Development of a New 1,1-Dioxo-1,2,4-Benzothiadiazine Type Yellow Coupler

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Abstract

We have developed a new yellow dye-forming coupler, which has a 1,1-dioxo-1,2,4-benzothiadiazine structure. The azomethine dye formed from the new coupler has a high molar extinction coefficient (ε) and high acid stability. The high ε is due to the high planarity of the chromophore moiety of the new dye. A new Fujicolor "Crystal Archive Paper Type II" has been commercialized by introducing this coupler. The new coupler technology helps to decrease the amount of silver halide and coupler in a blue sensitive layer and also helps to improve the image stabilities especially when in contact with acid gases.

Introduction

Acylacetanilide type yellow couplers, such as pivaloyl-acetanilide or benzoylacetanilide, have conventionally been used in photographic color papers and films. The molecular extinction coefficient (ε) of azomethine dyes formed by these couplers is lower than that of a magenta or cyan coupler, therefore a yellow coupler layer has required larger amounts of coupler and silver halide than a magenta coupler layer or a cyan coupler layer. Moreover, since the acid stability of the conventional yellow dyes is low, the image storability has been relatively inferior under conditions of high-temperature, high-moisture and coexistence of acid gases.

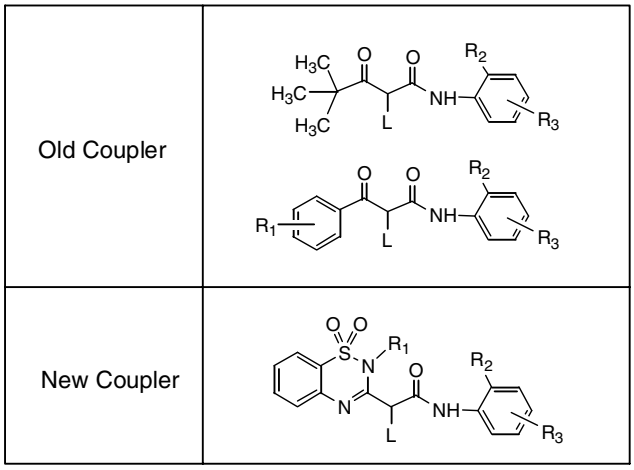
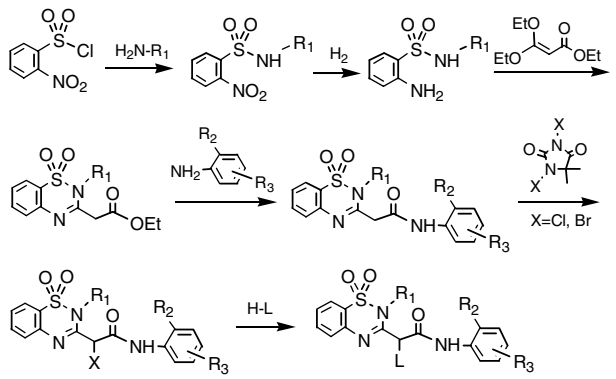


***Figure 1**. Structures of yellow couplers.*

In order to solve these problems, we investigated hetero-ring linked acetanilide type couplers, and have found that a 1,1-dioxo-1,2,4-benzothiadiazine type yellow coupler has excellent performance.

Results and Discussion

The structure of the new coupler is shown in Figure 1, and the typical synthetic route is shown in Scheme 1. The azomethine dye was formed from the coupler by an oxidative coupling reaction with phenylenediamine type developing agent.



***Scheme 1**. Synthetic route of a 1,1-dioxo-1,2,4-benzothiadiazine type coupler.*

The ε of the azomethine dye obtained from the new coupler is much higher than that of conventional pivaloylacetanilide type dye (Figure 2), and the new dye is superior to pivaloylacetanilide type dye as shown by the higher slope of the absorption curve at longer wavelengths (Figure 3).

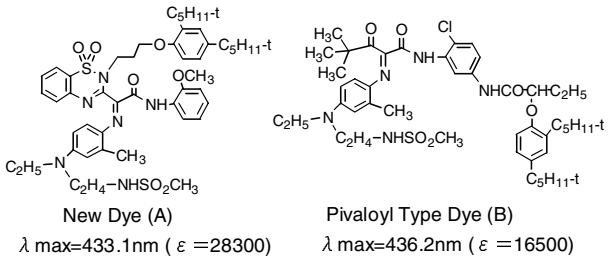


***Figure 2**. Structures of yellow dyes and absorption properties in ethyl acetate.*

The X-ray crystal structure analysis of the new azomethine dye was performed to analyze the extremely high observed. The twist angle of the benzene ring part of the developing agent in the new dye was 9° and smaller than that of pivaloylacetanilide type dye (about 37°). It was previously reported that the high planarity of the chromophore causes the high [1].

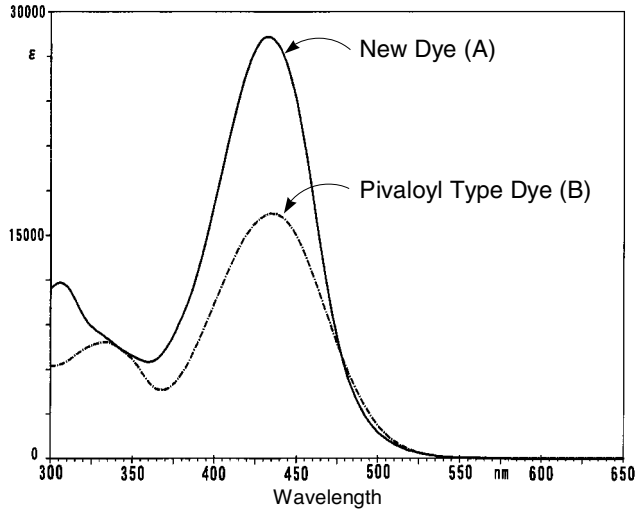


***Figure 3**. Absorption spectra of yellow dyes in ethyl acetate.*

It is believed that the size and shape of 1,1-dioxo-1,2,4-benzothiadiazine moiety is adequate to increase the planarity of the chromophore and rigidity of the new dye. This causes the high and the steep absorption curve.

Since acid hydrolysis is a main factor in fading of yellow azomethine dyes, the acid stability of the new dye was evaluated in the solution system. As a result, it has been revealed that the new dye has extremely high acid stability compared with conventional pivaloylacetanilide type dye (Figure 4). Actually this new coupler serves to improve image stability of new Fujicolor paper, especially when in contact with acid gases.

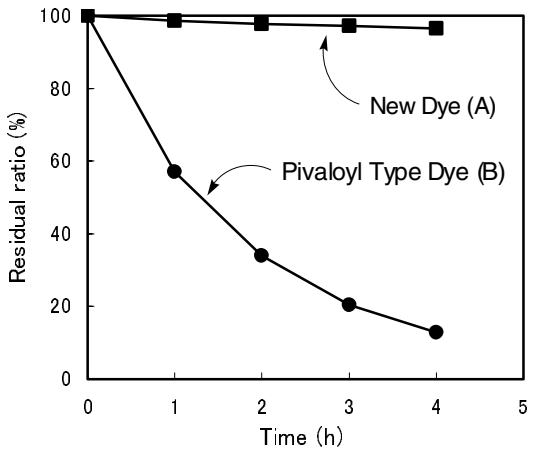


***Figure 4**. Acid stability of yellow dyes in acidic 1-methyl-2-pyrrolidone.*

Also, the light stability of the new dye was evaluated in the solution system. As a result, it has been revealed that like the conventional pivaloylacetanilide type dye, the new dye is stable (Figure 5).

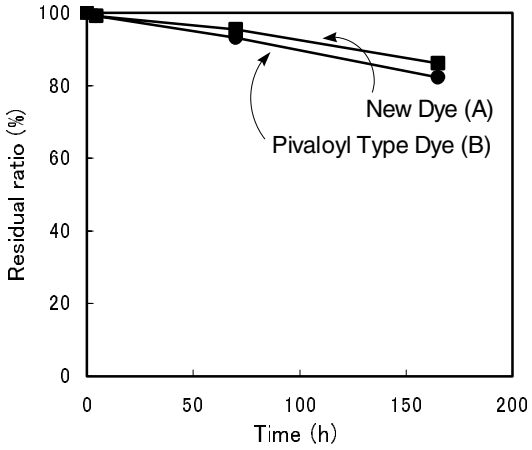


***Figure 5**. Light stability of yellow dyes in ethyl acetate.*

As for pKa of yellow couplers for conventional photographic color paper and film, the optimal range for color formation is between 6 and 9. This new coupler can adjust within the above-mentioned range by selecting substituents and a leaving group. With certain substituents and leaving groups, reactivity of the new coupler is higher than that of conventional couplers.

We have further exerted in-depth studies on this new-type structure and have developed a yellow coupler optimal for photographic color paper. The new-type coupler has been introduced in new Fujicolor "Crystal Archive Paper Type II".

Conclusion

We have developed a new yellow coupler, which has a 1,1-dioxo-1,2,4-benzothiadiazine structure. The azomethine dye formed from the new coupler has a high molar extinction coefficient and high acid stability. The new coupler technology allows a decrease in the amount of silver halide and coupler in a blue sensitive layer. Through introduction of this new coupler technology, the suitability of the color paper has been enhanced for rapid processing systems, and excellent image storability has been attained.

References

[1] S. Ichijima, H. Fukunaga, H. Kobayashi, M. Ishihara, and N. Koga, "Theoretical Study on the Structures and Absorption Properties of Yellow Azomethine Dyes", Bulletin of the Chemical Society of Japan, 76, 733(2003).

Author Biography

Kiyoshi Takeuchi graduated from the Tohoku University in 1986, and from graduate school at the same university, receiving a master's degree in chemistry in 1989. Since then he has worked in the Ashigara Research Laboratories at Fuji Photo Film Co., Ltd. in Minami-ashigara. His work has focused on the development of photographic materials. Now, he is a research associate at Synthetic Organic Chemistry Laboratories.