Image Stability of TA Paper

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Abstract

The image stability of TA (Thermo Autochrome) paper under dark storage conditions and display conditions was evaluated. "TA" direct thermal full color recording paper has three color forming layers: an outermost yellow color forming layer, a magenta color forming layer and an innermost cyan color forming layer. The yellow and the magenta color images were formed by an azo dye, and the cyan color image was formed by a leuco dye within the microcapsule in each color forming layer.

The dark stability at room temperature was predicted by an accelerated thermal test based on the Arrhenius law. The light stability under normal display conditions was evaluated by an accelerated light test which utilize a xenon arc lamp. The dark stability of the latest TA paper was improved by introducing a new leuco dye precursor, and the light stability was also improved by introducing an ultraviolet absorber precursor layer and a low oxygen permeability layer. The improvement of the image stability is evaluated in this paper.

Introduction

The TA system creates high quality continuous tone full color prints without any accompanying wastes such as an ink ribbon or an ink cartridge. In addition, the print is obtained by a complete drying process, and the printer is reliable due to the simplicity of its mechanisms.[1]

The TA paper was put on the market in 1994. Recently it becomes to be used widely for the output of the digital still camera. Therefore, we are taking an increasing interest in the image stability. In this paper we will evaluate the dark stability and the light stability to understand the image stability of the TA paper.

Mechanism of Image Formation

A simplified cross-sectional view of the TA paper is shown in Figure 1. The outermost layer is a heat-resistant protective layer. The yellow color forming layer is comprised of a microencapsulated diazonium salt compound, an organic base, and a coupler which react to form a yellow azo dye. The magenta color forming layer is comprised of a microencapsulated diazonium salt compound, an organic base, and a coupler which react to form a magenta azo dye. The innermost color forming layer is comprised of a basic leuco dye and a phenolic compound developer which react to form a cyan dye.

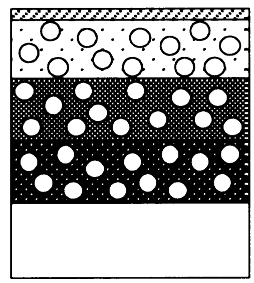

Figure 1. Simplified cross-sectional view of TA paper.

A full color print is obtained in a five-step printing process with the TA system. First, the yellow color forming layer reacts to low levels of thermal energy to generate the yellow portion of the image. Second, the entire print is exposed to a 420nm ultraviolet lamp, which decomposes a diazonium salt compound remaining in the yellow color forming layer. Third, the magenta color forming layer reacts to mid-range levels of thermal energy to generate the magenta portion of the image. Fourth, the entire print is exposed to a 365nm ultraviolet lamp, which decomposes a diazonium salt compound remaining in the magenta color forming layer. Finally, the cyan color forming layer reacts to high levels of thermal energy to generate the cyan portion of the image.

Evaluation Methods

Dark Stability

The dark stability at room temperature was predicted by an accelerated thermal test based on the Arrhenius law. The temperatures of the four specific test conditions were 70°C, 60°C, 50°C, and 40°C. And the relative humidity for all tests was 70%. The life of the image at room temperature was predicted by using the Arrhenius law from the result of accelerated thermal tests.

Light Stability

The light stability was evaluated by an accelerated light test which utilize a xenon arc lamp. In this test, exposure illuminance was 85klux with a Pyrex/soda lime filter to simulate outdoor sunlight through a windowpane. The light exposure cycle consisted of 3.8hour-light and 1-hour darkness.

Samples

Following samples were used for the evaluation.

Sample A: The initial product. (NC-1 printer paper, put on the market in 1994.)

Sample B: The latest product. (NX-70 printer paper, put on the market in 1998.)

The actual change of the image stored indoors in Okinawa, Japan was confirmed for sample A. (Average temperature and humidity during year was 25°C and 70%R.H.)

Results and Discussion

Dark Stability

The density of the cyan image decreased, and the stain increased in accelerated thermal tests. However, the density of the yellow and the magenta image didn't decrease under these test conditions. Arrhenius plots of the cyan image fading and the stain increase are shown in Figure 2 and Figure 3 respectively.

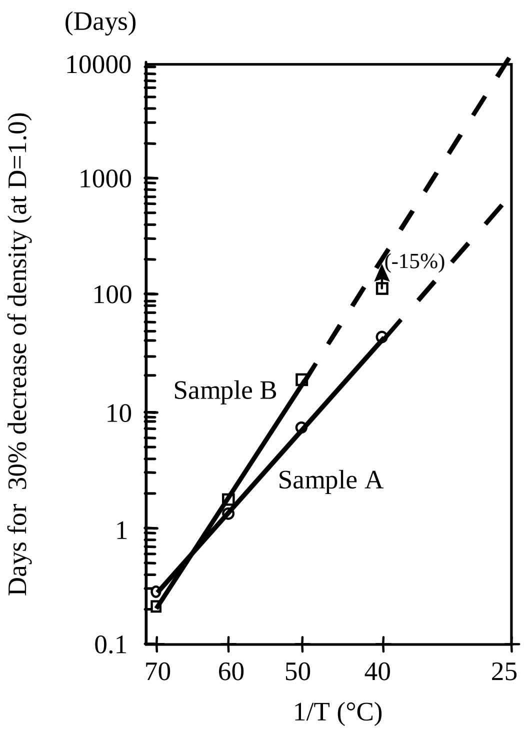

Figure 2. Arrhenius plot of the cyan image fading.

The color forming reaction of a leuco dye of the cyan image is a reversible reaction. The thermal decomposition of a leuco dye was verified in certain test conditions. But in other test conditions, a leuco dye might discolor according to the pH surrounding a leuco dye or the recrystallization of a phenolic compound developer. Therefore, we verified whether it was appropriate to predict the image stability at room temperature from test results at high temperatures. Predicted dark stability of the cyan image and the stain increase at 25°C and 70%R.H. by the Arrhenius law and the actual change of the image stored at room temperature are shown in Figure 4. Thus, it was confirmed that the prediction data of sample A almost corresponded to the actual change of the image at room temperature for both cyan image fading and the stain increase.

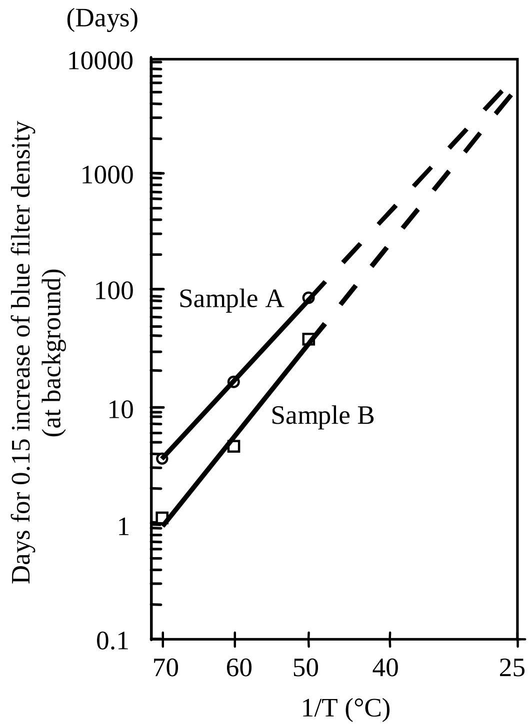

Figure 3. Arrhenius plot of the stain increase.

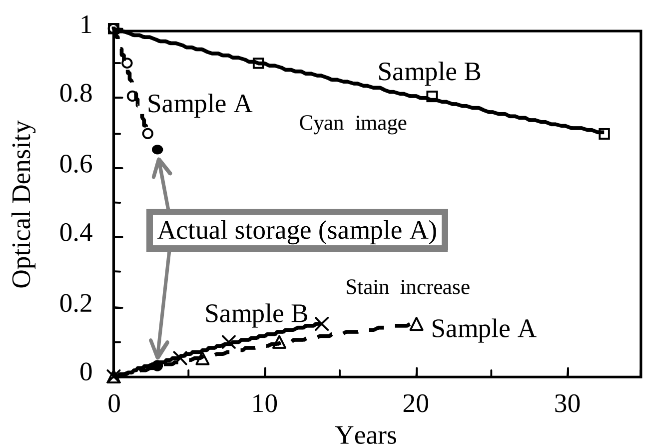

Figure 4. Predicted dark stability of the cyan image and the stain increase at 25°C 70%R.H.

The cyan image fading of sample A was remarkable, but the dark stability of sample B was improved mainly by introducing a new leuco dye precursor shown in Figure 5b. Activation energy of sample B was larger than that of sample A in Figure 2. It might be the reason that the intramolecular hydrogen bond was formed by means of changing the leuco dye's structure, and the thermal decomposition of the leuco dye was suppressed.[2] As a result, it was predicted that it is possible to preserve sample B for ten years or more at room temperature. Though some stains increase, this determines the life of the image. (In this prediction, 20 to 30% of the density decrease and +0.15 of the blue filter density in the stain increase assumed to be an allowable limit.)

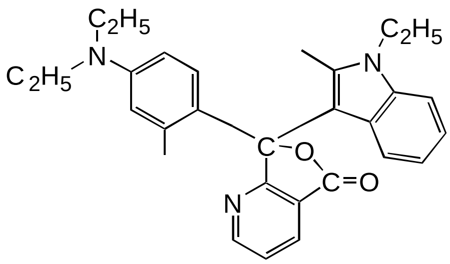

Figure 5a. Leuco dye precursor used in sample A.

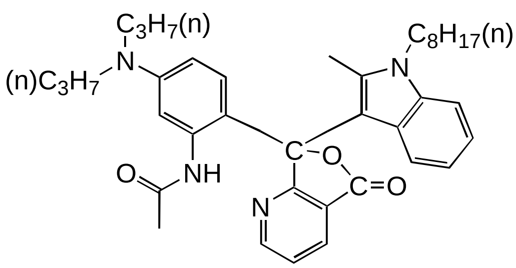

Figure 5b. New leuco dye precursor introduced in sample B.

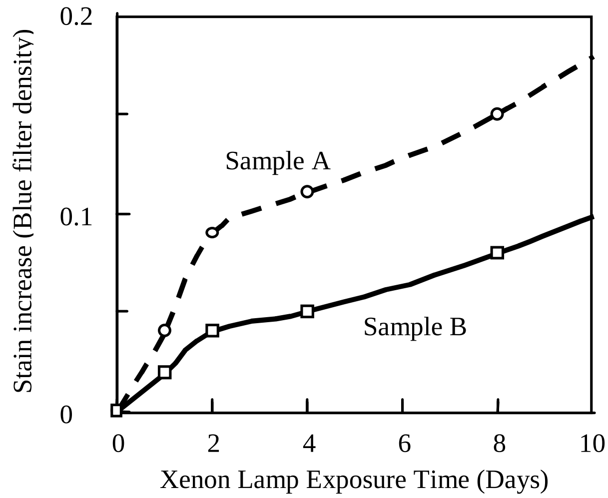

Figure 6. Light stability of background.

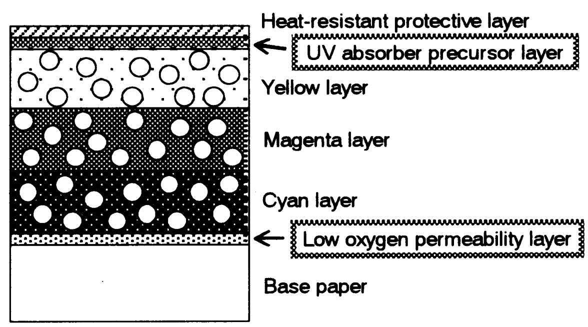

Figure 7. Simplified cross-sectional view of a new type of TA paper.

Light Stability

The accelerated test result of the stain in the light stability is shown in Figure 6. The stain increase has been improved to about 1/2 in sample B, though it was remarkable in sample A. The reason for this is that "a low oxygen permeability layer" was introduced between the cyan color forming layer and the base paper. Also, "an ultraviolet absorber precursor layer" which forms an ultraviolet absorber by light exposure was introduced between the heat resistant protective layer and the yellow color forming layer.[3] A simplified cross-sectional view of this new type of TA paper is shown in Figure 7. The exposure energy for one day in this accelerated test corresponds to that of about one week exposed to sunlight through a windowpane. (The illuminance was assumed 20klux and the irradiation time was assumed to be 12 hours a day.)

Conclusions

The dark stability and the light stability were evaluated, the image stability in the TA paper became clear. Especially, we found the dark stability of the cyan image was able to be predicted by the Arrhenius law. It was found out that the dark stability and the light stability had improved from an initial product by introducing several improved kind of technology.

In addition, the image is stable, does not transfer, does not blur, and does not discolor from plasticizers and solvents in comparison to other materials which utilize the movement of coloring agents. This is a result of the color image of TA paper being formed within the microcapsule in each color forming layer.

However, the improvement of the image stability will be required further, and we would like to concentrate on the development of technology which improves image stability.

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References

1. T. Usami and A. Igarashi, The Development of Direct Thermal Full Color Recording Material, *Journal of Inf. Recording*, **22**, 347-357(1996).
2. N. Yanagihara, H. Yamada and S. Higashi: New Cyan Dye Precursor for TA Paper, *The 4th International Symposium on Functional Dyes*, Osaka, Japan, May 31-June 4,1999 pp.53
3. S. Sano, K. Minami, A. Igarashi and M. Takashima: New Light Stability Technology in TA Paper, *Proc. IS&T's PICS Conference*, pp.106 (1998)

Biography

Eiichi Sakai joined Fuji Photo Film in 1987 after receiving his M.S. degree in materials science from University of Electro-Communications. From 1987 to 1991, he worked on the research and development of information recording materials. He is currently working on the research and development of a full color direct thermal recording system.

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Akira Igarashi joined Fuji Photo Film in 1975 after receiving his M.S. degree in polymer engineering from Tokyo Inst. of Technology. From 1975 to 1987, he worked on the research and development of a conventional thermal paper. He is currently working on the research and development of a full color direct thermal recording system.