribution of the transferred dyes in the dye receiving layer. SIMS can obtain the information of depth direction with argon spattering treatment.

The fluorescence spectrum of dyes that were transferred to the receiving layer was measured by a Fluorescence Spectrophotometer F-4010 (HITACHI).

Durability Tests of Print Images

Ci 35 Xenon Fade-o-meter (Atlas) was used for xenon light stability test with each printed sample which has gradation pattern. The samples were put in the fadeometer for 350 hours of the light exposure with a dosage of $1.2W/m^2$ at 420nm. Dye stiffness was evaluated as residual rates by measuring OD change of dye image after light exposure.

The influence of the surrounding environment on the print image was evaluated as an image density decrease. The printing sample was established into the container that introduced the active agents (acid, alkali, ethanol). The printing sample was tested in comparison with Ink jet print sample simultaneously.

Results and Discussion

Light Stability

Figure 1 shows the results of the xenon light exposure test regarding Pyrazoro-triazol dye. Dyes that were only transferred show a low residual density. The transferred dyes with OP-less ribbon treatment show the high residual density.

Also, transferred dyes with OP layer are showing higher residual density than the treatment of OP-less ribbon. This result is conceivable according to the effect by the UV absorption of the OP layer.

In the receiver layer that the dyes were dispersed beforehand, the residual density has a high value. From these results, it is understood that the heat-treatment by OP ribbon and also OP-less ribbon have improved the durability of the dyes that were transferred beforehand.

From the above results, it is estimated that the transferred dyes were stabilized by the re-diffusion process in OP layer transferring.

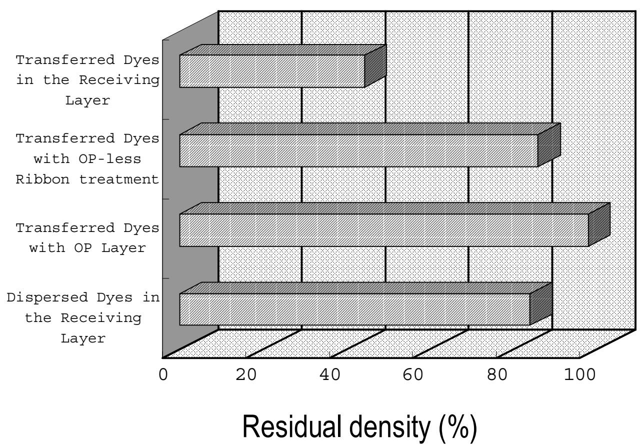

Figure 1. Light stability of various samples

Dye Existence Condition Analyses

Existence distribution of transferred dye in the receiving layer was measured. SIMS analysis of receiving layers that the dyes transferred to and that was treated by OP-less Ribbon after dye transfer are shown in Figure 2.

It is understood that the dye exists in the surface vicinity of the receiving layer after the dye transfer. The dye diffuses in deep into the receiving layer by the heat treatment of the OP-less ribbon. It is reported that dye deterioration is influenced by UV light and active oxygen strongly[1]. Also, the interaction between the dye and the dye receiving layer binder resin is important in durability performance. The dye and the dye receiving layer resin are chosen in terms of durability including light stability in addition to the dyeing performance. The dispersed dye in the dye receiving layer is stabilized compared to conditions where the dye is condensed.

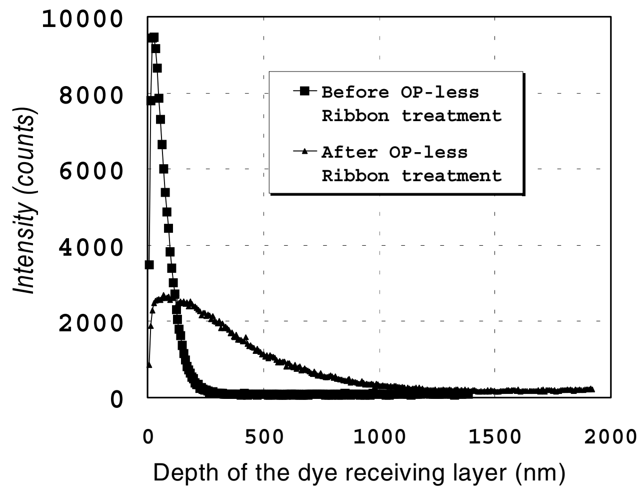

Figure 2. Distribution of transferred dye in the dye receiving layer

Fluorescence spectrum analysis was measured to evaluate the condition of the transferred dye in the dye receiving layer. By measuring the fluorescence spectrum of the fluorescence dye (Kayaset Yellow SF-G) that was transferred, the influence of the heat treatment by the OP-less ribbon was evaluated. Figure3 shows that the fluorescence spectrum strength of the transferred dye. It is understood that spectrum strength increases remarkably by heat-treatment of OP-less Ribbon.

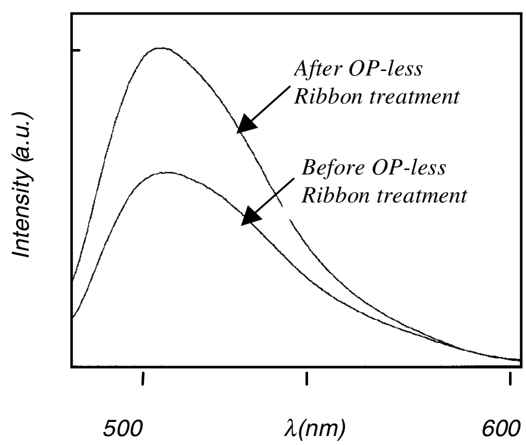

Figure 3. The fluorescence spectra of the transferred dye before and after OP-less Ribbon treatment

According to the OP-less ribbon heat-treatment, transferred dyes diffuse in the dye receiving layer. It is speculated that spectrum strength increased by making the dyes molecule state.

Dyes that were just transferred to the dye receiving layer are condensed in the surface of the dye receiving layer. Therefore, dyes are easy to receive the influence of

UV and surrounding oxygen at the time of the irradiation of xenon light.

As a results of SIMS and fluorescence analyses, dyes diffuse deeply by heating at the time of transfer of the OP layer. The transferred dyes are considered to be stabilized more by heat transfer of the OP layer.

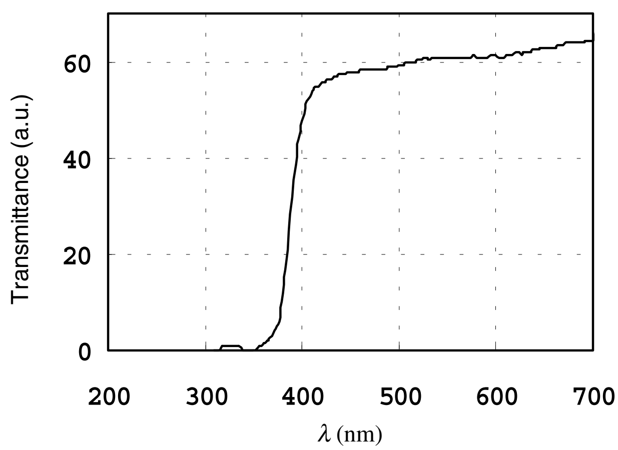

Figure 4. The absorption spectrum of the OP layer

Table 1. Durability to the active agents

Sample	Hydrochloride acid	Ammonia water	Ethanol
Thermal Dye Transfer	Good	Good	Good
Ink Jet	Poor	Poor	Fair

Over Protect Layers

The absorption spectrum of the OP layer that is used with thermal dye transfer printing is shown in figure 4. The light under 400 nm range is absorbed and the OP layer protects the receiving layer from UV light. Also OP layer protect the transferred dye image from fingerprints, plasticizer and humidity.[2] Generally dyes are week for active agents like a active oxygen. Transferred dye image with OP layer is hardly affected by the air within the saturated active agents, acid, alkali or alcohol. Table 1 shows the results of durability to the active agents. It is understood that the transferred dyes image with OP layer has a good performance for the durability to the active agents.

Conclusion

The durability of the dye image in thermal dye transfer printing has been studied. It is understood that the condition of the transferred dye is important for durability.

The transferred dyes diffuse toward the depth of the dye receiving layer by heat treatment of the OP layer transfer. The dispersed dyes in the dye receiving layer are stabilized. Furthermore, the transferred dye image with OP layer is protected from UV light and the surrounding environment including active agents.

Dye itself and the combination of dyes and the dye receiving layer resins are important in the point of the durability. Developed thermal dye transfer materials contribute to the durability of the transferred dye images. Accordingly, it is conceivable that a better image stability is obtained by the strength of dyes and the dye receiving layer materials and an optimized OP layer.

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References

1. N. Kuramoto and T. Kitao, J.S.D.S.,98,334(1982)
2. H. Saito, Proceedings of IS&T's 15th International Conference on Digital Printing Technologies, 251 (1999).

Biography

Noritaka Egashira received his Masters Degree from Chiba University of Japan in 1982.

He has worked for Dai Nippon Printing Co. since 1982. He has studied imaging materials and imaging systems. He received Doctor Degree from University of Tokyo Agriculture and Technology in 1993.