

# The Effect of Polymeric Addenda on Dark Fading Stability of Cyan Indoaniline Dye

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## Abstract

An investigation on the heat-decomposition mechanism of indoaniline dyes suggested that preventing the reaction between dyes or between dyes and heat-decomposition products is important to improve dark fading stability of cyan Indoaniline dyes. This has led to the development of the polymer-protected coupler (PPC) technology incorporated in all Fujicolor Super FA papers.

This paper describes the effect of polymer addenda on indoaniline dyes in terms of an assumed mechanism for heat-decomposition of cyan indoaniline dyes and physical properties of polymers.

## Introduction

In color papers, cyan image is the most vulnerable to heat among three dyes: yellow, magenta and cyan.

The cyan couplers used in color papers can be divided into two main types: 2-acylamino-5-alkylphenol and 2,5-diacylamino-phenol type cyan couplers.

Couplers of 2-acylamino-5-methylphenol type have the disadvantage that the dyes formed from them have poor heat fastness while they have good light fastness. Further, cyan dyes formed from couplers having 2 or more carbon atoms substituted on the 5-position have improved heat-fastness, but is still insufficient.

Couplers of 2,5-diacylaminophenol type give dyes of excellent heat fastness but of poor light fastness and, in addition, with absorption wavelengths too short to be used without a combination with 2-acylamino-5-alkylphenol type coupler.

Thus, there traditionally was a trade-off between light and heat fastness of cyan indoaniline dye.

Polymer protected coupler (PPC) technology, applied to a light-stable-dye forming 2-acylamino-5-alkylphenol type coupler, has solved this problem and achieved the strong heat- and light-fastness, contributing to excellent dye stability of Fujicolor Super FA prints.

In order to investigate the mechanism of heat-decomposition of the dyes and evaluate the effect of polymer addenda, the dye (C-1) obtained from coupling reaction of 2-( $\alpha$ -2,4-di-tert-amylphenoxybutanamido)-4,6-dichloro-5-methyl phenol and oxidized 4-amino-3-methyl-N-(2-methane-sulfonamido-ethyl)aniline(CD-3) was used. The

experiments were done with the test tube as well as a single-layer coating format containing dyes and addenda.

## Result and Discussion

### Heat-decomposition of Cyan Indoaniline Dye.

To investigate the decomposition reaction of the dye in a simple system, we adopted the dye (C-1) dissolved in solvent (S-1) with the ratio of 1:1(wt/wt) and observed the heat-decomposition behavior of the mixture under 140°C.

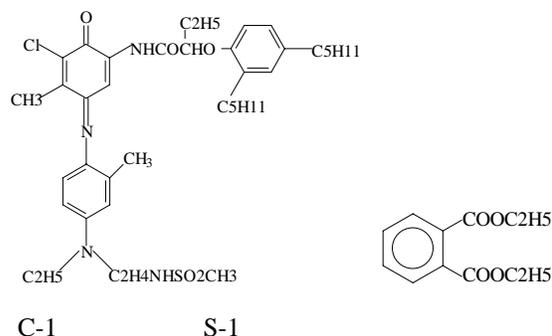


Figure 1. Cyan dye and solvent for analyzing the behavior of heat-decomposition

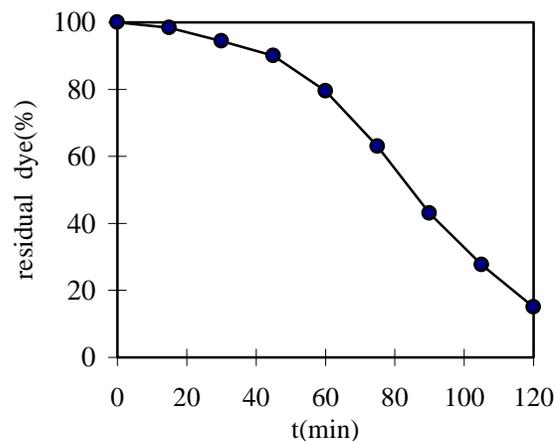


Figure 2. Heat-decomposition profile of cyan indoaniline dye

The percentage of residual dye to initial amount which is plotted against heating time is shown in Figure 2. This shows that in the early stage, the decomposition rate is slow but becomes faster as the reaction proceeds, suggesting that the decomposition products may accelerate the reaction. In order to prove this, the effect of decomposition products on the reaction was investigated. The decomposition products prepared beforehand was added to the dye solution (C-1/S-1=1/1(wt/wt)) and the heat-decomposition behavior of the dye was observed. Figure 4 shows that decomposition product of the cyan indoaniline dye accelerates the heat-decomposition of the dye.

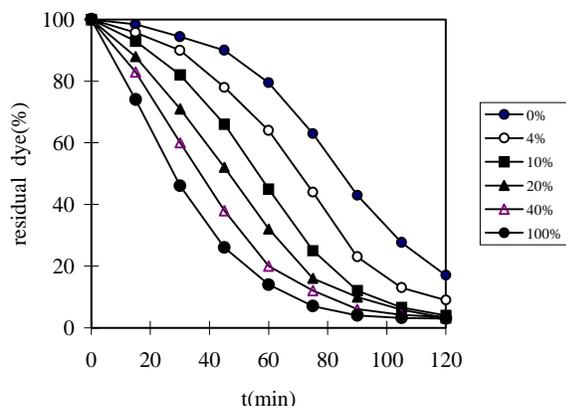


Figure 4 Heat-decomposition of cyan indoaniline dye accelerated by adding its decomposed product (140°C 2hr) to the dye.

Among the decomposition products of the indoaniline dye, we found the leuco form of the dye. For the further qualitative analysis, the heat-decomposition experiment was made under nitrogen gas environment to prevent the colorless leuco dye from being oxidized to the corresponding dye by oxygen.

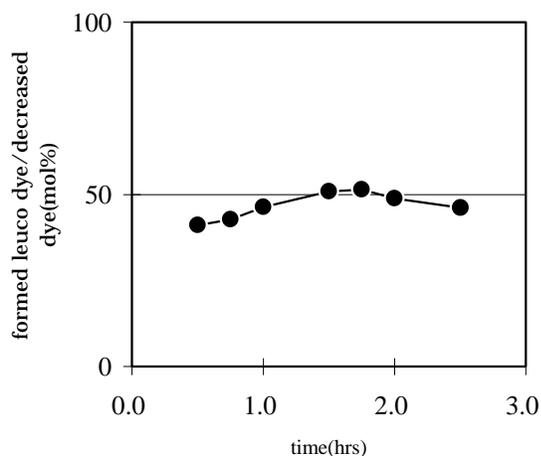


Figure 5 Formed leuco dye / decreased dye (mol%)

Figure 5 shows that the ratio of the leuco dye to the decreased dye was about 50mol% at each observed time from the early stage of the decomposition. This indicates that the heat-decomposition reaction of cyan indoaniline dyes involves the redox reaction between two dye molecules, yielding one leuco dye (reduced form) molecule and one oxidized form molecule.

### Improved Dye-stability by Polymeric Addenda

The results obtained above suggests that preventing the reactions between the dyes and/or the dye and the decomposition product is effective to improve the heat-fastness of indoaniline dyes. To achieve this physically, we attempted to decrease the mobility of the dyes and the decomposition products by replacing oil formers with polymers. In this experiment, the cyan indoaniline dye (C-1) and either of a oil former (e.g.S-2) or a polymer(e.g.P-1) were dissolved together with ethyl acetate, the solution was emulsified in an aqueous solution containing gelatin and surfactant to give fine particles. The emulsions were coated on a transparent PET support and used for the dye-stability study. The effect of the polymer (P-1) compared with the oil former(S-2) is shown in Figure 7.

This figure clearly shows that the dark-stability(heat-fastness) of cyan indoaniline dyes can be greatly improved by the polymer and the acceleration process of the decomposition seems to disappear in the case of the dye with the polymer:P-1. This means that the polymer efficiently prevents the reaction involving the decomposition product.

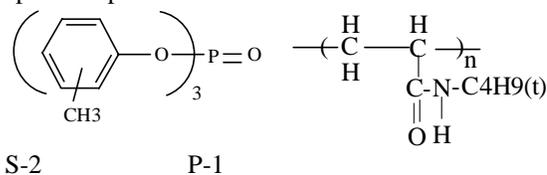


Figure 6. trityl phosphate and poly(t-butylacryl amide)

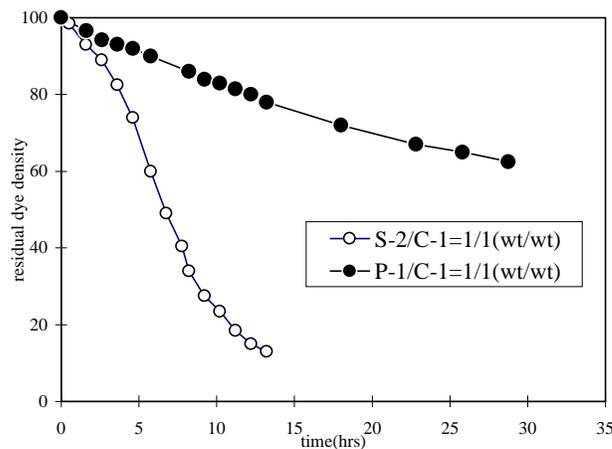


Figure 7 The improved heat-fastness of cyan indoaniline dye by poly(t-butylacrylamide)(at 120°C)

Glass transition point(Tg) of polymer is known to be closely related to the mobility of polymer chains. The mobility of polymer chains are more restricted as Tg rises.

We studied the relation between the heat-fastness of cyan indoaniline dye (C-1) and Tg of polymers used together with the dye. Figure 8 shows there is a strong correlation between them. This can be explained that polymers with high Tgs suppress the motions of dye molecules and decomposition products by lodging them in the polymer matrix to retard the decomposition reaction.

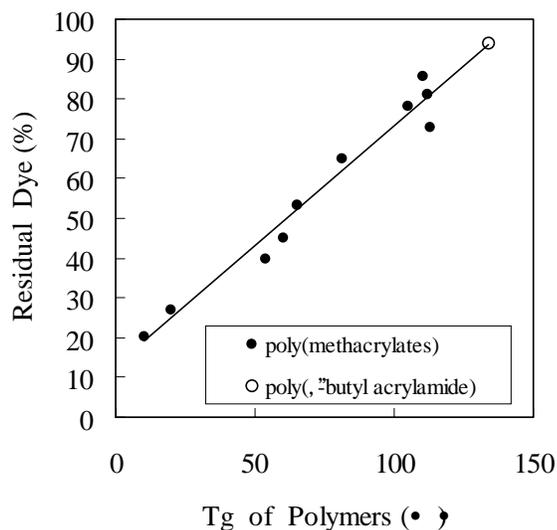


Figure 8 Relation between heat-fastness of cyan indoaniline dye and Tgs of polymers(80°C 180days)

## Summary

Studies of cyan indoaniline dyes have shown that preventing the reactions between the dyes and between the dye and the decomposition product is the key point to improve heat-fastness of indoaniline dyes. Polymers with high glass transition temperatures were tested with an aim of decreasing the mobility of the dyes and the decomposition products. They proved to be effective stabilizers for indoaniline dyes.

## References

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