

# A Pigment Precursor for Inkjet Inks

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There are two general categories of water-based inkjet inks: dye-based inks and pigment-based inks. Pigment-based inks provide images with comparatively greater stability when subjected to light or to chemically reactive materials such as oxidizing gases. However, pigment-based inks typically fail to provide image gloss and resistance to abrasion. In response, we have developed a novel inkjet ink that employs a new water-soluble pigment precursor. During printing, this pigment precursor ink behaves much like a dye-based ink. But once this ink has been applied to the print medium, a simple treatment triggers the provision of pigment particles. The result is an image that possesses not only high image stability but also high gloss and high resistance to abrasion.

## 1 Introduction

Recent years have seen marked technical advances in inkjet printing, with the image quality and the image stability of inkjet prints approaching those of photographic prints.

Many efforts that have borne on bringing high image quality and high image stability together have been made. Bauer, Baumgart, and Zoller surveyed a number of water-soluble magenta dyes.<sup>1)</sup> Bugner and Burmel studied the effect of particle size in pigment inks on such characteristics as printing reliability, image quality, and durability.<sup>2)</sup> Tsutsumi, Sawada, and Nakano developed an emulsion colorant involving a water-based polymer emulsion that contained a water-insoluble dye or pigment.<sup>3)</sup> Zhimin and Abul developed a solvent-soluble pigment precursor (latent pigments).<sup>4)</sup> And Parazak examined the application of latent pigments to inkjet printing<sup>5)</sup>.

We join these efforts with a method in which a water-soluble pigment precursor penetrates the surface of the printing medium and then releases a pigment. This combines the high gloss and resistance to abrasion of a dye-based ink with the superior light stability of a conventional pigment-based ink.

## 2 Experimental

Our work may be viewed in four segments:

1. The design and synthesis of a new water-soluble pigment precursor,
2. The preparation of an ink containing that water-soluble pigment precursor, and printing an interim image with that ink,

3. The post-printing treatment of the medium to release the pigment from the pigment precursor, and
4. The evaluation of the terminal image.

### 2. 1 Design and synthesis of pigment precursor

We selected a quinacridone pigment (CI Pigment Red 122) as our color material because magenta presents the greatest challenge to simultaneously achieving optical brightness and high image stability.

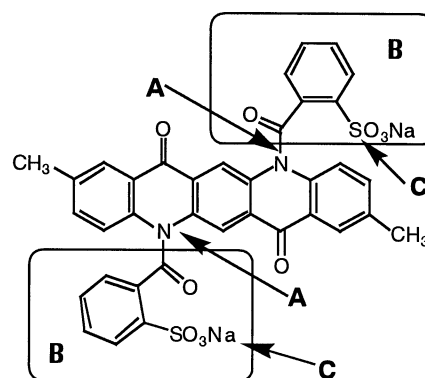


Fig.1 Pigment precursor

In the pigment precursor that we designed and synthesized (Fig. 1), the nitrogen atoms (A) are protected by groups (B) to increase water solubility, which is accomplished by preventing the aggregation of molecules. The groups contain a water-soluble radical (C). The composition of the groups (B) is designed to afford ease of synthesis and stability in water. Compared to an m-sulfonic acid salt type, this o-sulfonic acid salt type precursor is easy to synthesize and provides good stability; in this, the steric effect of the o-sulfonic acid salt is likely involved.

The pigment precursor was synthesized from CI Pig-

ment Red 122 and o-sulfobenzoic anhydride, using NaH in HMPA or N-methylpyrrolidone (**Fig. 2**). The com-

pound obtained was identified as the target compound through NMR and mass spectra.

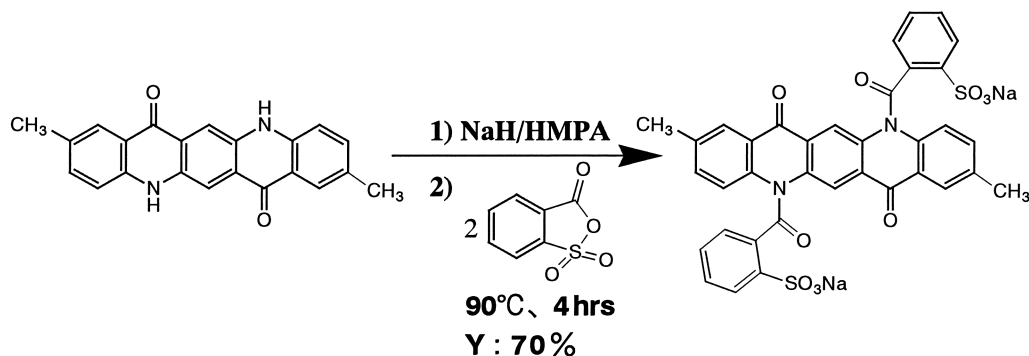


Fig.2 Synthesizing the pigment precursor

The pigment precursor was dissolved in water to approximately a 10% solution, the solution was colored yellow, and the stability of the pigment precursor was then studied at various pH values. The pigment precursor was stable in alkali (**Fig. 3**) and neutral conditions, while in acidic conditions (in a pH 1.68 buffer), the precursor was slowly hydrolyzed at room temperature, and a red precipitate appeared.

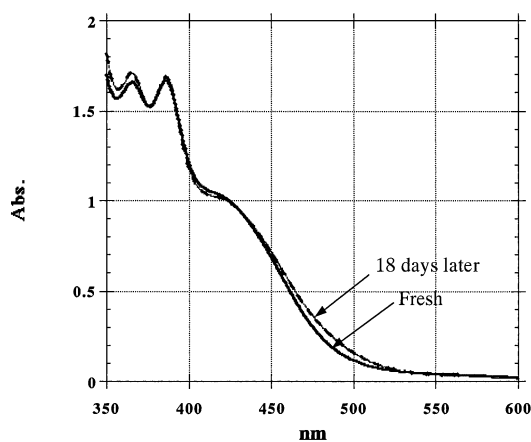


Fig.3 Stability of the pigment precursor (pH10.0)

## 2. 2 Ink preparation and printing

We prepared an ink containing the pigment precursor, consisting of the following:

- Pigment precursor (6%)
- Diethylene glycol (10%)
- Glycerol (10%)
- Triethylene glycol mono-n-butyl ether (10%)
- Nonionic surfactant (0.1%)
- Deionized water (63.9%)

With this ink, we printed on a porous medium (Konica Inkjet Paper Photolike QP) with a commercial inkjet printer (Piezo type) and obtained a yellow image (**Fig. 5**).

## 2. 3 Post-printing treatment

Prints were sprayed with diluted sulfuric acid or p-toluene sulfonic acid aqueous solution, and heated to 90-130°C for several seconds with a commercial laminator. This post-printing treatment caused the pigment precursors to be hydrolyzed and thus to release the pigment particles (**Fig. 4**). Consequently, from the yellowish, interim image, the reddish, terminal image emerged.

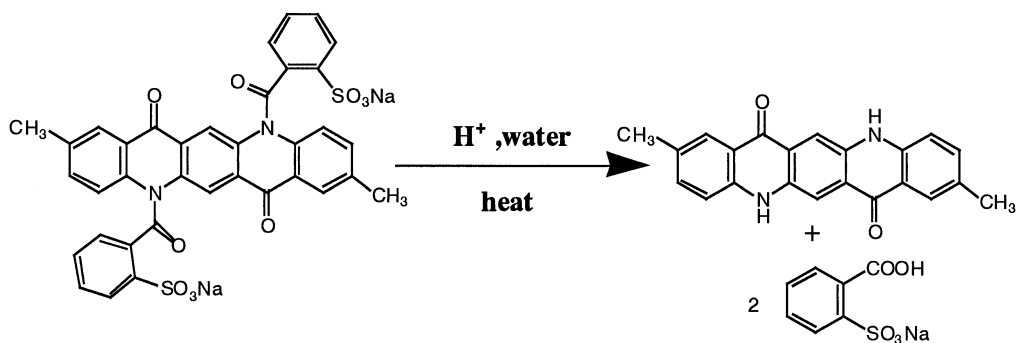


Fig.4 Synthesizing the pigment precursor

## 2. 4 Evaluation the image

We measured the reflection spectra of the terminal image and compared it with that of an image printed with conventional CI Pigment Red 122 water-based ink (Fig. 5). The two spectra were nearly identical.

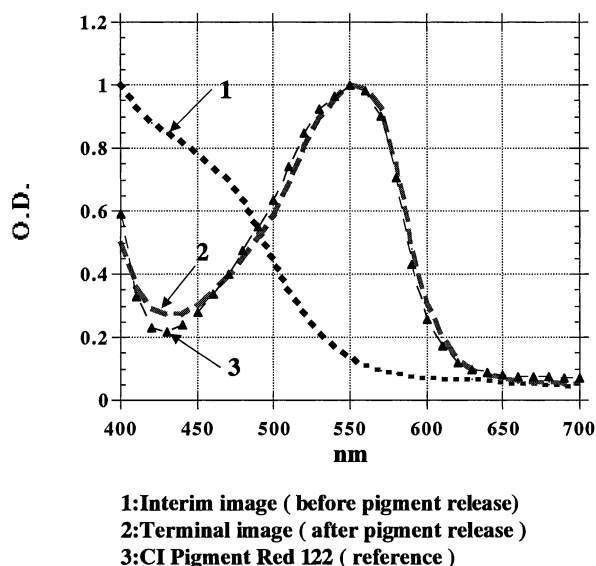


Fig.5 Reflection spectra

Extending our comparison to encompass an appropriate dye image, we evaluated the gloss, light stability, and resistance to abrasion resultant from the three types of inks (Table 1). The pigment precursor image exhibited the high gloss and resistance to abrasion of the dye image while it approached the light stability of the conventional pigment image.

Table1 Image evaluations

Type of ink	Gloss	Resistance to abrasion	Light stability
Pigment precursor	High	High	High
Conventional pigment	Low	Low	Very high
Dye	High	High	Low

To determine how the pigment precursor image managed to simultaneously avoid the low gloss and resistance to abrasion of the conventional pigment image and the low light stability of the dye image, we examined microscopic, cross-sectional views of each image (Fig. 7).

Pigments naturally provide high light stability. However, with a conventional pigment image (Fig. 7 A), the pigment lies chiefly on the surface of the medium. Because the average size of the pigment particle is roughly 100-150nm, the pigment particle is prevented from penetrating the surface. The result is a surface roughness that both limits gloss and leaves the image susceptible to abrasion.

In contrast, dye images (Fig. 7 B), by their nature, do not provide sufficient light stability. However, because dye images penetrate the surface of the medium, they do allow high gloss and high resistance to abrasion.

In the pigment precursor image (Fig. 7 C), the pigment precursor deposits the pigment well below the surface of the medium; thus, just as with dyes, gloss and resistance to abrasion are high. But at the same time, by virtue of being true pigments, light stability is also high.

It should be observed that the light stability of our experimental pigment precursor images, while exhibiting the characteristically superior light stability of a pigment image, does not yet match the performance of a conventional pigment-based ink (Fig. 6). As we address this challenge, we note that the light stability of a pigment image generally increases with the size of the pigment particles.

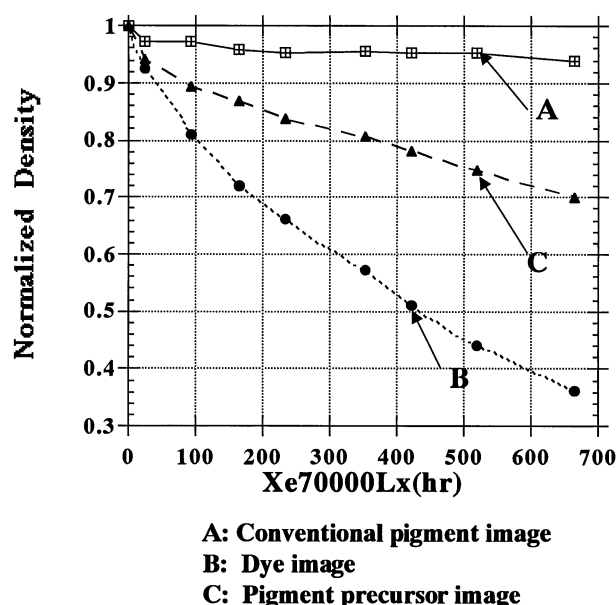


Fig.6 Light stability

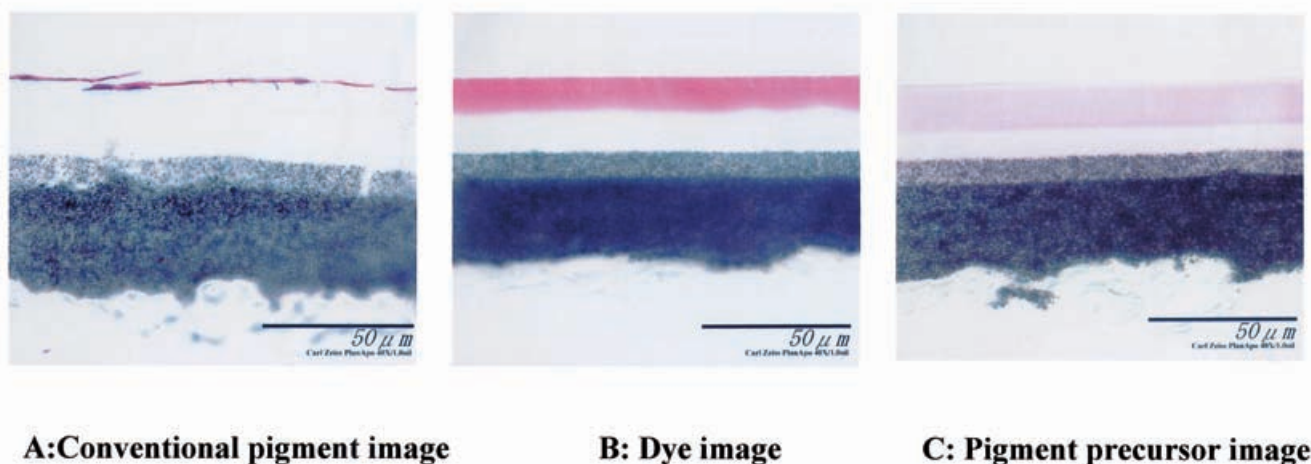


Fig.7 Cross-sectional views of images

### 3 Conclusion

We synthesized a quinacridone type water-soluble pigment precursor and evaluated its performance. Our results indicate that inkjet inks using pigment precursors promise to combine the high gloss and resistance to abrasion of dye-based inks with the high light stability of conventional pigment inks.

#### References

- 1) Wolfgang Bauer, Dieter Baumgart, and Walter Zoller, IS&T's NIP12: International Conference on Digital Printing Technologies, Proceedings, pp.59-65 (1996)
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- 5) Dennis P. Parazak, Japanese Patent Publication Open to Public Inspection No. 11-246809