Highly Compatible Pigment Preparations for Aqueous Ink Jet Inks

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Abstract

In recent years, pigment-based inks have become more and more attractive for office and wide format ink jet applications. This non-impact printing technology does pose special requirements, not only for pigment preparations, but also for the pigments themselves. Besides the exploration of new dispersants and the optimization of the dispersant system, tailoring the properties of the pigments, such as particle size distribution, surface charge and polarity, morphology, and especially purity, is key. As a result, the desired features of preparations and inks such as transparency, hue, viscosity and storage stability (no flocculation or sedimentation) can be improved, as well as the elimination of cogation or abrasion in the printhead. New test methods for ink jet applications and new concepts for production processes such as microreactor technology or finish treatment can significantly improve the suitability of specific organic pigments for ink jet printing and the performance of the resulting inks.

Introduction

In recent years, pigment-based inks have become increasingly attractive in ink jet applications. This is mainly due to the fact that pigments generally exhibit superior water and light fastness properties when compared to dyes.

The ink jet market, represented by the ink manufacturers, especially the refillers, nowadays are demanding simple solutions, which means concentrated pigment preparations that can be formulated into ink jet inks by simply adding a few additives and "magic ingredients" to yield inks that meet the stringent demands of high-performance ink jet printing.

Figure 1 depicts the principal in the manufacturing of such aqueous pigment preparations. The first step is the choice of the right color pigment. Ink jet printing usually requires a four-color set comprising a black (carbon black), a magenta, a cyan, and a yellow ink. Thus, a pigment has to be selected that matches in shade one of the desired colors. To the pigment powder or presscake are added water, dispersant(s), and other additives, and the mixture is stirred to allow homogenization and wetting of the pigment surface. The pigment particles, comprising agglomerates and aggregates, are then broken down into their primary particles, e.g., by means of bead milling, microfluidizing or other suitable dispersing equipment. The primary particles are stabilized against re-agglomeration and settling by the dispersant molecules thereon due to sterical and/or electrostatical repulsion. The pigment concentrate thus produced is filtered and can be diluted by adding water, co-solvents (humectants), and other ingredients, such as biocides, chelating agents, etc. It has to be stressed that the pigment employed in the first step substantially influences all of the following steps of the pigment dispersing process discussed above.

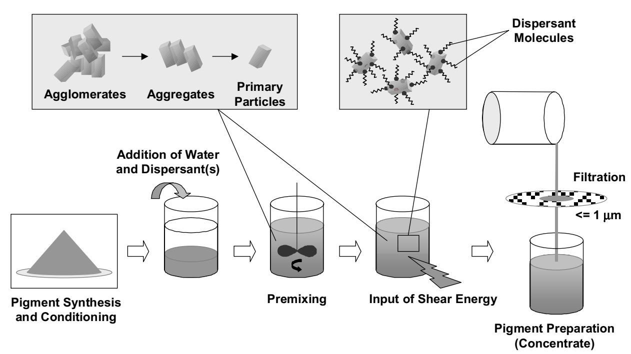


Figure 1. Principle steps in the manufacturing of aqueous pigment preparations.

While the properties of dyes are mainly influenced by their chemistry, the properties of pigments are influenced by chemical and physical parameters. Consequently, besides the exploration of new dispersants and optimization of the dispersant system, tailoring the physical properties of the pigments, such as the particle size distribution, surface charge and polarity, morphology, and especially purity is key to obtaining pigment preparations that are suitable for modern ink jet printing technologies. Thus, the desired features of the resulting preparations and inks, such as the transparency, hue, viscosity, storage stability (no flocculation or sedimentation), and absence of cogation or abrasion in the printhead can be achieved.

The present manuscript demonstrates concepts of either synthesis, finish, or post-finish treatment that can significantly improve the suitability of specific organic pigments for ink jet printing. Also presented are examples of the manufacturing of preparations based on such pigments and their performance in ink jet inks.

Conditioning of Pigment Properties

A) Particle Size Distribution

A very important physical property of a pigment is its particle size and connected with this the specific surface area [m^2/g]. The particle size, for example, directly influences the shade, the transparency, the chroma, the optical density, and the light fastness of an ink jet ink when printed on a medium. Figure 2 shows the dependency of several ink properties on the particle size of the corresponding pigments. The average or mean particle size distribution (in the following referred to as d_{50}) should be around 100 nm with a narrow particle size distribution curve. If the d_{50} value is considerably higher, printing reliability is impaired by large pigment particles or agglomerates clogging the channels and/or nozzles of the ink jet heads (diameter typically in the range of 10-50 µm). In bubble-jet printheads, short-term temperatures of up to 500°C may occur. This can be considered as a quasi-finish process: the pigment is heated in the presence of one or more solvents (ink additives) which may lead to unwanted particle growth or re-agglomeration. Larger particles also result in ink jet prints with low transparency and low chroma.[1]

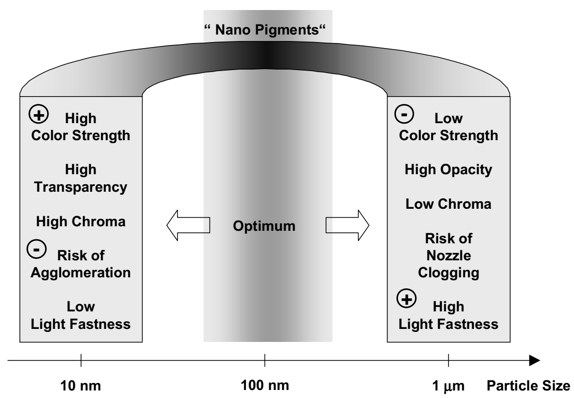


Figure 2. Dependence of ink jet printing parameters on pigment particle size.

On the other hand, very small particles in pigment preparations tend to re-agglomerate due to their larger surface and, thus, much stronger inter-particle interactions. As a result, the viscosity may increase and the storage stability may drop. It is important to note that the high fastness properties of pigments vary: some are extremely lightfast, while others fade almost as quickly as dyes. However, there is a general tendency that the light fastness drops with particles significantly smaller than 50 nm.[2]

In summary, there is an optimum pigment particle size for ink jet and the quality of its printed images which is somewhere in the range of d_{50} = 100 nm. Organic pigments with such particle sizes are denoted in the following as nano color pigments.

An important step is the so-called finish process. The finish process ("finish") is understood to be a post-synthesis process step where the raw pigment is heated in the presence of one or more organic solvents. This process involves the growth of the pigment particles. The degree of this particle growth depends on temperature and duration of the finish for a certain solvent. As a general rule, the higher the temperature and the longer the finish process, the larger the particles become. Figure 3 demonstrates the influence of the finish temperature on the primary particle size of P.Y. 155.

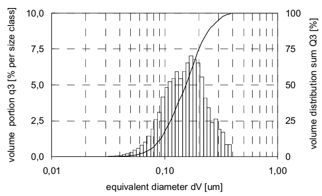
The distribution curve for Type I represents a sample of P.Y. 155 finished at higher temperature, while the chart on the right is based on a sample finished at lower temperature (Type II). As shown, a lower temperature leads to a smaller average particle size and a narrower distribution curve.

Table 1 shows the corresponding particle sizes of both types of P.Y. 155 (Type I and Type II) of the powder pigment and of aqueous pigment preparations. Apparently, Type II is much closer to the desired 100 nm range when compared with Type I and, thus, preferable in office ink jet applications.

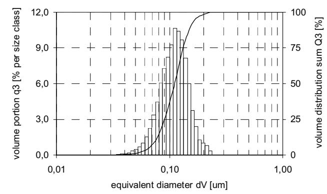
Table 1. Particle sizes of P.Y. 155 as powder and in aqueous preparation.[3]

	Powder[a]			Preparation[b]		
	d_{25} [nm]	d_{50} [nm]	d_{75} [nm]	d_{25} [nm]	d_{50} [nm]	d_{75} [nm]
Type I	113	155	202	86	150	222
Type II	90	111	132	62	96	142

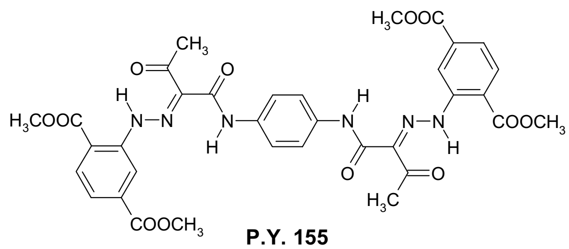
[a] [nm] measured by TEM
[b] [nm] measured by CHDF



Type I



Type II



P.Y. 155

Figure 3. Influence of the finish temperature on pigment particle size: finish at higher temperature (Type I) and finish at lower temperature (Type II).

In conclusion, to obtain small particles in pigment preparations it is essential to employ pigments that already possess small primary particles in the powder or presscake (wetcake) form.

B) Surface Charge and Polarity

Surface charge and polarity are strongly dependent on morphology and chemistry of a pigment. The polarity of an organic pigment surface can be highly unpolar (hydrophobic) or highly polar (hydrophilic) or in between. Surface polarities of pigments can be calculated from contact angle measurements (tensiometry) with different solvents.[4] The polarity of a pigment surface is an important factor in the dispersion process (Figure 1). To ensure excellent wetting behavior of a pigment, the right combination of pigment and dispersing medium has to be found. Figure 4 shows an example of two samples of P.Y. 180 with quite different surface polarities. Type A is quite hydrophobic, consequently floating on water. Type B (pigment on bottom) is highly hydrophilic which provides for excellent wetting in a water-based system. On the other hand, for a better wetting behavior in hydrophobic (solvent-based) media, Type A is more appropriate. In other words, the surface polarity of a pigment has to be optimized for each application, and this has to be achieved in the pigment manufacturing step.

Type A

Type B

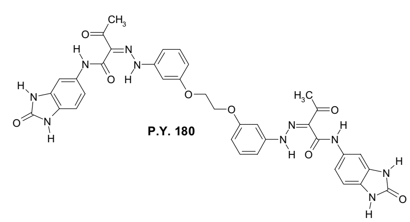


Figure 4. Two types of P.Y. 180 with hydrophobic (Type A) or hydrophilic (Type B) surface characteristics.

C) Purity

A further parameter that qualifies organic nano pigments for use in ink jet is a high degree of purity. Amounts of residual organic and/or inorganic impurities in a range of just a few ppm (parts per million) are desirable. It is well known that, for example, chloride ions promote corrosion of the printheads. Some cations are known to form insoluble complexes with a number of dispersant molecules, thereby impairing the stability of a pigment preparation. An ink containing such ionic impurities may exhibit flocculation or sedimentation upon storage, causing nozzle clogging in the printhead. One process to manufacture pure pigments is based on micro reactor technology (MRT).[5]

The following demonstrates how these nano color pigments can be used to prepare aqueous pigment concentrates for high-performance ink jet inks.

Preparation of Pigment Concentrates

The pigment concentrates were manufactured according to the following process. The pigment was premixed with the dispersant, a glycol, a biocide, and demineralized water by means of a dissolver and then subjected to milling until the desired particle size distribution was reached. The resulting aqueous pigment preparation was filtered with an appropriate filter to remove coarse particles.

The physical properties were checked to prove their suitability for ink jet applications. Even at higher pigment loads, the pigment preparation should have a low viscosity (preferably < 50 mPas) which means that they exhibit good flowability. The dispersed pigment particles should be very small, i.e., the average d_{50} particle size should be around 100 nm or less. Table 2 compiles the physical data obtained for the four nano color pigment preparations.

The pigment preparations given as examples in Table 3 all exhibit the desired excellent flowability properties due to their very low viscosity. The viscosities after preparation are in a range below 10 mPas and do not significantly increase upon storage at elevated temperature, proving their shelf-life stability. Good shelf-life properties are key for high ink stability and excellent printability. The d_{50} value for the mean particle size of all preparations is below 100 nm (CHDF), which makes them fulfill the requirements of pigment concentrates for ink jet applications.

Table 2. Physical data obtained for aqueous preparations based on nano color pigments.[6]

Color	Pigment	Pigment Content	pH	d_{50} [nm][a]	Viscosity [mPas]		
					fresh	7 d/et	28 d/et
Yellow	P.Y. 155	20%	8.6	96	7.9	11.7	10.1
Magenta	P.R. 122	20%	9.0	68	7.7	7.4	9.4
Cyan	P.B. 15:3	20%	8.7	84	5.7	5.6	6.4
Black	P.Bk. 7	15%	8.4	64	4.9	5.6	6.5

[a] measured by CHDF
[et] = elevated temperature

Printing Tests

Knowledge of just the physical parameters, however, is not sufficient to decide whether a pigment preparation is suitable for ink jet applications or not. Especially in thermal ink jet printing (bubble jet), the high (short-term) temperatures and the high shear forces should not lead to decomposition of the ink due to desorption of the dispersant molecules from the pigment surface. Such decomposition processes could result in agglomeration of pigment particles, cogation, or nozzle clogging.

Based on the pigment concentrates listed in Table 2, test inks were prepared, which were then printed on coated and uncoated paper. All test inks showed excellent printing performance with regard to reliability, jetting stability, and optical density of the resulting test prints.

Conclusions

Once again, it is the optimized interaction between ink, printhead, and substrate (paper) that is the prerequisite for excellent results in high-performance ink jet printing. One approach to meet this desired quality is that of the nano color pigments described in this paper and preparations based on such pigments.

References

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3. The mean particle sizes measured by the CHDF method (capillary hydrodynamic fractioning) for the preparations correspond to the data obtained by TEM (transmission electron microscopy) for the pigment powders. It has to be noted that these two methods result in different values due to the different physical principles on which they are based on. However, the ratio is more or less the same, represented by a factor of CHDF:TEM ≈ 1:1.4.
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Biography

Klaus Saitmacher received his Ph.D. degree in organic chemistry from the Friedrich-Wilhelms University in Bonn / Germany in 1989. He began his career in the textile dyes business unit at the former Hoechst AG / Frankfurt. In 1998 he joined Clariant GmbH Division Pigments & Additives. He worked on several azo pigment development projects and was in charge of production quality. Now in Clariant's Non-Impact Printing group he focuses as a project manager on the development of pigment preparations for ink jet applications.