

# The Physicochemical Environment of Acid Red 249 Insolubilized in an Ink-Jet Paper

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## Abstract

The physicochemical environment of the dye in the printed image influences the image quality. In this investigation, the environment of the dye in the ink-receiving layer has been deduced from the results of studies of the interaction between a dye and certain inkjet chemicals. The interaction among the dye Acid Red 249, silica as a white pigment, Polyfix 601 as a dye-fixing agent that is a cationic polymer, and polyvinyl alcohol as a binder has been investigated in aqueous solution and in the solid state. We conclude that Acid Red 249, printed on a receiving paper that includes Polyfix 601, mainly forms an ionic complex with Polyfix 601 dispersed in the polyvinyl alcohol layer; some dye remains as a solid layer on the surface.

## Introduction

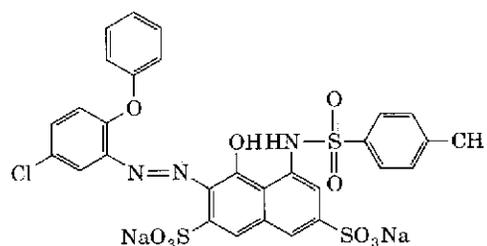
Inkjet printing is a nonimpact printing system wherein aqueous ink droplets are transferred from a printhead to a receiving paper. The advantages of the inkjet printing system are ecological safety, quiet running, high speed, and high resolution. The market is growing for both black-and-white and full-color systems.

For high-quality printing, high color density, high water resistance, and limited dot spreading with water-soluble dyes, an ink-receiving layer is employed at the surface of the recording paper. Typically, the receiving layer includes a white pigment, a dye-fixing agent, and a binder polymer.

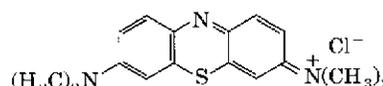
After printing, the environment of the dye within the receiving layer determines the properties of the dye image, such as the hue and the stability against water and light. Therefore it is very important to know the optimum environment for the dye.

The physical behavior of the ink in a paper, i.e., ink penetration speed,<sup>1</sup> and its effect on print quality<sup>2</sup> have been studied extensively. However, less work has dealt with the microscopic distribution, or, in other words, the environment of the dye on a molecular scale in the receiving layer of an ink-jet paper. In this report, we deduce the state of the dye in the receiving layer from our

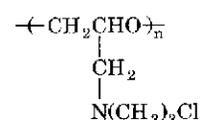
studies on the interaction between the dye Acid Red 249 (AR), and certain inkjet chemicals silica as a white pigment, Polyfix 601 (PF) as a dye-fixing agent (polycation) and polyvinyl alcohol (PVA) as a binder, both in aqueous solution and in the solid state. For comparison with the anionic dye, the cationic dye methylene blue was used.



AR  
Anionic dye



Methylene blue  
Cationic dye



PF (ca. n = 8 to 10)  
Polycation

## Experimental

### Materials

The purity of AR (Polar Brilliant Red B; Ciba-Geigy Ltd., Basel, Switzerland) was confirmed by liquid chromatography. Methylene blue (Wako Pure Chemical Industries, Ltd., Japan) was used without further purification. Synthesized fine powder silica (Type 244; W.R. Grace Co. Florida), polyvinyl alcohol (63018; Riedel de Haen AG, Seelze, Germany), and a polycation (Polyfix 601; Showa Highpolymer Co., Ltd., Japan) were used without further purification.

Throughout the experiments, deionized water, Ion Pure-12 (Nihon Millipore Ltd., Japan) was used. The zeta

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potential was measured by a Laser Zee Meter Model 501 (Pen Kem, Inc., New York).

## Tests and Results

### Adsorption of Ionic Dyes onto Silica

The adsorption properties of AR and methylene blue from their aqueous solutions onto silica were characterized.

Silica was added to separate aqueous dye solutions of AR and methylene blue. The concentrations were controlled so as to make their peak absorbance in the visible spectral region around 1 in a cuvette of 10 mm light-path length. After shaking the samples for a few days, silica and adsorbed dye were separated by centrifugation and the supernatant solutions were collected. The amount of the adsorbed dye was determined by absorbance measurements before and after the treatment. As indicated in Table I, the absorbance of methylene blue was lower after the treatment, indicating that 0.41 g/L silica had adsorbed  $1.0 \times 10^{-5}$  mol/L of methylene blue from aqueous solution. Thus  $2.4 \times 10^{-5}$  mol of methylene blue was adsorbed per gram of silica. On the other hand, no decrease of the absorbance was observed for AR, suggesting that the anionic dye could be adsorbed onto silica. Instead, a small increase of the absorbance was observed, and this is explained by exclusive adsorption of water onto silica.

### Formation of an Insoluble Product from AR and PF

When both AR and PF are dissolved in water, an insoluble red precipitate is formed. The amount of AR precipitated from  $3.9 \times 10^{-2}$  g/L aqueous solutions of AR were measured at various concentrations of PF. After shaking the mixed solutions for a few days, the precipitates were removed by centrifugation. The amount of the precipitated dye was determined from the absorbance difference between the solution after treatment and a solution of AR without PF.

Figure 1 shows the amount of precipitated AR plotted against the concentration of PF, which is given as the ratio between the mass of PF and that of AR initially included in the solution, the AR concentration being held constant throughout the experiment.

The amount of precipitated AR increased linearly with the PF concentration. At the ratio 0.31, almost 100% of the AR formed a precipitate. Then the amount of precipitated AR sharply decreased upon further addition of PF.

### Formation of an Insoluble Product from AR and PF in the Presence of Silica

The effect of the presence of silica on the AR-PF precipitation curve obtained above was studied. The amount of AR precipitated from its  $2.9 \times 10^{-2}$  g/L aqueous solution was measured at various concentrations of PF in the presence of 0.6 g/L of silica. The amount of precipitated AR was determined in the same way as for the experiment without silica. As in the case without silica, precipitation of AR increased with PF concentration, and excessive PF decreased the amount of precipitation, as shown in Fig. 2. In this case, however, the

maximum precipitation was observed at the PF/AR wt ratio of 0.52, which is 0.21 higher than that without silica.

**Table 1. Change of Absorbance of Dye Solutions by Adsorption on Silica**

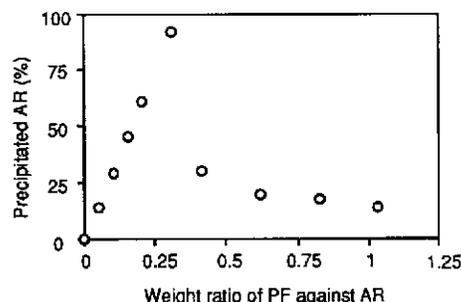
Dye	Initial dye concentration (mol/L)	Absorbance		Amount adsorbed (mol/L)
		Before	After	
Acid Red 249	$4.8 \times 10^{-5}$	1.246	1.368 <sup>*</sup>	—
Methylene Blue	$2.0 \times 10^{-5}$	1.551	0.738 <sup>†</sup>	$1.0 \times 10^{-5}$

<sup>\*</sup>Concentration of silica is 67 g/L. <sup>†</sup>Concentration of silica is 0.41 g/L.

### Adsorption Property of PF on Silica

To characterize the adsorption property of PF on silica, the zeta potential of silica was measured in aqueous suspension at various concentrations of PF (Fig. 3). For the suspension of silica alone, a zeta potential of -0.100 V was observed. It increased with concentration of PF and became zero at PF concentration 0.25 wt %. In the region of higher PF concentration, the zeta potential became positive.

The amount of PF adsorbed on silica was also studied. Aqueous solutions (100 mL) containing 2 g of silica and 10 to 200 mg of PF were prepared. After shaking the suspensions for a few days, silica and adsorbed PF were removed by centrifugation, and the concentrations of PF in the supernatants were determined by chemical oxygen demand (COD) measurement. The amounts of PF adsorbed were calculated from the concentration difference of PF before and after the treatment. Figure 4 indicates that the amount of PF adsorbed increased with PF concentration up to 100 mg of PF, where 20 mg of PF was adsorbed, and further addition of PF did not increase the amount adsorbed. From this result, we concluded that PF equivalent to 1 wt % of silica could be adsorbed onto silica.



**Figure 1.** Change of the amount of precipitated AR (39 mg/L) with increasing concentration of PF.

### Absorption Spectra of AR in Films

Films containing AR were prepared by applying aqueous solutions of (a) AR and PVA, (b) AR, PF, and PVA, and (c) AR on polyethylene terephthalate (PET) film, using a wire bar coater, and subsequently drying at room temperature overnight. Curve a in Figure 5 shows the absorption spectrum of the dye coated with PVA, with peaks at 520 and 555 nm. In the presence of PF, the absorption intensity decreases, particularly at the longer

wavelength peak (Curve b). AR in the solid state shows a new absorption around 490 nm (Curve c).

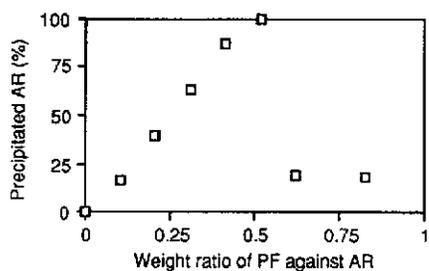


Figure 2. Change of the amount of precipitated AR with increasing concentration of PF in presence of silica. AR, 29 mg/L; silica, 0.6 g/L.

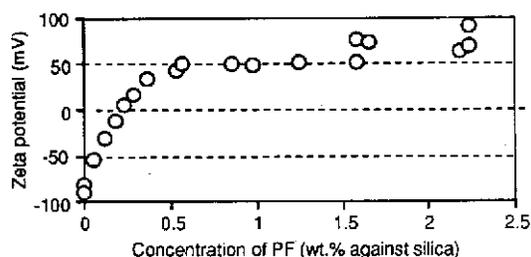


Figure 3. Change of zeta potential of silica with additional PF.

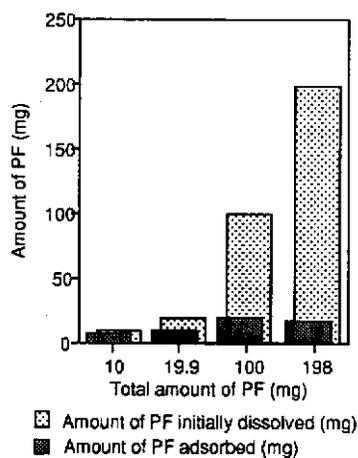


Figure 4. Amount of PF absorbed on 2 g of silica from aqueous solution

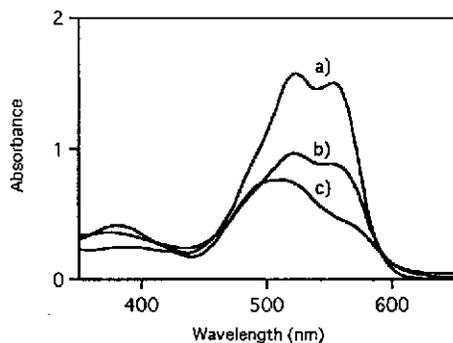


Figure 5. Absorption spectra of AR in solid state. a) AR, 0.3 g/m<sup>2</sup>, PVA, 3.5 g/m<sup>2</sup>; b) AR, 0.3 g/m<sup>2</sup>, PF, 1.2 g/m<sup>2</sup>; PVA, 3.5 g/m<sup>2</sup>; and; c) AR, 0.4 g/m<sup>2</sup>

To investigate further the state of the dye in the printed image, the following multilayer systems were studied as simplified models: PVA films with and without PF were prepared by coating PET film with a PVA solution or a mixed solution of PVA and PF, again using a wire bar coater and subsequent drying. A 2% aqueous solution of AR was spincoated on the PVA films thus prepared. To investigate the penetration of AR into PVA layer, the cross-sectional distribution of AR was studied. The films were etched by oxygen plasma, and spectral changes were measured. For the film including PF (Figure 6), the initially observed absorption around 490 nm decreased and the shoulder around 580 nm became prominent after etching, suggesting that AR molecules spin-coated on PVA/PF film have two different environments that influence the absorption spectra, and the abundance depends on the depth. Without PF (Figure 7), the spectral features showed no clear differences with depth, suggesting that all AR molecules in the film are in the same environment.

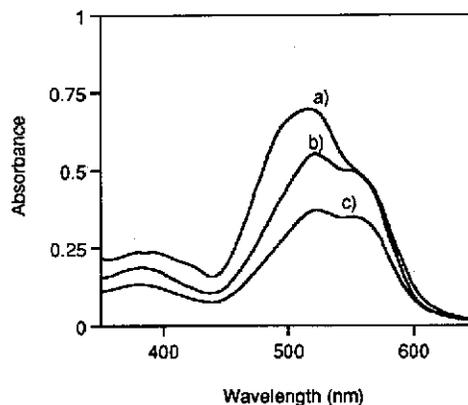


Figure 6. Absorption spectra of AR spin-coated on PF/PVA film. a) Before etching; b) after 10 min of etching; and c) after 20 min of etching.

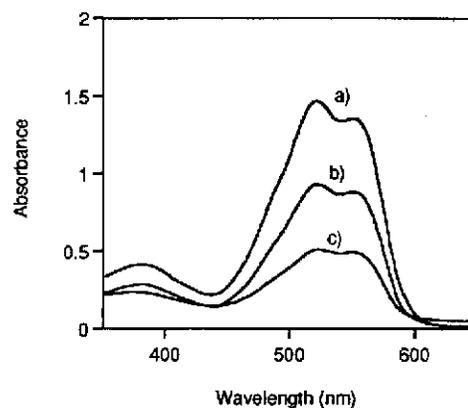


Figure 7. Absorption spectra of AR spin-coated on PVA film. a) Before etching; b) after 8 min of etching; and c) after 16 min of etching.

The amount of AR removed by the etching was calculated from the loss of the absorbance. The loss is plotted against the depth calculated from the loss of sample weight during etching and the sample density (supposed to be 1) in Figure 8. By using this method, the vertical distribution of AR at submicrometer intervals can be determined. The distribution of AR in the film containing PF is not described in a region shallower than 0.4  $\mu\text{m}$  because of the spectral change of AR during the etching described above.

## Discussion

### Interaction of the Ink-Jet Dye (AR) and the Chemicals in the Ink-Receiving Layer of the InkJet Paper

Silica has silanol (Si-OH) groups on its surface, and their protolytic dissociation in an aqueous suspension makes silica weakly acidic. Silica employed in the present work had been treated with weak alkaline solution in the manufacturing process to provide a neutral property. The silica adsorbs methylene blue from aqueous solution, as described in the earlier section. AR, on the other hand, shows no adsorption onto silica. This can be explained by taking into account the negatively charged silica surface, which repels an anionic dye.

AR forms a precipitate from aqueous solutions in the presence of PF, and the amount of the precipitate increases linearly with the PF concentration. Maximum precipitation is observed at PF/AR wt ratio of 0.31. At this concentration, the anionic charges of AR and the cationic charges of PF in the solution are calculated to be almost equal, taking the molecular weight of AR to be 748.1 with two anionic groups in a molecule and that of PF 151.5 per monomer unit possessing one cationic group. The above result suggests that the precipitation is caused by a stoichiometric ionic complex formation between the anion of AR and the cation of PF, rather than by a salting-out effect of PF. If an excess amount of PF is present, the amount of AR precipitated decreases. This decrease can be explained by a solubilizing effect of the free cationic charges on the excess added PF in the AR-PF complex, as shown in Scheme 1. The hydrophilicity of dissociated and hydrated cationic moiety exceeds the hydrophobicity in this region of PF/AR ratio.

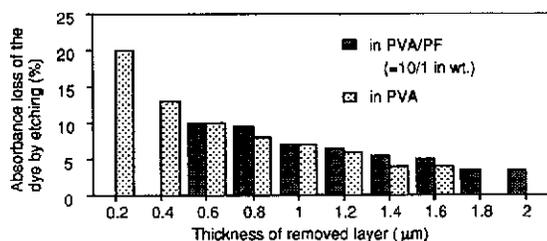
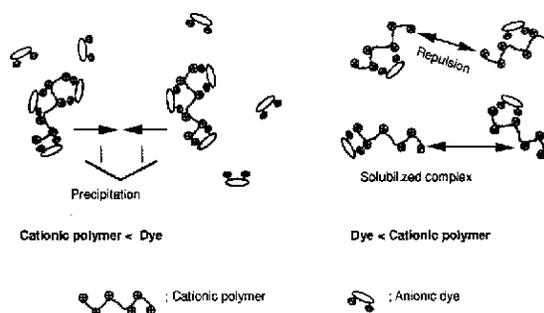


Figure 8. Depth profile of diffused AR spin-coated on PVA film

In the presence of 0.6 g/L silica, the PF concentration at the precipitation maximum increased from 0.31 to 0.52. This additional PF required, 0.21, is equal to 6.1 mg/L, corresponding to 1 wt % of silica.

The zeta potential measurements (Figure 3) show that silica has a negatively charged surface attributable

to dissociation of silanol groups ( $-\text{SiO}^-$ ). Addition of PF at 0.25 wt % of silica shifts the potential to 0, indicating that the cationic charge of PF neutralizes the dissociated silanol group. Further PF can be adsorbed on silica and make the potential positive.



Scheme 1.

From the quantitative experiment using COD measurements, we found that silica could adsorb PF equivalent to 1 wt % of silica (Figure 4). The results obtained by the zeta potential and the adsorption measurements suggest that PF equivalent to 0.25 wt % of silica neutralizes the dissociated silanol on silica, and PF equivalent to 0.75 wt % of silica can be further adsorbed on silica, rendering the silica surface positive. This excess adsorption of PF on silica is thought to be attained by the contribution of a loop or tail layer in the adsorbed PF. From these results on zeta potential and COD measurements, we concluded that an amount of PF equivalent to 1 wt % of silica is adsorbed on silica and that the adsorbed PF cannot form an insoluble complex with AR.

In another experiment, we found that the presence of tetramethylammonium chloride or ammonium chloride, each forming cations in aqueous solution, does not precipitate AR. This finding suggests that multiple cationic groups along a polymer chain are necessary to form an insoluble precipitate of AR. The observation that PF adsorbed on silica cannot form an insoluble precipitate with AR can be explained by assuming that the polymeric character of PF is lost when it is in the adsorbed and immobilized condition on silica.

### The Physical State of the Dye in an Ink Jet Image

From the above results on the interactions among chemicals for the inkjet printing system in dilute aqueous solutions in the equilibrated condition, we conclude that the interaction of AR with silica is negligible. Therefore the complex structure of the printed ink-receiving layer can be simplified, using a model sample that involves AR, PF, and PVA to make quantitative measurement of absorption spectra feasible.

AR spin-coated on a PVA film including PF shows an absorption spectrum (Curve a in Figure 6) that is equivalent to a superposition of the absorption of the dye dissolved in PVA (Curves a and b in Figure 5) and an extra absorption around 490 nm, which corresponds to the absorption band of solid AR (Curve c in Figure

5). The absorption around 490 nm disappears with etching (Curves b and c in Figure 6), indicating the presence of solid dye at the surface. These results show that most of the dye is dissolved into PVA and that a small portion of it forms a solid dye deposit on the surface of the PVA film in the presence of PF.

On the other hand, AR spin-coated onto a PVA film without PF (Figure 7) shows a spectrum similar to that of AR dissolved in PVA (Curve a in Figure 5), and the spectral change with etching is negligible. This result reveals that, without PF, AR dissolves totally in the PVA layer, even with a short drying period.

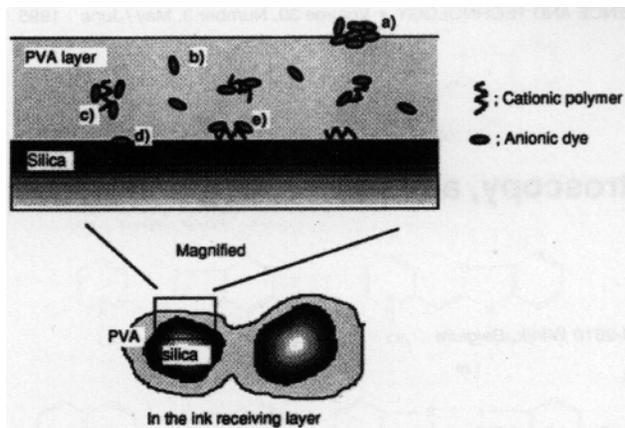


Figure 9. Estimation of states of anionic dye in the ink-receiving layer

## Conclusion

Generally speaking, the following five models might be proposed as possible environments or states of AR in the ink-receiving layer of a printed sample (Figure 9): (a) a solid AR layer on the PVA surface; (b) AR dissolved in PVA; (c) AR complexed with PF dispersed in PVA; (d) AR adsorbed on silica; and (e) AR adsorbed on silica with PF. Among the proposed five states, (d) and (e) are denied by the results obtained in aqueous solutions, which show that AR is not adsorbed on silica, even in the presence of a polycation. We have confirmed that PF, other than that adsorbed onto silica, aggregates with AR to form an insoluble precipitate. By studying the state of AR in the AR spin-coated PVA films, we have found that most of the AR forms a complex with PF dispersed in PVA (Case c), and that the rest remains as a solid AR layer on the surface (Case a). From our study, we conclude that (c) is the dominant state of AR in the ink-receiving layer of the inkjet paper.

## Acknowledgment

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