The Influence of Pigment Selection on Particle Size and Migration Stability in Aqueous Inkjet Inks

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Abstract

The aqueous pigmented inkjet ink formulator is faced with a large number of potential commercially available grades of organic pigment. This paper presents data that explores the link between the properties of some commercially available organic pigments and (i) the particle size achievable in dispersed form and (ii) the subsequent effects on the stability of the dispersion to particle migration. Different grades of the same organic pigments from several manufacturers were dispersed under equivalent conditions and particle sized using Photon Correlation spectroscopy. Ink jet inks were formulated from these dispersions and the propensity to settling was measured using a Turbiscan stability analyser. The results show a clear correlation between rate of sedimentation and particle size. The effects of particle size are less pronounced as ink viscosity increases. Correlation with the available physical parameters of the pigment powder is not always clear, however the study shows the importance of selection of the appropriate grade of pigment in optimising the achievable particle size. Examples are shown that illustrate the colouristic advantages of reduced particle size.

Introduction

Pigments are continually emerging as the colorant of choice in a wide range of Ink Jet printing applications. This has always been the case in outdoor graphics and signage applications, but with the development of new technology inks and paper substrates we are beginning to see the same trends in desktop.[1,2] Recent developments in piezo print head technology provide further opportunities for pigments and we are now seeing the expansion of Ink Jet into industrial sectors.[3] Organic pigments tend to satisfy the requirements of most printing inks, but selecting a suitable type or grade for Ink Jet is not necessarily straightforward. The range of commercial pigments is enormous and although some manufacturer's technical specifications can provide some guidance this information is not always readily available. This is further complicated by the different methods of analysis that each of the manufacturers employs to characterize pigments.

The effectiveness of dispersion determines the key properties of pigmented inks in their end application and in this paper we will show how different properties can be obtained from seemingly comparable grades of commercial organic pigments. Ink Jet applications generally require very fine particle size and stable pigment dispersions. For low viscosity inks there is a greater tendency for particle migration to occur during storage. To control and monitor particle sizes, methods such as PCS (photon correlation spectroscopy) are used, but techniques like this alone are not entirely effective in the assessment of pigment dispersion quality or stability. The emergence of the Turbiscan however provides an additional technique, which now allows the assessment of dispersion stability to be carried out in a comparatively short period of time. In this study it will be shown how particle migration and tendency to sediment is influenced by pigment selection and the particle sizes achieved through the dispersion process.

Experimental

The Formulaction Turbiscan is able to analyse the stability of a wide range of colloidal systems and is particularly suited to the evaluation of pigmented ink jet inks.[4] Test samples are placed in a cylindrical glass tube and scanned from bottom to top using a pulsed near infrared light source (850nm). This provides transmission and backscatter data and over a given period of time changes can be monitored. Colloidal stability is assessed through changes in backscatter (delta) when compared to a reference, which is usually a scan taken from the beginning of the analysis. The backscatter of a colloidal system is influenced by several key factors; particle size, concentration, relative refractive index and colour/absorbency. The key areas of interest are the top, middle and bottom of the tube and changes in these regions are consistent with creaming, particle growth and sedimentation.

The pigment classes selected for evaluation were Phthalocyanine Blues, Quinacridone Reds and Azo yellows, and these have all found widespread use in a range of Ink Jet applications. The pigments were all commercially sourced and have been recommended for this application. The technical specifications are presented in Table 1.

Table 1. Pigment Grades & Manufacturers Technical Specifications.

Pigment Type	Pigment Class	Bulk density g/cm^3	BET m^2/g	Primary size (nm)
Magenta 1	Quinacridone	1.49	63	-
Magenta 2	Quinacridone	1.45	97	60
Cyan 1	Phthalocyanine	1.59	48	85
Cyan 2	Phthalocyanine	1.64	130	-
Yellow 1	Disazo	1.40	50	90
Yellow 2	Disazo	1.40	63	47
Yellow 3	Disazo	1.50	90	-
Yellow 4	Monoazo	1.20	47	65

Aqueous pigment dispersions (20% solids) were prepared using a Microfluidiser and filtered prior to ink formulation to remove any oversized particles that remained after processing. The dispersant types were alkali neutralised acrylic copolymers that were known to be effective stabilisers for each pigment. Mean particle sizes were determined through a Polymer Laboratory LSP analyser which uses Photon Correlation Spectroscopy. Pigment dispersions were let down into ink formulations that contained a mixture of glycols, resins, surfactants and a suitable pH buffer. The colorant concentration in the ink was between 2 – 5% depending on the pigment type. The inks were also subjected to a final 3-micron filtration step. The physical properties for each of the inks evaluated are presented in Table 2.

Table 2. Ink Physical Properties.

Pigment Ink	pH	Viscosity cps	Surface Tension Dynes /cm	Mean Particle Sizes (nm)	BET m^2/g
Magenta1	8.6	2.46	32	130	80
Magenta2	8.5	2.63	36	108	97
Cyan 1	8.4	2.65	32	129	48
Cyan 2	8.4	2.54	36	86	130
Yellow 1	8.6	2.33	36	160	50
Yellow1a	8.9	14.0	30	210	50
Yellow 2	8.5	2.86	35	120	63
Yellow 3	8.9	3.21	36	140	90
Yellow 4	8.4	2.43	35	111	47

Ink stability analysis through a Turbiscan "thermo" model was carried out over 24 hours at 30°C with scans every 15 minutes. In parallel with this activity inks were also stored at 70°C for 7 days to assess pigment stability through the more traditional means of an accelerated ageing test. An Encad 700 wide format printer was used to evaluate the performance of ink sets on a wide range of media types.

Results & Discussion

In Figure 1 the particle sizes of the pigment dispersions are plotted against the pigment manufacturer's BET surface areas. There is clearly very little correlation ($R^2 = 0.30$) between the data and although the pigment BET can offer guidance these results confirm that it does not necessarily predict what particle sizes will be achieved in dispersion. The chemical and physical nature of the pigment types (e.g. degree of agglomeration, surface treatment) and the type of process used to disperse will be major factors also influencing the end result.[5]

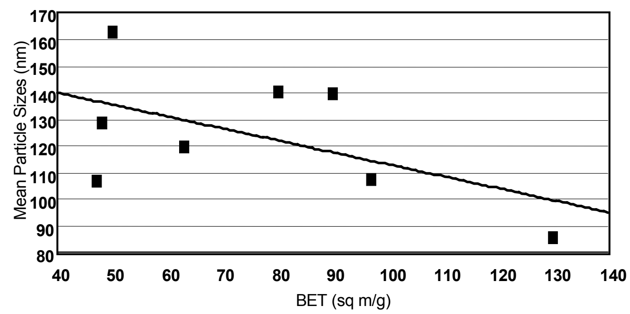

Figure 1. Mean Particle Sizes Achieved in Dispersion Compared with the Pigment BET Surface Area.

The results of the Turbiscan ink stability analysis are summarised in Table 3. Also included in the table are the mean particle sizes for the inks stored at elevated temperature for 7 days. The 0hrs % backscatter value (in the 10-30mm mid tube zone) correlates with the measured particle size of each ink. The 24hrs % backscatter in the same zone is virtually unchanged for all inks thus confirming no particle size increases during the analysis. Stability results at elevated temperature largely followed the same trend, although for yellow inks 2 and 3 these conditions have promoted instability (increased particle sizes).

Table 3. Summary of the Pigment Ink Stability Analysis.

	% Backscatter Zone 10-30mm		Migration Velocity (mm/min)	Mean Particle Sizes (nm)	
	0hrs	24hrs		25°C	70°C
Mag 1	47.1	47.3	6.66×10^{-4}	130	128
			1.61×10^{-3}		
Mag 2	15.9	16.8	7.26×10^{-5}	108	110
Cyan 1	39.6	39.2	5.59×10^{-4}	129	133
Cyan 2	26.4	26.3	5.71×10^{-4}	86	86
Yel 1	68.1	67.4	1.39×10^{-3}	160	156
			2.02×10^{-3}		
Yel 1a	72.9	73.4	3.06×10^{-4}	210	225
Yel 2	34.3	34.3	1.79×10^{-4}	144	317
Yel 3	39.6	39.7	1.72×10^{-4}	140	212
Yel 4	29.1	29.2	1.94×10^{-4}	111	137

Although no particle size increases were seen in the Turbiscan analysis, clear differences in the % backscatter at the top and bottom of the tube were observed indicating particle migration. In some of the inks two migration rates were observed indicating bimodal population of particles. Figure 2 compares the migration rates for each of the inks calculated from the delta backscatter at the top of the tube. There is reasonable correlation (R^2 = 0.58) with the measured particle sizes. Faster migration rates were observed in inks that have larger average particle sizes. These low viscosity inks will show a greater tendency to settle on storage.

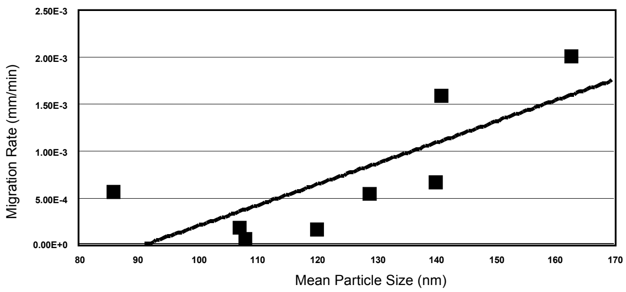

Figure 2. The Influence of Particle Size on Migration Velocity

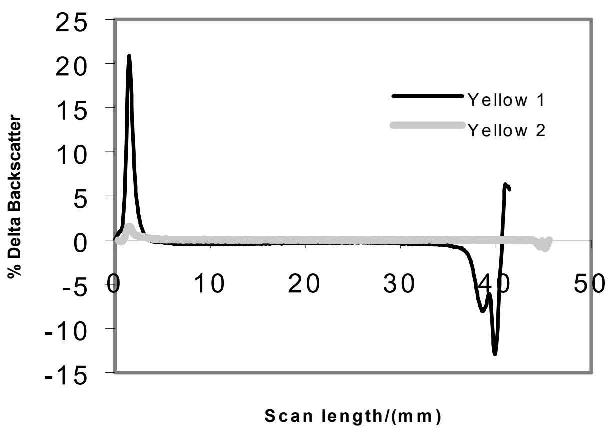

Figure 3. Turbiscan Delta-Backscatter for Yellow Ink 1 and 2

Figure 3 shows Turbiscan Delta Backscatter data after 1 and 24hrs for yellow inks 1 and 2, which contain different grades of the same pigment chromophore. This further illustrates the importance of pigment selection and shows that the finer particle sized ink will exhibit better keeping properties on storage. Further analysis of backscatter data reveals the different migration rates for the two ink types and these have been overlaid in Figure 4.

This analysis confirms the instability of Yellow ink 1 and shows that this particular formulation is very susceptible to particle migration. However, taking the same pigment dispersion and modifying the viscosity as in Yellow ink 1a has had a profound effect on stability. The same pigment in a different formulation is now giving a much reduced tendency to settle as a result of increased viscosity.

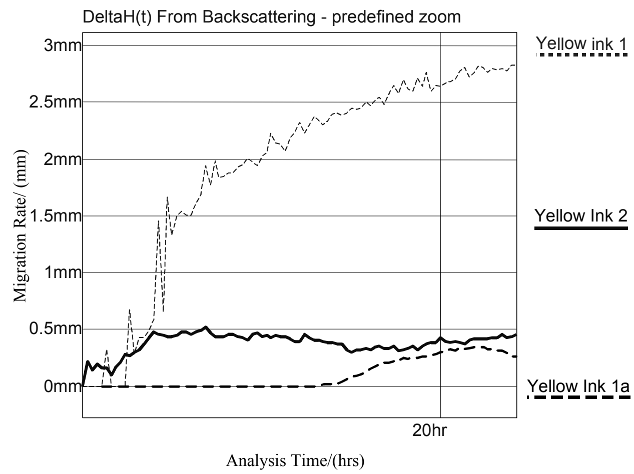

Figure 4. Turbiscan Analysis Comparing Particle Migration for Yellow Ink 1, the more viscous Ink 1a and Yellow Ink 2

Table 4. Colour Gamut Data for three Ink Sets printed on a Range of ILFORD Media.

Ink Set	ILFORD Media	Colour Gamut Data						
		Total	Y	R	M	B	C	G
Magenta 1	Glossy	22329	3884	3037	4783	3195	3289	4141
Cyan 1	Semi Gloss	21601	3836	2894	4573	3012	3252	4034
Yellow 1	Canvas	14403	2659	2180	3050	2039	1912	2562
	Vinyl	12098	2325	1928	2508	1840	1441	2055
	Scrim	14126	2957	2316	2877	1892	1614	2470
	Fine Art	16059	2825	2303	3503	2414	2348	2667
Magenta 2	Glossy	28332	4484	4140	5977	3813	4272	5646
Cyan 2	Semi Gloss	29281	4896	4269	5937	3821	4348	6010
Yellow 3	Canvas	16527	3181	2668	2951	2034	2316	3376
	Vinyl	14362	2793	2467	2569	1827	1828	2877
	Scrim	15093	3062	2485	2804	1960	1907	2874
	Fine Art	17510	3461	2789	2980	2119	2534	3627
Magenta 2	Glossy	33452	6700	4966	6059	3837	4348	7542
Cyan 2	Semi Gloss	34048	6783	5034	5971	3843	4448	7968
Yellow 4	Canvas	16746	3475	2662	2969	2062	2214	3364
	Vinyl	13542	2794	2358	2454	1733	1680	2523
	Scrim	14480	3142	2305	2656	1831	1763	2784
	Fine Art	18387	3739	2834	3278	2331	2570	3635

The discussion has so far focused on choice of pigment and how this influences stability, but the selection is also important in optimizing printed image quality on a range of media types. Table 4 shows the achievable colour gamut's for three ink sets on a range of Ilford Inkjet media.

These results show that the pigment inks with finer particle size give higher gamut in most colour sectors particularly on glossy and semi glossy media. Unlike the cyan and magenta pigments which are the same chromophore, the yellow pigments are different. Yellow 4 is tinctorially stronger than Yellow 1and this will have contributed to the improvement in colour gamut in Y,R & G sectors, whereas Yellow 3 is tinctorially weaker and so the gamut improvement here is clearly particle size related. Although less pronounced, similar improvements are also observed on some of the other more absorbent medias. The differences in colour gamut on glossy nanoporous media are illustrated in Figures 5 and 6. This confirms the increase colour gamut that the finer particle size inks offer on this media type.

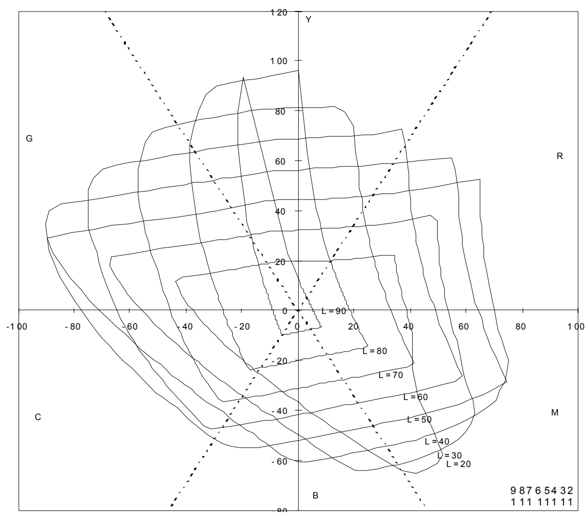

Figure 5. Colour Gamut for Magenta 2, Cyan 2 and Yellow 4 Printed on ILFORD Glossy Media

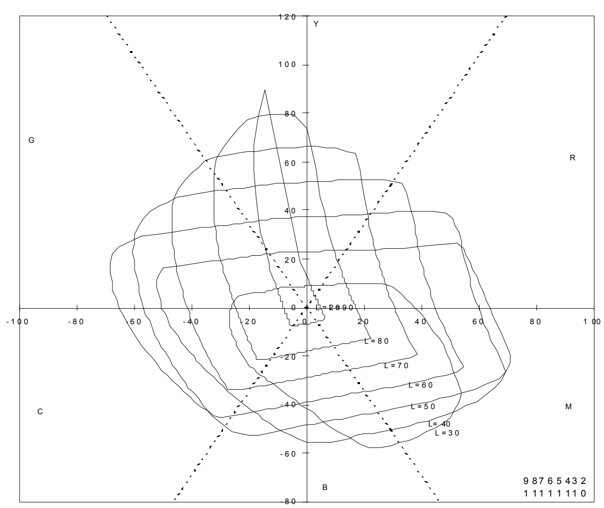

Figure 6. Colour Gamut for Magenta 1, Cyan 1 and Yellow 1 Printed on ILFORD Glossy Media

Conclusion

The Turbiscan analysis has shown that migration stability of aqueous pigmented inkjet inks is greatly influenced by the choice of pigment grade. Seemingly comparable pigment grades recommended for this ink application have given rise to different stability results. Pigments that produced coarser particle sizes in dispersion showed a greater tendency to settle when formulated into inks. These results were true for low viscosity inks, but as expected the formulation of a more viscous ink slowed down the rate of particle migration and improved stability. The finer particle size inks gave greater colour gamut when printed on a wide range of media types.

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Biography

Peter Rose holds a BSc degree in applied chemistry from St John Moores University Liverpool. He has worked with ILFORD Imaging since 1983, initially in research and development of photographic film and since 1996 has worked on aqueous pigmented inkjet inks and dispersions. He holds several patents relating to inkjet pigments, dispersants, dispersing processes and ink formulations.