Organic Pigments for Ink Jet Applications: Key Properties and Impact on Ink Performance

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Abstract

Dye and pigment inks for ink jet applications usually strive for different parts of the non-impact printing market, where their respective key benefits can be fully exploited (brilliancy vs. fastness). The use of pigments as ink jet colorants, instead of dyes, usually provides an adequate answer to image degradation caused by environmental factors such as light, moisture and atmospheric pollutants, and enables the production of digital graphics that meet the stringent durability criteria required for outdoor display.

However, the particularities of ink jet technology (firing of tiny droplets through ultra fine nozzles, low ink viscosity…) makes the formulation of pigment inks quite demanding and an accurate selection of the key ingredients is crucial to reliably performing inks and high quality, colorful prints.

This paper will review the prerequisites for effective pigmented ink jet inks and give hints to proper pigment selection in terms of chemistry, particle size, surface modification and chemical purity.

Introduction

The digital printing market is dynamic and technology is fast moving forward as new applications are developed. The major, rapid shift towards digital printing is driven by advances in printer technology and in improved materials, i.e. chemicals. Flexible, reliable, relatively fast and cost effective, ink jet printing has gained broad acceptance and is further growing in popularity in various market segments.

The wide-ranging applications for ink jet give rise to many different requirements. Though such requirements might vary depending on the final application, it is universally desired to get colorful images that will maintain high quality during the time they are displayed or stored. However, ink jet graphics are prone to fading when exposed to natural or artificial light or to atmospheric pollutants like ozone. Depending on the receptive layer system (polymer or porous) and the colorant (pigment or dye) the permanence can vary over several orders of magnitude. Water fastness is another issue for aqueous (dye based) inks, should the print come into contact with water. Since nearly all components in ink jet ink and receiving layer formulations will contribute to the overall image stability, it is crucial to select them cautiously.

Essential ink components are the colorants, which can be either dyes or pigments. Quite often, a trade-off has to be made between brilliancy and fade resistance, since dyes - which are able to impart vibrant colors - usually suffer from poor fastness to light and/or ozone, whereas pigments - which often exhibit outstanding durability - tend to yield duller images.

Multicolor industrial printing applications (wide format graphics) have triggered a demand for ink jet inks combining good light-, weather- and waterfastness with a high brightness and color gamut. Clearly, this can only be achieved with pigment inks, given the stringent durability constraints. Meeting those requirements supposes the realization of a pigment ink formulation with stable particle sizes around 100 nm and high color strength, while maintaining all the fastness advantages normally inherent to high performance pigments, which is a quite challenging task.

Selecting the appropriate pigment based on chemistry (chromophore) and particle size considerations is obviously well known and customary in the ink jet industry. However, other essential pigment features like surface treatment and purity are rather unfamiliar to the ink formulator and are thus often overlooked when devising pigmented ink jet inks, which can lead to ink failure. Also, other ingredients present in waterborne ink jet inks, like co-solvents, can detrimentally interact with the pigment dispersion and should be carefully selected/optimized according to the pigment-dispersant system.

Chromophore and Particle Size

There is a common belief that pigmented ink jet inks contain coarse particles which might plug the nozzles. However, properly dispersed inks do not contain any particles larger than the nozzle diameter – which is usually at least 10 microns – and are thus not likely to clog the nozzles. Only accidental drying of the ink in the nozzle would lead to jet deviation and eventually to total obstruction, but this is true for dye-based inks as well.[1]

Although jettability might not be impaired by the presence of micron-wide particles, much smaller particle size is required to obtain vibrant colors from a CMYK ink jet ink set. Indeed, in order to achieve high chroma, the inks must be transparent and must not scatter light. Those criteria are fully fulfilled with pigment particles which are less than half the shortest wavelength of visible light, i.e. less than 200 nm. Image brilliancy and color gamut can thus be greatly enhanced by reducing pigment particle size down to 200 nm and smaller. However, the particle size reduction is often detrimental to image durability, the photo permanence of most pigments being related to the particle size and the total surface area (figure 1).[2] Thus only pigment chemistries with inherent high light and weather stability, i.e. high performance pigments, can offer a good balance between attractive colors and image durability with the smallest particle size.

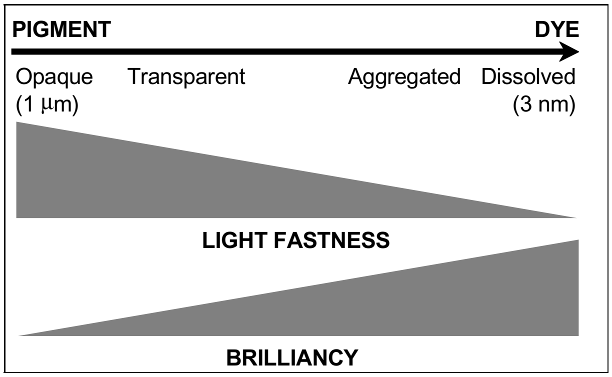
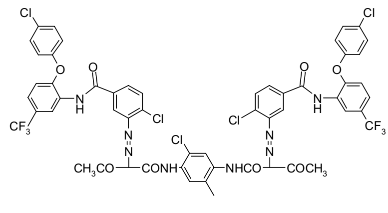
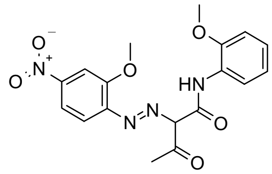
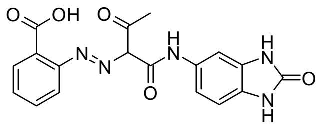
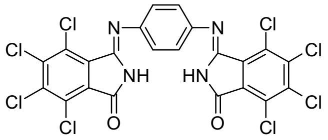
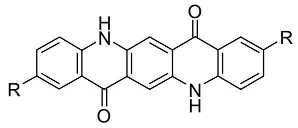
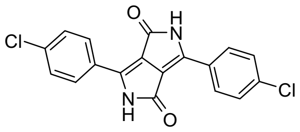
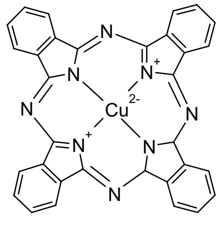


Figure 1. Pigment vs. dyes: permanence and brightness

Table 1 lists the main pigments commonly used in aqueous and solvent borne ink jet applications. For each pigment type, there are a wide variety of different single products available, differing in crystal modification, shape, size, size distribution, surface modification... Most of the pigments in table 1 are high performance pigments that offer high chroma combined to outstanding light- and weather-fastness, even at particle sizes around 100 nm or less. Only such pigments are suitable for most demanding ink jet applications, like outdoor wide format. Yellow pigments like P.Y. 128 or P.Y. 110 thus offer excellent color strength combined to outstanding durability. A pigment like P.Y. 74 is widely used in aqueous ink jet applications. It shows very high chroma but clearly lacks light fastness and, therefore, doesn't meet the requirements for outdoor use. Magenta shades are typically obtained using quinacridone pigments (P.V. 19, P.R. 122, P.R. 202) that are optionally blended together or shaded off with a yellow-shade magenta like P.R. 254 (solvent-based inks). Cyan pigment ink jet inks are always based on copper phthalocyanine compounds (P.B. 15), which are classical pigments offering high performance properties.

Table 1. Usual Pigments for Ink Jet Applications

P.Y. 128	
P.Y. 74	
P.Y. 151	
P.Y. 110	
P.V. 19 (R = H) P.R. 122 (R = CH$_3$) P.R. 202 (R = Cl)	
P.R. 254	
P.B. 15	

Small particle size, and - even more important - narrow particle size distribution, can be achieved either by inhibiting the growth of the pigment crystal during synthesis or by milling and kneading technologies, like salt-kneading. In the salt-kneading process, pigment particles are crushed in a high-shear mode by hard salt crystals and yield a finely divided pigment with broad particle size distribution. In a second step, a carefully controlled amount of a suitable solvent dissolves the finest particles and helps to heal (i.e. re-crystallize) the wounded pigment particles into a fine-grade pigment with narrow particle size distribution. Separation from the kneading media and drying completes the procedure. Salt-kneading of high performance pigments thus provides colorants that fulfill the requirements for most challenging applications, i.e. high chroma (small particle size), good dispersibility (narrow particle size distribution) and high durability.[3] Figure 2 illustrates the impact of kneading on P.Y. 128 and table 2 gives the primary particle size and fastness properties of some commercial fine grade pigments suitable for aqueous ink jet applications.

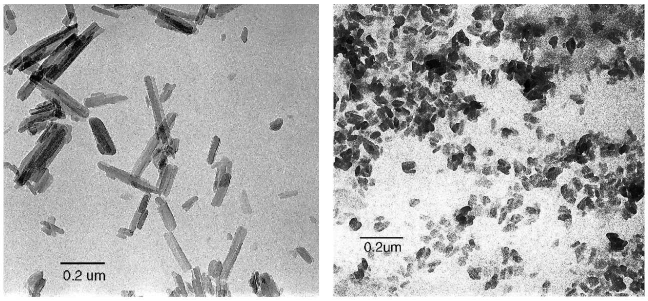


Figure 2. TEM images of P.Y. 128 particles before (left) and after (right) kneading

Table 2. Properties of Pigments for Aqueous Ink Jet Inks

Color Index	**Particle size D_{max} (micron)**	**Light fastness** BW scale (1-8)
Pigment Yellow 128	0.108	7
Pigment Red 122	0.090	7
Pigment Blue 15:3	0.039	8

Dry powder pigments unfortunately never exist as primary particles. They are typically strongly agglomerated and it takes quite a lot of energy to obtain a finely dispersed system. For this reason, the market also offers specialized pigment preparations in which the pigment is pre-dispersed so as to distribute easily and uniformly in the application medium without extensive shear. Here also, stringent particle size control through accurate grinding enables production of high performance pigment preparations with significantly improved application properties. The benefits of accurate particle size distribution control in the case of pigment preparations for solvent borne ink jet inks is illustrated in figure 3 and table 3. The type A preparations show a smaller particle size and narrower size distribution when compared to the coarser type B preparations (based on the very same pigments), which results in much improved coloristic properties with preserved permanence.

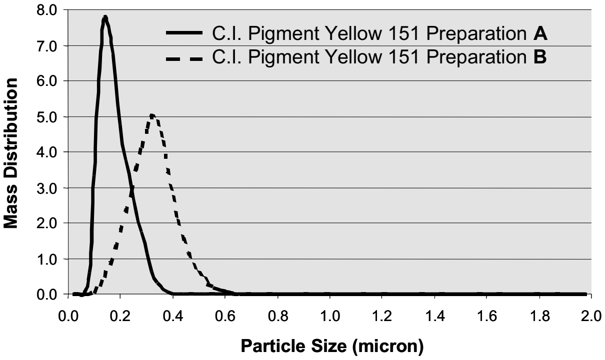


Figure 3. Particle size distribution of commercial P.Y. 151 pigment preparations for solvent borne inks

Table 3. Properties of Pigment Preparations for SB Inks

Color Index	**Particle Size D_{max} (micron)**	**Color Strength**	**Light Fastness** (1-8, BW scale)	**Weather Fastness** (1-5, ISO 105-A02)
P.Y. 151 Preparation A	0.173	100%	7	2-3
P.Y. 151 Preparation B	0.333	73%	7	2-3
P.B. 15 Preparation A	0.044	100%	8	5
P.B. 15 Preparation B	0.087	88%	8	5

Surface Treatment

The modification of pigments by treating their surface is well known in all the major application areas for organic pigments, i.e. printing inks, coatings and plastics. Such treatment serves to control and/or improve a variety of properties of the ink, paint or plastic medium into which the pigment is incorporated. Beneficial effects on such properties like color strength, hue, gloss, transparency, rheology or deflocculation are typically noted. Especially, surface modification methods in which the pigment is surface-treated with one of its own derivatives has proven very successful in ink applications. In the pigment derivative treating method, a polar group is introduced as a substituent into a pigment molecule of the same type as the pigment to be treated, to give a pigment derivative which is allowed to be adsorbed onto the pigment surface.[4] In aqueous systems, such as waterborne ink jet inks, a more polar surface is expected to result in improved dispersibility, due to better wetting properties and lower flocculation/reagglomeration tendency resulting from stronger electrostatic repulsion forces between individual particles.

For instance, quinacridone pigments have a great affinity for their polar substituted derivatives. Thus, quinacridone pigments have been treated with a variety of quinacridone derivatives such as the mono and disulfonic acids, amide derivatives of the sulfonic acids, carboxylic acids, phthalimidomethyl, dialkylaminoalkyl derivatives, etc… to increase the polarity of the pigment surface. In aqueous ink jet ink formulations, pigments like P.R. 122 are generally dispersed using specific polymeric dispersants, which allow greater stability of the dispersion. Very fine pigments particles - as utilized in ink jet applications - have a stronger tendency to flocculate due to higher surface energies and consequently tend to impart higher viscosities relative to larger, opaque pigments. In that case, the chemical nature of the polar substituted derivatives, such as those previously mentioned, and of the polymeric dispersants, is critical in reducing the system's viscosity and assure its stability, compared with untreated pigments and/or dispersions not containing polymeric dispersants. Polymeric dispersants usually contain basic, acidic or nonionic moieties. These can associate individually with the solvent, the binder (if any), the pigment, or a combination of these ingredients. Clearly, a pigment treated with an acid derivative of the compound that makes the pigment, which is adsorbed onto the surface of the pigment, referred to as the anchor group, would have a great propensity to react with a polymeric dispersant which has a built-in basic moiety (chemisorption). The opposite is true when the pigment surface is treated with a derivative carrying a basic substituent. Thus, in the dispersion process of initial pigment wetting followed by particle deaggregation, individual particles treated with the anchors become exposed and available for reaction with the polymeric dispersants, which in most cases are block copolymers of specific molecular weight.

The impact of an anionic surface treatment on viscosity and flocculation/reagglomeration stability of aqueous ink jet formulations based on a small-particle size P.R. 122 (surface area of 90 m^2/g) and a suitable block polymeric dispersant is shown in figures 4 and 5. Pigment concentration is 2.6% and polymeric dispersant concentration is 1.3%. Dispersion is done with a bead mill and the coarse particle fraction (less than 2%) is removed by ultracentrifugation. All formulations are binder free and differ only in the concentration of butyldiglycol (diethyleneglycolmonobutylether). Such glycol ether co-solvents are typically included in waterborne ink jet formulations, where they function simultaneously as humectant, viscosity modifier and solubilizing agent. Obviously, the untreated pigment shows poor storage stability at high butyldiglycol concentration (> 5%), as evidenced by a marked increase in particle size (an indication of reagglomeration) and viscosity (flocculation). The inks made from surface treated pigment appear less affected by the butyldiglycol and thus offers lower initial viscosity and much improved storage stability at the highest butyldiglycol concentrations.

The glycol ether co-solvent, by its intrinsic amphiphilic nature, is believed to weaken the affinity between the block copolymer and the pigment surface and thus to interfere with its stabilising action. The surface treatment probably acts as a mediator between the pigment surface and the block copolymer, making the latter more resilient against desorption. Furthermore, even in a dewetted state, surface treated pigment particles are less prone to reagglomeration due to electrostatic repulsion between polar surfaces (charge stabilization).

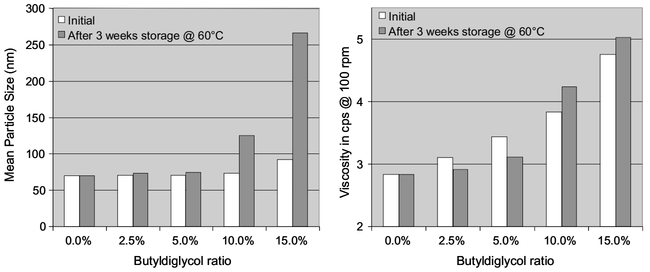


Figure 4. Change in particle size and viscosity in P.R. 122 ink jet inks upon incubation at 60°C (no surface treatment)

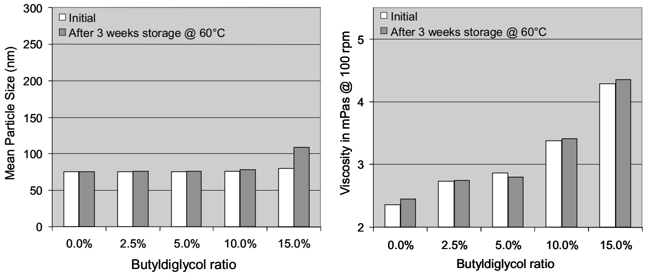


Figure 5. Change in particle size and viscosity in P.R. 122 ink jet inks upon incubation at 60°C (anionic surface treatment)

Even though in the specific case presented here, there is clear evidence for the beneficial effect of the surface treatment on dispersion stability, a cautionary note should be indicated. Proper functioning of inkjet printheads relies on the nozzles remaining free of any traces of adhering material, since this results in jet deviation or failure of jetting. If materials used in surface treatment are present in excess, or their solubility is enhanced by the carrier fluid composition, there is a risk of some deposition on the nozzle rim in the course of an extended print run. The carrier phase should be as free as possible of dissolved species, and every ink system should be submitted to extended runnability tests in addition to the determination of colloidal stability.

Chemical Purity

Organic pigments are usually obtained via multi-step synthesis, followed by finishing to optimize the physical properties such as crystal shape, crystal size and crystal quality, as well as particle size distribution.[5] The synthesis of azo pigments, like monoazo, disazo or benzimidazolone yellows (P.Y. 74, P.Y. 155, P.Y. 151), comprises two main steps: a diazotation reaction, leading to diazonium salt formation, followed by azo coupling, which is responsible for the formation of the azo pigment. Subsequent finishing typically involves heating the of the crude pigment suspension or the salt-free pigment presscake in water and/or organic solvents to temperatures of 80°C to 150°C. Synthesis of isoindolinone and isoindoline azo methine and methine yellow pigments (P.Y. 128, P.Y. 139) involves a condensation step. Industrial scale production of quinacridone magenta pigments (P.R. 122, P.R. 202, P.V. 19) typically includes total synthesis of the central aromatic ring, a process consisting of numerous intermediate steps. Production of copper phthalocyanines (P.B. 15) is somewhat more straightforward and involves heating phthalonitrile with metallic copper/copper salts, or heating phthalic anhydride with a copper salt and urea in the presence of a catalyst.

The complexity of organic pigment manufacture, including further processing (finishing), drying and pulverizing, makes it quite cumbersome to achieve a product with the purity and physical properties that are required for the intended use. Thus, pigments differ greatly from dyes in the form in which they emerge from the manufacturing process. Dyes are soluble in the reaction mixture and are precipitated from the (aqueous) solution by salts, whereas pigments come out from the manufacturing process as almost insoluble substances. The purity of the starting materials is therefore a major concern to the producer, as is the avoidance of any residual reaction intermediates that might be adsorbed at the pigment surface of the particles or, even worse, trapped into the crystal structure. Contamination of the pigment with impurities present in raw materials or with intermediate products/pigment precursors potentially soluble in the application medium can negatively affect the pigment's application properties. Reproducibility of the manufacturing process has to include particle and interface characteristics, such as ease of dispersion.

The relevance of pigment contamination in ink jet applications is illustrated in figures 6 to 8. In this study, various batches of a small-particle size pigment (surface area of 150 m^2/g) showing different (low) levels of contamination with a pigment precursor were formulated into a standard aqueous ink jet ink. The pigment was dispersed via ball milling with a polymeric dispersant (50% by weight of pigment). The ink formulations were subjected to incubation for a total of 4 weeks at 60°C. Particle size and viscosity of all samples were monitored weekly. As shown in figures 6/7, the pigment precursor was clearly found to promote particle size growth and viscosity increase. Thus, in the case of a precursor impurity level of about 0.4 % by weight of pigment, the mean particle size and viscosity almost doubled during the 4 weeks incubation period. Furthermore, analysis of the particle size distribution shows that the size distribution after storage ranged from 50 nm to 800 nm, whereas it spanned from just 80 nm to 200 nm before incubation (figure 8). Processing the pigment to reduce the precursor level to about 0.1% by weight of pigment or less enables to suppress almost completely particle growth and thus to obtain an ink with outstanding ageing properties. The broadening of the particle size distribution in presence of higher levels of precursor contaminant can be explained by extraction and recrystallization of the precursor. The resulting precursor crystals would account for the fraction of smaller particles seen in the particle size analysis after incubation, whereas larger particles would arise through "gluing" of the dispersed pigment particles by the smaller precursor crystals. Besides, the formation of small amounts of larger precursor crystals/aggregates (in the micron range), not seen in the particle size analysis via dynamic light scattering, cannot be excluded. Also, it should be noted that glycol ether co-solvents (see previous section) were found to play a key role in promoting particle growth, since crystal growth could be markedly reduced - and in some cases fully inhibited - by modifying the glycol ether type or suppressing glycol ether co-solvents from the formulation.

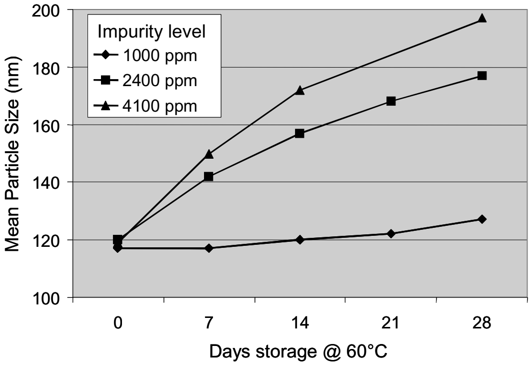


Figure 6. Particle size change of pigment inks upon incubation at 60°C as a function of pigment batch

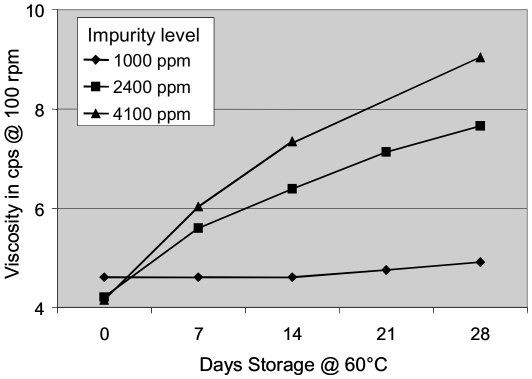


Figure 7. Viscosity change of pigment inks upon incubation at 60°C as a function of pigment batch

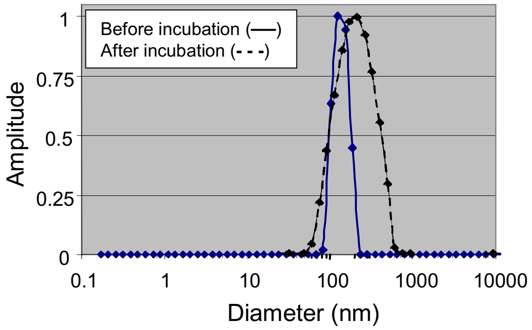


Figure 8. Change in particle size distribution upon incubation (impurity level = 4200 ppm)

Conclusion

The permanence of images produced by ink jet is a key issue in an increasing number of applications, since enhanced image quality offered by latest printer technology increases the print value and thus the desire to be able to store or display prints for a prolonged period. For the most demanding applications, where both brilliancy and durability are required, pigmented inks based on specialized pigments are currently the only viable option.

The combination of appropriate chromophore choice and rigorous particle size control is the first step to superior pigmented ink jet inks. Ultrafine pigments obtained through accurate particle size reduction of high-performance chemistries are thus proving well suited for both indoor and outdoor applications due to their outstanding brightness and fastness properties. Predispersed variants, which allow the ink formulator to eliminate the complex dispersion step, have become commercially available and open the door to a broader implementation of pigment ink jet inks. Besides pigment chemistry and particle size, other crucial but less familiar factors have been shown to have a potential impact on the performance of pigmented ink jet formulations. Thus, surface modification and chemical purity of the pigment should be carefully considered, as they might affect colloidal stability and in turn compromise ink reliability. In addition, some usual aqueous ink ingredients like glycol ether co-solvents, have been found to impair specific pigment dispersions by promoting particle growth and flocculation.

The discussed issues definitely show that finishing (particle sizing, surface modification, purification…) and formulation of ink jet pigments are potentially more challenging than synthesis.

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Biography

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