

INK JET DYE FIXATION AND COATING PIGMENTS

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ABSTRACT

Ink jet printing is a rapidly growing method of documentation and communication, due to low equipment cost and color reproduction. Accordingly, many papermakers have developed and are developing papers that are compatible with this process. Because ink jet printing is quite new and different from established processes like offset, gravure, and flexographic printing, little mechanistic work has been published to help with paper design. A unique feature of current ink jet printing is that ink setting depends on direct fixation of colorants on the paper surface. No viscous resins are present to control colorant movement. This report describes the fixation of commercial ink jet inks using thin layer chromatography. It is shown that silica based coating pigments and specialty precipitated calcium carbonate pigments fix ink jet dyes by different mechanisms. It is hypothesized that the differences stem from different interactions between the pigment surfaces and carboxylic and sulfonic acid groups on the dyes.

INTRODUCTION

Typical home ink jet printing is unique among important paper printing processes in the amount and mobility of the applied inks. Offset, gravure, flexo, and newsprint inks are applied in layers about 1 μm - 5 μm in thickness for each color; ink jet ink layers may be 15 μm or more in thickness for each color [1 - 3]. Offset, gravure, and flexo inks have binders to hold the colorants in position; most aqueous ink jet inks have none. Binder containing inks increase markedly in viscosity when small amounts of solvent are removed; ink jet inks remain mobile even when most of their solvent volume is removed.

Most ink jet color inks are dilute solutions of one or more acid dyes [4]. The solvents account for up to 98% of the ink weight and are blends of water and various organic materials, typically high boiling alcohols. For good printed appearance, the dyes should be fixed on the paper's outer surface with only enough lateral spreading from the position of drop impact to merge adjacent drops in solid colors. In fact, proper dye fixation is the key to several components of ink jet print quality including (1) high optical density or intensity of the color, (2) high resolution or sharpness of ink boundaries, (3) low image print through to the back side of the paper, and (4) high resistance of the image to smearing when wetted.

Several papermaking approaches to properly fix the dyes are practiced. Uncoated paper is treated with sizing agents to balance lateral ink spreading and z-direction penetration. Higher quality can be obtained with pigmented coatings. These provide the well known benefits of finer pore structure and surface smoothness but require the dyes to adhere to non-cellulosic coating ingredients: pigments, coating binders, and functional additives.

For coatings, silica pigments are most commonly used. Several grades of silica have found application including precipitated, fumed, and gel. Recently, pigments based on clay and precipitated calcium carbonate (PCC) have been offered. It is the contention of this paper that, depending on pigment, different mechanisms are used to fix ink jet dyes. The literature suggests that silica coatings work by providing pore volume to trap the entire ink volume and, as a second step, provide surface area on which the dye can deposit and adhere as the solvent evaporates. Chapman has shown that higher silica pore volume, even with lower surface area, causes faster ink jet ink setting [5]. This mechanism is based on high affinity of the silica surface for the ink solvent. It will be shown that specialty PCC fixes ink jet ink dyes by an almost opposite mechanism.

EXPERIMENTAL

Thin Layer Chromatography

To obtain high color intensity, high edge acuity, and low print through, it is important for the ink jet dyes to immobilize on the paper's outer surface at the point of ink jet drop impact. After drying, the dyes should stay fixed even if the surface is rewetted. We hypothesize that fixation depends on the relative affinity of the dye for the coating surface versus the ink solvent or rewetting fluid. Because interactions of solutes, solvents, and solid surfaces are exactly the province of chromatography, we selected a chromatographic method to study ink jet dye fixation.

Thin layer chromatography (TLC) is inexpensive to perform, easily analyzed, and rather closely related to the ink jet printing process on coated paper [6]. Others have used paper chromatography to investigate ink jet printing on uncoated paper.[7].

We used a #60 rod to apply a $75 \pm 25 \mu\text{m}$ thick layer of pigment or coating (after drying) on borosilicate glass plates. The plate dimensions were 10 cm wide x 20 cm high for room temperature experiments and 6 cm wide x 12 cm high for temperature bath experiments. The coatings were dried with a heat gun. Parallel score lines, about 1 cm apart, were scraped in the coating so that several measurements could be made simultaneously on each plate. A 0.1 μl drop of ink jet ink was placed with a micro pipette near one end of each band of coating. As quickly as possible, the plate was held vertical and placed in a vapor tight, solvent saturated container with the edge nearest to the ink drop immersed in a puddle of solvent.

As solvent rose through the coating layer by capillary action, it passed the ink drop and carried the dyes along with it, a step known as development of the plate. Development was usually stopped when the solvent rose to about 75% of the plate height. Plates with very slow moving solvent fronts were stopped before the solvent reached 75% of the plate height.

Figure 1 illustrates the method of analysis. The distance from the dye's addition point to its final position was measured and divided by the distance from the dye's addition point to the final solvent front. This distance ratio, called relative affinity and referred to as R_f , was used for all subsequent interpretation of results. The migrating dye spot enlarged as it ascended the plate so the spot center was estimated and used for the R_f measurement. When the ink fractionated into several spots at different positions on the plate, a separate R_f was determined for each spot.

During TLC plate development, dye molecules attach to and detach from the pigment with some frequency. The most direct interpretation of R_f is that it is the fraction of dye molecules that are not attached to the pigment surface at a given time (see appendix).

$$R_f = \frac{N_{\text{Mobile Dye}}}{N_{\text{Total Dye}}}$$

A large R_f implies that the dye has a low relative affinity for the solid surface and spends little time fixed on the surface. A small R_f has the opposite meaning.

Figure 2 shows two examples of developed plates. One shows large R_f values and the other shows small R_f values. These examples were well behaved with fairly sharp spots. Frequently, the spots were more spread out and less sharp edged.

Relative affinity does not give a complete picture because either a small number of strong binding sites or a large number of weak binding sites could cause the same R_f . In the appendix it is shown that, if a number of assumptions are made, Langmuir thermodynamic analysis may be used to estimate the energetics of dye fixation [8,9]. In the simplest case (see appendix) the following equation results:

$$\ln \left[\left(\frac{R_f}{1-R_f} \right) \right] = \frac{\Delta H^\circ}{RT} + \ln \left[K(n)e^{-\Delta S^\circ/R} \right]$$

On the left is a term that contains only R_f and is completely determined by the TLC measurement. On the right is reciprocal temperature, which can be measured, and several constants. ΔH° and ΔS° are the thermodynamic enthalpy and entropy, respectively, of dye adsorption.

ΔH° is the most accessible value because it can be determined without evaluating all the constants grouped in $K(n)$. ΔH° is found by measuring R_f at two different temperatures and plotting the left hand term against reciprocal temperature. $\Delta H^\circ/R$ is the slope of this plot. If ΔH° is negative, heat is released so the adsorption is exothermic. A large exothermic value implies strong binding of the dye on the pigment surface.

Materials

For pigments, we have selected an amorphous precipitated silica, Degussa FK 310[®], and a precipitated calcium carbonate that is specially made for ink jet use, Specialty Minerals JETCOAT[™] 30 precipitated calcium carbonate (PCC). We have not made optimized coatings with either pigment but only simple blends with one or two other coating materials to illustrate the difference in mechanisms of action.

For other coating materials we used a fully hydrolyzed, low viscosity, polyvinyl alcohol, Air Products Airvol 107[®], and a cationic polymer, Ontario Specialty Coatings OSC - 470.

For inks, we purchased cartridges marketed by the printer manufacturers for their own printers. The colors and true black inks were used as received and spotted on TLC plates.

The focus of the experimental data presented herein is initial fixation of the dye after ink drop contact with a coated surface. Therefore our interest is in dye dissolved in its own ink solvent. To simulate specific ink solvents, we mixed water and organic materials to approximate the fluid phase of each ink jet ink. This required analysis of the inks' fluid phases. Water content was determined by Karl Fischer titration. The major organics were identified and quantified by GC-MS. Proportions in the fluid phase were first determined by calibrating peak intensities with standards of known concentration. Then the proportions were confirmed by mixing the calculated quantities of fluid phase ingredients and comparing the resulting peak sizes to those of the inks. There were large differences in composition in inks for different printers. There were smaller differences from color to color in the same cartridge. Because there was some commonality among the yellow, cyan, and magenta inks in the same cartridge, an "average" simulation of the ink liquid phase was made for each color cartridge. This average liquid was used to develop the TLC plates that were spotted with the corresponding cyan, magenta, and yellow inks.

RESULTS

Role of Pigment

Our contention is that silica coatings hold the fluid phase including the dye of ink jet ink whereas specialty PCC holds only the dye and allows the fluid phase to pass through. The first experiment dealt with pigments alone and in combination with polyvinyl alcohol (PVOH) binder. Figure 3 shows cross sections of the specialty PCC and silica pigment layers with no binder, cast on glass plates. The specialty PCC macro pore structure is much finer than the silica macro pore structure. These structures match the separate mechanisms. Silica provides space to hold large volumes of ink solvent. Immediate contact between dye molecules and the pigment surface is not required. Specialty PCC provides fine pores with high surface to volume ratios so that dye molecules have a high probability of making contact with the pigment surface in a short time. Capacity to hold a large volume of fluid phase is not required. In practice, a relatively low coat weight is needed since only the dye remains in the coating layer.

Figures 4 - 6 show results from the pigment and binder experiment. Silica and PVOH were blended in combinations ranging from no PVOH up to a typical level of PVOH used in silica coatings, 30 weight percent. Specialty PCC and PVOH were blended in combinations ranging from no PVOH up to a typical level of PVOH used in specialty PCC coatings, 7 weight percent. Each blend was drawn down onto a glass plate. Colored inks were taken from a Hewlett Packard 600C printer HP 51649A cartridge, spotted on the TLC plates, and developed with "average" Hewlett Packard solvent. After development, R_f values were measured.

Several of the inks contain more than one species of dye; these different species tend to migrate differently. A developed plate may exhibit several dye spots at different distances from the origin. Magenta inks are especially prone to this behavior. For simplicity, the following discussion will focus on the most rapidly moving dye component, i.e., the component with the largest R_f value. The average "largest" R_f values for cyan, magenta, and yellow are graphed in Figures 4, 5, and 6 respectively. The error bars show \pm one standard deviation in 3 - 5 replicate measurements.

The first striking feature of these plots is that the R_f values for specialty PCC are much lower than those for silica. The lower R_f means more of the dye and less of the solvent is bound to the pigment surface. This demonstrates that the mechanisms of action are different. It appears that silica has a higher relative affinity for the solvent components whereas specialty PCC has a higher relative affinity for the dye components in the ink.

Role of Binder

The second observation in Figures 4 - 6 is that the binder can play a role in dye adsorption. PVOH, at high concentration, provides some sites for dye binding as evidenced by reduced R_f values. Binder also tends to slow the solvent movement up the TLC plate. For example, 5 % PVOH more than doubled the development time relative to no PVOH.

Role of Cationic Additive

Many of the dyes used in ink jet inks contain sulfonic or carboxylic acid groups that make the dyes soluble in water and may aid in binding to cellulose [10]. At ink pH these groups are ionized and anionic and attracted to cationic sites. A common practice is to add a cationic quaternary amine to an ink jet coating formulation in order to provide binding sites in the non-cellulosic coating.

TLC films were cast containing silica alone, silica in combination with 1% of a proprietary cationic additive, PCC alone, or PCC in combination with 1% proprietary additive. These were spotted with ink from three different equipment manufacturers. Each manufacturer's inks were developed with an "average" solvent that approximated the ink solvent composition of their color cartridge. After development, largest R_f values were measured. The averaged results of 3 - 5 replicates are listed in Tables I, II, and III.

Table I gives R_f values for inks from the Hewlett Packard 600C series of printers. Several features stand out. Color R_f values for the specialty PCC are lower than silica indicating that more of the ink dyes are bound to the PCC surface. The black ink R_f values are zero in all cases. This is because the HP 51629A colorant is a dispersed pigment rather than a soluble dye. The cationic additive reduces the high R_f values for silica, whereas it does not produce a consistent effect on the lower R_f values of specialty PCC. This suggests that the specialty PCC already has dye binding sites and that cationic additive, if needed, is needed in a lower amount.

Table II gives R_f values for inks from the Canon BJC 210 printer. Again, specialty PCC exhibits lower R_f values in the absence of cationic additive. In this case, the additive reduces R_f values for both the silica and specialty PCC pigments; however the effect on the silica pigment is much larger. The Canon inks are very compatible with the selected cationic additive.

Table III gives R_f values for inks from the Epson Stylus Color 600 printer. As with the other inks, specialty PCC exhibits lower R_f values than silica. The cationic additive reduces the R_f values for all the inks, but it has a much larger effect on cyan and magenta ink than on black or yellow, possibly due to different acid moieties.

These experiments support the conclusion that specialty PCC and silica fix dyes by different mechanisms. PCC without cationic additive retards dye migration more than silica. Addition of cationic additive further retards dye migration with both pigments; however, less additive is needed for PCC. This suggests that PCC has dye binding sites even without cationic additive.

Binding Energy

In the appendix, it is shown that the energetics of dye fixation can be estimated from temperature experiments. All the data presented so far was collected at room temperature. In order to estimate binding energy, we carried out TLC experiments in temperature baths.

Dye adsorption onto a surface from solution is complicated by the solvent. For a dye molecule to fix on a binding site, it must displace one or more molecules of solvent. Therefore, any energy released during binding is a measure not just of the dye - pigment bond energy; it is a measure of the difference between the dye - pigment bond and the solvent - pigment bond or bonds that are simultaneously broken. Strong dye - pigment binding could be masked by strong solvent - pigment binding.

Specialty PCC and silica films were cast on glass plates and spotted with inks made for the Canon BJC 210 printer. In this case, the TLC plates were developed in jars that were emersed in temperature baths. Some were developed at 8 °C and others at 40 °C. R_f values were calculated after the plates were developed. Results are shown in Tables IV and V. Two of the spots were analyzed slightly differently from the rest. When R_f is well over 0.9, the denominator of the ratio: $R_f / (1 - R_f)$ becomes small and the ratio becomes very sensitive to error in R_f . In those cases, R_f was calculated from the average of all spot components in the > 0.8 range rather than on only the most mobile spot. This gave smaller R_f values with smaller experimental errors in the enthalpy calculations.

Table IV shows the effect of temperature on R_f values and the adsorption enthalpies for the dyes on silica. The cyan dye releases less energy due to adsorption on silica than the other dyes. The specific reason is unknown but is almost certainly related to the cyan molecule's structure. The magenta, yellow, and black bond energies are comparable to hydrogen bond energies. The technique described in the preceding paragraph was used for the silica with black and cyan inks. All other analysis was done on the most mobile component as described earlier.

Table V shows the effect of temperature on R_f values and the adsorption enthalpies for the dyes on specialty PCC. Here, the cyan and magenta dyes show small net energy changes due to adsorption. The black dye adsorbs in the hydrogen bond range and the yellow dye releases much more energy.

These results confirm the specificity of dye adsorption. In the presence of excess solvent, the Canon yellow and cyan dyes exhibit stronger bonding on PCC than on silica. The black dye energetics were similar for both pigments, and magenta dye exhibited stronger bonding on silica.

CONCLUSIONS

Although there are similarities between ink jet printing and TLC, there are significant differences. One difference is that much more solvent is present in the case of TLC. This extra solvent washing over the pigment surface creates an exaggerated migration tendency. Moreover, the simple formulations used here have not been optimized for dye binding. Accordingly, no direct claims about potential ink jet print quality are put forward. The goal of this report is to demonstrate a relatively accessible technique by which to study the mechanism of fixation of ink jet dyes.

The major conclusion of this work is that different coating pigments interact with and fix ink jet inks by different mechanisms. Specialty precipitated calcium carbonate pigment tends to fix ink jet dyes even in the presence of excess ink solvent. Silica, according to the literature, tends to hold the solvent component of ink jet inks.

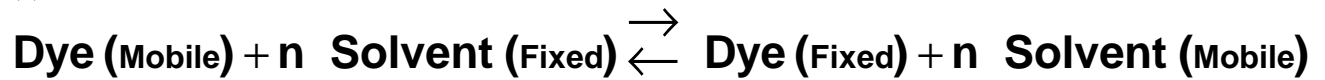
Specific conclusions from the described experiments that support the major conclusion are:

1. Silica films contain more fluid holding capacity than specialty PCC films.
2. Specialty PCC films retard ink jet dye movement more than silica films
3. Cationic additive further retards ink jet dye movement.
4. Dye binding strength, in most cases, is greater on specialty PCC than on silica.

APPENDIX

Under certain conditions, it is possible to extract some thermodynamic information from thin layer chromatography (TLC) [6]. Begin with a description of dye fixation on a pigment surface. Since the fixation occurs in solution and a dye must displace solvent molecules to adsorb:

(1)



When a dye molecule fixes on the pigment surface, it displaces some number, n , of solvent molecules. If only one, abundant, solvent species competes with the dye, and if all the binding sites and dye molecules and solvent molecules are identical, unchanging, and non-interacting, and ideal so that one equilibrium constant describes everything and concentrations can be used in place of activities, if equilibrium conditions prevail throughout the dye spot, if competing solvent molecules in solution are uniformly dispersed through the pore volume at a single concentration, $S_{\text{Mobile Solvent}}$, in units of (moles/meter³_{pore}) and the fixed solvent molecules are uniformly distributed over the pigment surface at a single concentration, $S_{\text{Fixed Solvent}}$, in units of (moles/meter²_{pigment}), and dissolved solvent molecules vastly outnumber the fixed solvent molecules so $S_{\text{Mobile Solvent}}$ is essentially constant during the TLC process, if all the added dye molecules are in the dye spot, if the dissolved dye is uniformly dispersed through the pore volume in the spot at the single concentration, $C_{\text{Mobile Dye}}$, in units of (moles/meters³_{pore}), and if the fixed dye is distributed over the pigment surface at the single concentration, $C_{\text{Fixed Dye}}$, in units of (moles/meter²_{pigment}), then equilibrium can be described with the following formula [11]:

(2)

$$K_a = \frac{\left(C_{\text{Fixed Dye}} \right) \left(S_{\text{Mobile Solvent}} \right)^n}{\left(C_{\text{Mobile Dye}} \right) \left(S_{\text{Fixed Solvent}} \right)^n}$$

An assumption of TLC is that a dye molecule spends its time cycling between two conditions. Either it is dissolved in the solvent or it is fixed on the pigment. If it is in the solvent, it is moving up the plate at the same velocity as the solvent. If it is fixed, its velocity is zero. Therefore, R_f is the fraction of time that the dye molecule spends in solution. The next assumption is that the time course of one dye molecule is experienced randomly by all other dye molecules; therefore, R_f is also the fraction of dye molecules in solution at any one time. As the dye spot moves up the TLC plate it will cover an area on the plate, A , measured in units of (meters²_{plate}). The plate subscript is present to distinguish plate area from pigment surface area. If the pigment layer is everywhere uniform in thickness, porosity, and interactive properties, then the pigment will exhibit a surface area, SA , expressed in (meters²_{pigment}/meters²_{plate}) and the structure will provide a pore volume, V , expressed in (meters³_{pore}/meters²_{plate}). Under these conditions the following formula can be derived:

(3)

$$\frac{(C_{\text{Fixed Dye}})}{(C_{\text{Mobile Dye}})} = \frac{V_1}{V_2} \left(\frac{1 - R_f}{R_f} \right)$$

This equation connects equilibrium concentrations with quantities that can be measured. Further equations can be written that specify conservation of dye molecules, solvent molecules, and binding sites. The number, N, of each of these conserved entities in units of (moles) are:

(4)

$$N_{\text{Total Dye}} = V \cdot A \cdot (C_{\text{Mobile Dye}}) + SA \cdot A \cdot (C_{\text{Fixed Dye}})$$

(5)

$$N_{\text{Total Solvent}} = V \cdot A \cdot (S_{\text{Mobile Solvent}}) + SA \cdot A \cdot (S_{\text{Fixed Solvent}})$$

(6)

$$N_{\text{Total Sites}} = SA \cdot A \cdot (C_{\text{Fixed Dye}}) + \frac{1}{N} SA \cdot A \cdot (C_{\text{Fixed Solvent}})$$

Combining equations (2) through (6) and grouping measurable constants into B, the ratio of dye molecules to binding sites, and K(n), the ratio of solvent molecules to binding sites when n = 1 and something more complicated when n > 1, as follows:

(7)

$$B = \frac{N_{\text{Total Dye}}}{N_{\text{Total Sites}}}$$

(8)

$$K(n) = \frac{V_1}{SA} \left(\frac{(S_{\text{Mobile Solvent}}) SA \cdot A}{(n N_{\text{Total Sites}})} \right)^n$$

gives an equation that describes the equilibrium constant in terms of measurable quantities and constants.

(9)

$$K_a = K(n) \left(\frac{1 - R_f}{R_f} \right) \frac{1}{(1 - B (1 - R_f))^n}$$

The equilibrium constant is related to the thermodynamic enthalpy and entropy via the method of Langmuir [7]:

(10)

$$\ln(K_a) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

In equation (10), R is the gas constant, 1.987 (calories/mole K°) and T is the Kelvin temperature. ΔH° is the enthalpy or heat change in (calories/mole) due to dye adsorption on the pigment surface. If ΔH° is negative, heat is evolved and dye adsorption is an exothermic process. ΔS° is the entropy or disorder change in (calories/mole K°) due to dye adsorption. If ΔS° is negative, disorder is reduced by adsorption.

If ΔH° and ΔS° are constant, equation (10) is linear in the form of $y = mx + b$. The dependent variable, y, is $\ln(K_a)$ and the independent variable is reciprocal temperature, $1/T$. If K_a is determined at two different temperatures and $\ln(K_a)$ is plotted against $1/T$, then the slope will be $-\Delta H^\circ/R$ and the intercept will be $\Delta S^\circ/R$. A large negative value of ΔH° would imply a strong binding site.

The simplest condition occurs when binding sites outnumber dye molecules, $B = 0$, and one dye molecule displaces one solvent molecule, $n = 1$. If these assumptions are incorporated into equation (9) and (9) is inserted into equation (10) and rearranged, the equation given in the experimental section results.

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Table I. Effect of cationic additive, 1% by weight, on R_f factors. Hewlett Packard HP 51629A and HP 51649A cartridge inks.

Ink Color	Silica	Silica + Cationic	PCC	PCC + Cationic
Cyan	.99	.78	.61	.47
Magenta	.97	.76	.75	.76
Yellow	.95	.87	.62	.22
Black	.00	.00	.00	.00

Table II. Effect of cationic additive, 1% by weight, on R_f factors. Canon BC-02 and BC-05 cartridge inks.

Ink Color	Silica	Silica + Cationic	PCC	PCC + Cationic
Cyan	.96	.04	.65	.01
Magenta	.97	.05	.18	.03
Yellow	.89	.05	.20	.02
Black	.97	.05	.71	.02

Table III. Effect of cationic additive, 1% by weight, on R_f factors. Epson S 020093 and S 020089 cartridge inks.

Ink Color	Silica	Silica + Cationic	PCC	PCC + Cationic
Cyan	.99	.03	.71	.02
Magenta	.99	.16	.24	.04
Yellow	.97	.70	.55	.45
Black	.97	.91	.86	.66

Table IV. Enthalpies of adsorption on silica pigment. Inks from Canon BC - 02 and BC - 05 cartridges.

Color	T (° C)	R_f	ΔH^0(Kcal/mole)
Cyan	8	.90 ± .02	- 0.6
	40	.91 ± .03	
Magenta	8	.82 ± .02	- 4.3
	40	.91 ± .05	
Yellow	8	.81 ± .03	- 4.7
	40	.91 ± .06	
Black	8	.87 ± .04	- 4.7
	40	.94 ± .04	

**Table V. Enthalpies of adsorption on specialty PCC pigment.
Inks from Canon BC - 02 and BC - 05 cartridges.**

Color	T (° C)	f_R	ΔH°(Kcal/mole)
Cyan	8	.66 ± .08	- 2.3
	40	.74 ± .12	
Magenta	8	.16 ± .07	- 0.8
	40	.18 ± .05	
Yellow	8	.07 ± .02	- 18.8
	40	.70 ± .03	
Black	8	.54 ± .13	- 5.6
	40	.74 ± .03	

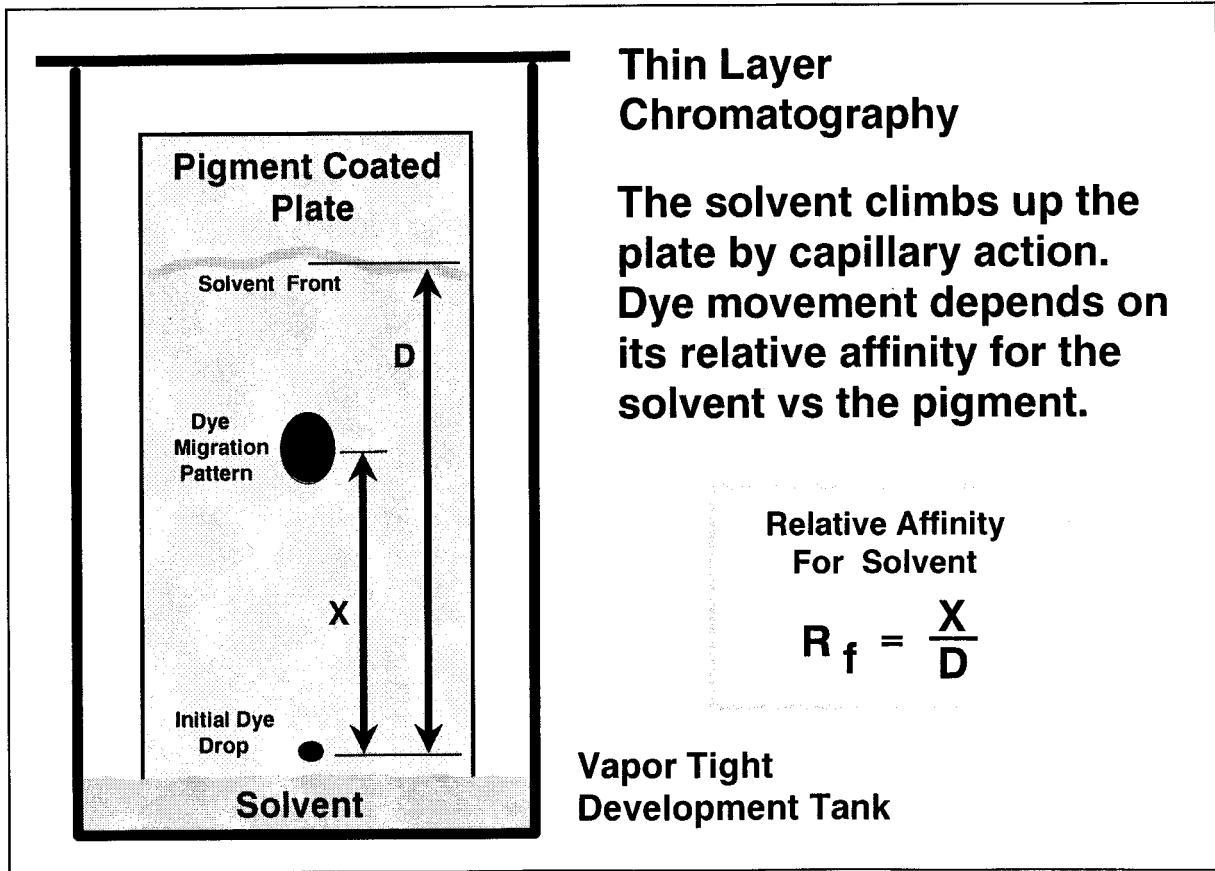


Figure 1. Schematic representation of a thin layer chromatographic plate.

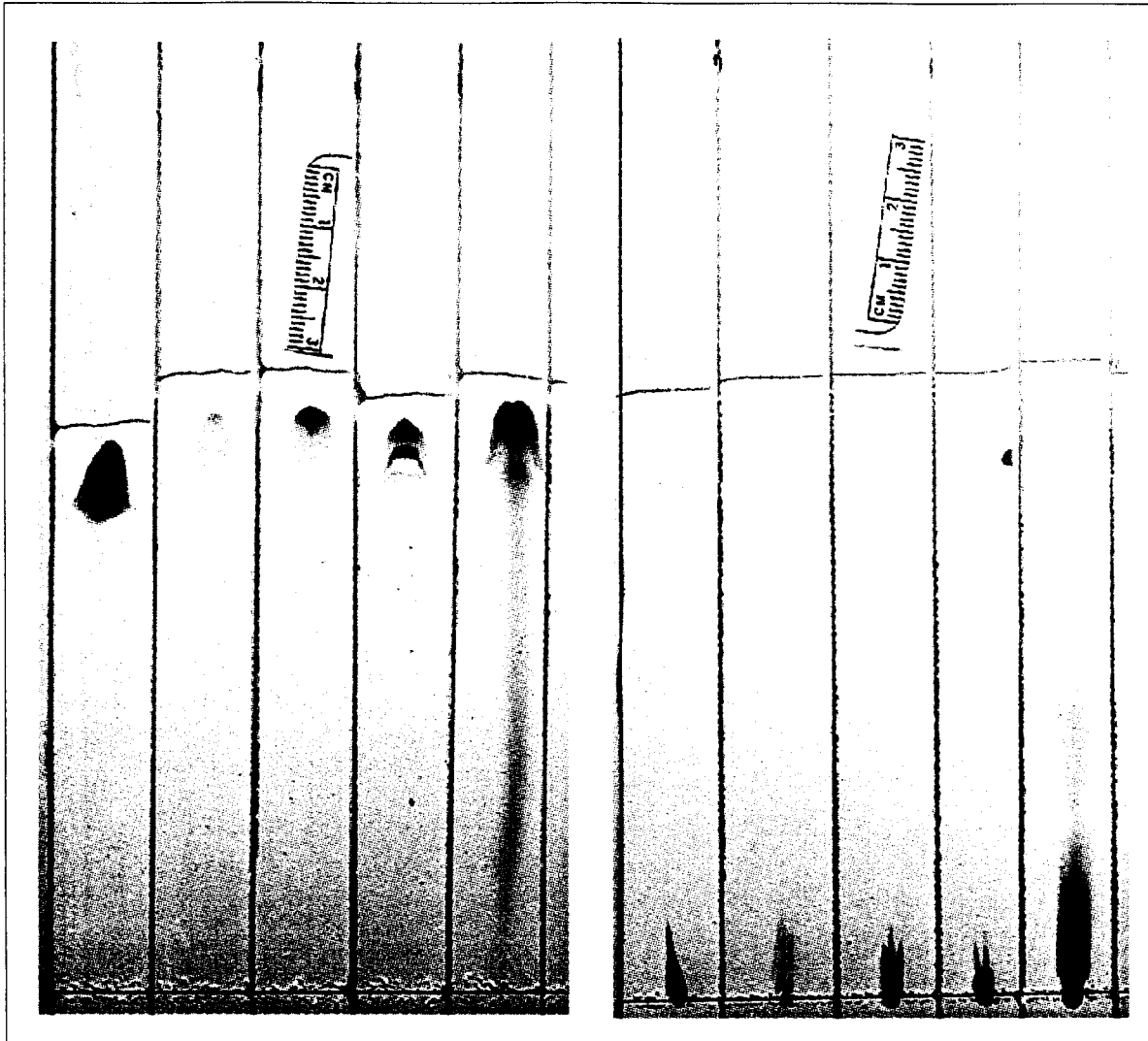


Figure 2. Thin layer chromatographic plates exhibiting large (left) and small (right) values of R_f .

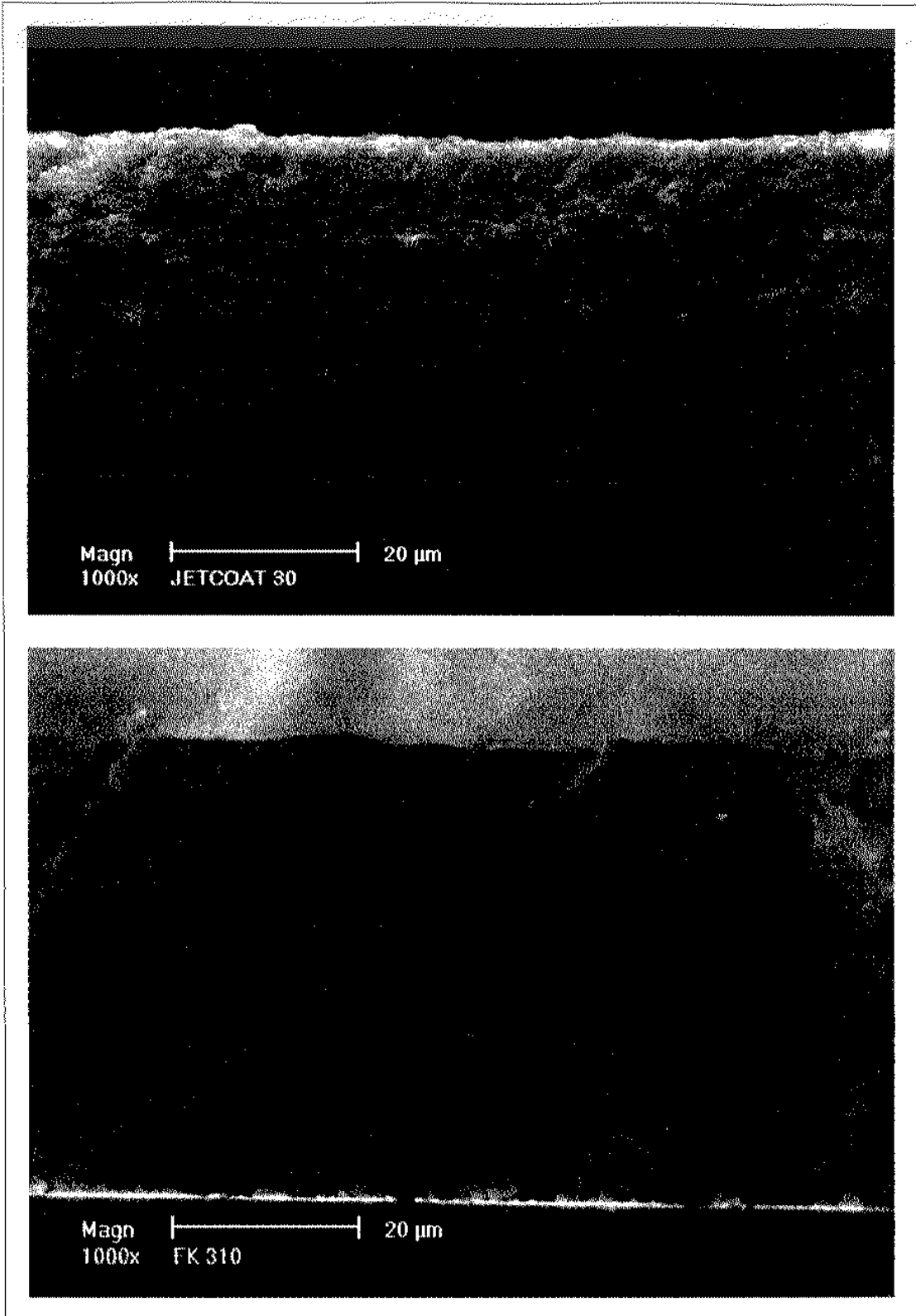


Figure 3. Cross sections of specialty PCC (above) and silica (below) pigment films on glass plates. 1000 X.

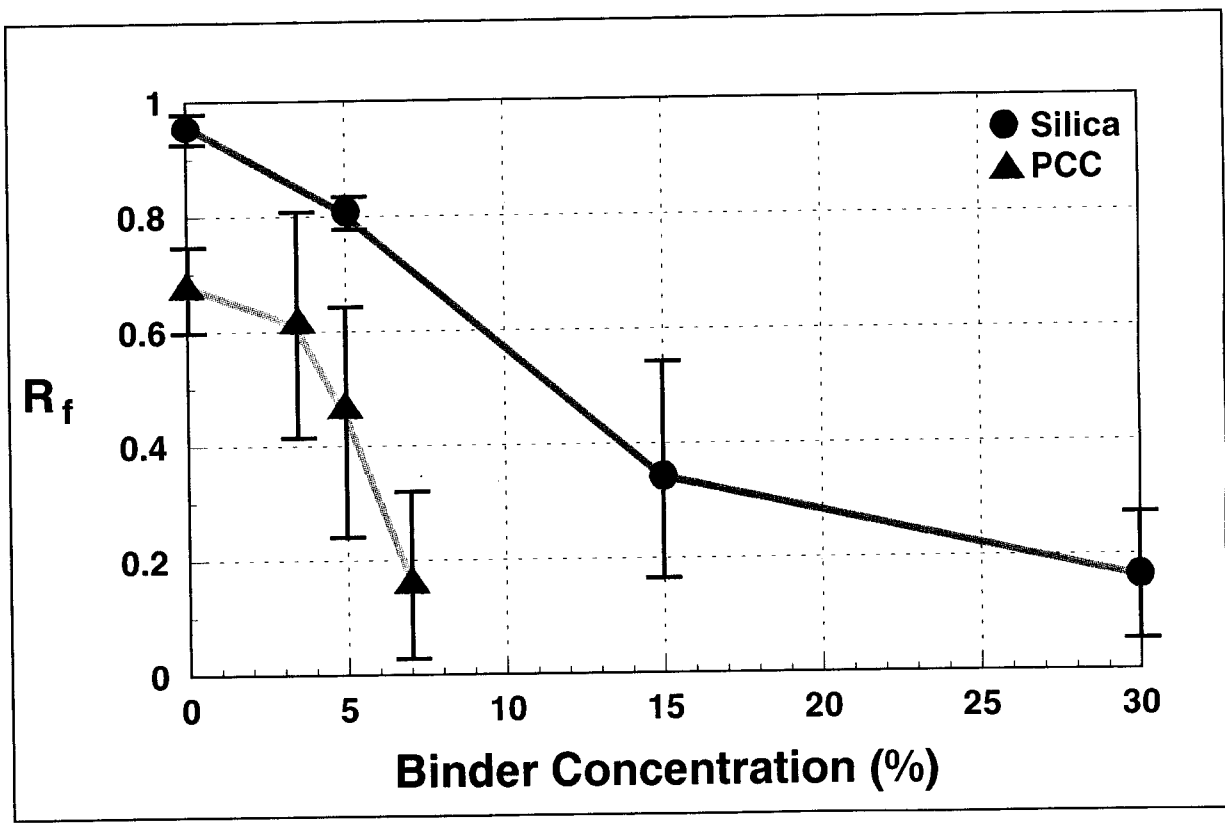


Figure 4. Effect of binder concentration on R_f for silica and specialty PCC pigments. HP 51649A Cyan Ink.

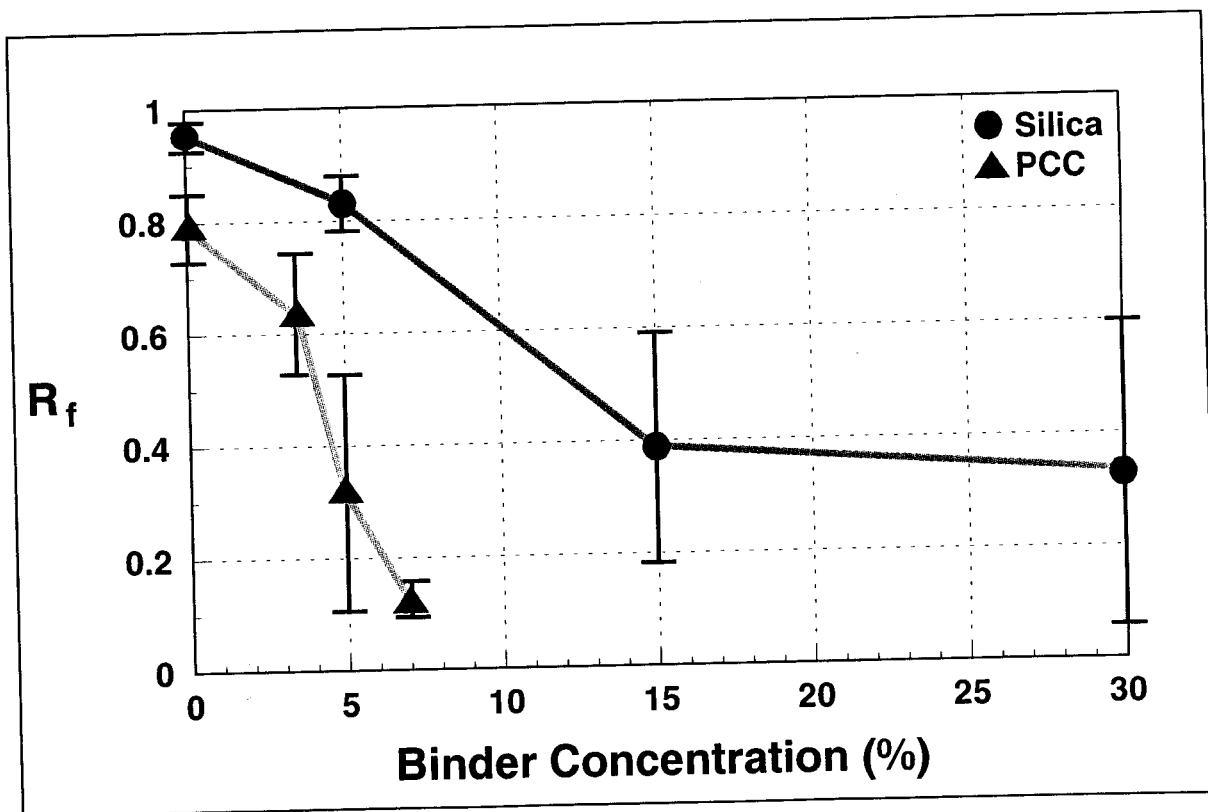


Figure 5. Effect of binder concentration on R_f for silica and specialty PCC pigments. HP 51649A Magenta Ink.

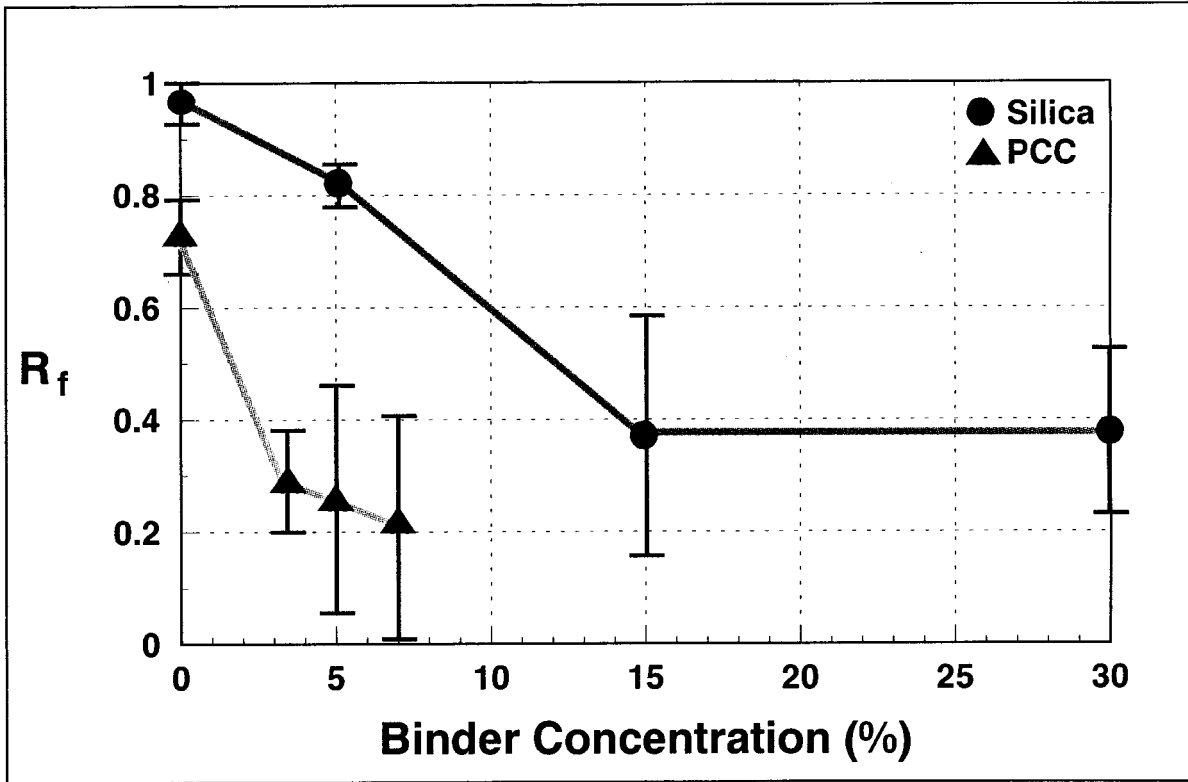


Figure 6. Effect of binder concentration on R_f for silica and specialty PCC pigments. HP 51649A Yellow Ink.