

# Crystal Engineering of Pigments for Permanence

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## Abstract

Continuously improving demands upon the permanence of inkjet colorants have seen an increasing trend towards the use of pigments rather than dyes for applications such as outdoor signage printing. Appropriate selection of pigments for the formulation of YMC inks must be made to ensure that all components fade uniformly in order to preserve image colour quality for the longest possible duration. The permanence of a pigment can be influenced by control of the primary particle size distribution, which is well known to have a great bearing upon the resistance and coloristic properties. As primary particle size increases, a reduction in gloss, transparency and colour strength are observed, combined with an increase in permanence. Armed with this knowledge it is possible to "size engineer" pigment particles that will allow specific degrees of colour permanence to be achieved. Experimental work was carried out to manipulate the particle size of pigment Yellow 151 into small, medium and large size forms, which were then compared to one another in terms of permanence, gloss, opacity and colour strength. Physical reaction parameters used in synthesis were employed to control the pigment particle size. Small sized particles were synthesized by inducing rapid, homogeneous nucleation of the pigment. Large particles were formed by reducing the rate of nucleation followed by controlled crystal growth.

## Introduction

Light fastness is the property of a pigment in a binder system to remain unchanged after exposure to light. Weather fastness encompasses not only the changes due to light exposure, but also includes temperature, humidity, pollution, rain etc. There are many factors that influence the light and weather fastness and this means that it is impossible to compare any two sets of test data unless they have been measured under exactly the same conditions, at the same location over the same time period. Some of the factors affecting the fastness of a pigmented ink system include:

1. Chemical constitution of the pigment molecule.
2. Binder system of the ink.
3. Substrate on which image is printed.
4. Pigment concentration.
5. Film thickness.
6. Pigment particle size.

Generally the chemical structure of a pigment dictates its basic light and weather fastness properties, and the presence of certain groups in a molecule are well known to add to the permanence properties. For example in azo pigments, the introduction of halogen or nitro groups into the amine molecules from which the pigment is built, tend to give improved light fastness. Likewise the presence of electron donating groups such as methyl and methoxy in the coupling component molecule, also provide enhanced fastness. The presence of the carbonamide group, metal complexation and a high degree of intra- and inter-molecular hydrogen bonding will provide additional light fastness benefits.

The inherent permanence of a pigment molecule can also be altered to a high degree by manipulating the particle size distribution of a pigment powder. The light radiation responsible for degradation and fading of pigments can only penetrate a small way into the pigment particles, so molecular layers of the pigment are sequentially destroyed by light. This means that a large pigment particle has more layers of molecules and thus greater light resistance than a small pigment particle. A pigment powder with large particle size distribution also presents a lower surface area to light than an equal mass of a pigment powder with a small particle size, which means that it will fade more slowly.

In addition to the manipulation of pigment particle size, the light fastness of a formulation can also be affected by pigment concentration, film thickness, binder system and substrate. As pigment manufacturers we have no control over these areas, but can make developments to specific pigment grades in accordance with their required end use.

Pigments are primarily used in exterior ink jet printing applications because of their superior light fastness over dyes, and the correct selection of pigments for yellow, magenta and cyan inks is critical for image durability and performance. The majority of magenta inks are formulated using quinacridone pigments (e.g. CIP Red 122) while cyan inks are formulated from phthalocyanine derivatives (e.g. CIP Blue 15:3). Both of these pigment selections give high light fastness and durability, which the selection of a yellow pigment based ink must strive to maintain, in order that all components of an image fade uniformly. Yellow pigments as a group typically have poorer light and weather fastness than the other colour groups of pigments. This is because the vast majority of yellow pigments tend to be based upon simple azo chemistry with small molecular size with less inter-molecular hydrogen bonding than other pigment

classes, to give stabilization in the presence of light. The result of this is that the use of high performance chemistries are required when selecting yellow pigments, such that the permanence of the magenta and cyan pigments are of the same level. Ink jet applications also have the additional burdens of very low pigment concentration used in ink and very thin layer thickness of the final ink jetted onto a substrate, both of which detrimentally affect light fastness.

In this paper we look at the high performance benzimidazolone yellow pigment CI Pigment Yellow 151 (CIP Y151) that has excellent light fastness (according to Florida testing) due to the high degree of hydrogen bonding inherent in its crystal structure. We explore the effect of particle size upon the light fastness of the CIP Y151 pigment with all other factors being kept equal.

## Experimental

Three CIP Y151 pigments were synthesized in small, medium and large particle size forms by control of reaction conditions. The medium particle size Y151-M was synthesized using a standard formulation while the small particle size form Y151-S was made using a very rapid reaction and limited heat treatment of the pigment. The large particle size Y151-L was synthesized according to the standard formulation and then particles were grown by heat treatment of the aqueous pigment slurry under the action of elevated temperature and pressure. The pigments were washed, filtered dried and ground ready for analysis.

Particle size analysis was performed using a Coulter LS 230 Particle Size Analyzer and pigment samples were prepared by dispersing pigment (0.05g) in de-ionized water (100ml) with a small quantity of Surfynol CT-324 surfactant. The dispersions were treated in an ultrasonic bath for 5 minutes before measurement of the volume particle size distribution.

SEM images of the pigment powders were taken by The University of Guelph, Laboratory Services, at 40,000 times magnification.

Water based ink formulations, at 15% pigment loading, were prepared to generate colour displays. The formulation contained: Joncryl 61 resin (45.3%), Water (37.5%), Pigment (15.0%), 10% Ammonia solution (2.0%), Tego Foamex 1435 (0.2%). The pigment was dispersed using a Red Devil Shaker for 45 min. using steel balls as the grinding media. A tint was prepared by taking a standard TiO<sub>2</sub> white formulation (90.9%) and Y151 mill base (9.1%), that were mixed on a Red Devil Shaker for 20 min. Ink displays were prepared by drawing down the three Y151 inks, in masstone and tint, with a #4 Meyer rod on Leneta 3NT-3 coated test paper. Displays were also prepared using a knife scrape down onto bond paper, and these were used for light fastness evaluation in an Atlas Color Fade-o-Meter. Testing for 18 cycles, or 432 hours was performed according to ASTM

Colour measurement was performed using a Gretag Macbeth Color-Eye 3100 spectrophotometer with 10° observer function, D<sub>65</sub> illuminant and taking an average of 4

measurements. CIE L\*a\*b\*C\*h° and reflectance values across the spectrum (400nm to 700nm) were recorded and colour strength K/S, was determined at a wavelength of 420nm. Gloss measurements were taken using a Gene Q inc. Novo Gloss Meter NG 2060, at a measurement angle of 60°.

## Results and Discussion

Volume particle size data is given in Table 1. and the distributions are plotted in Figure 1. SEM images of the three pigments are illustrated in Figures 2, 3 and 4.

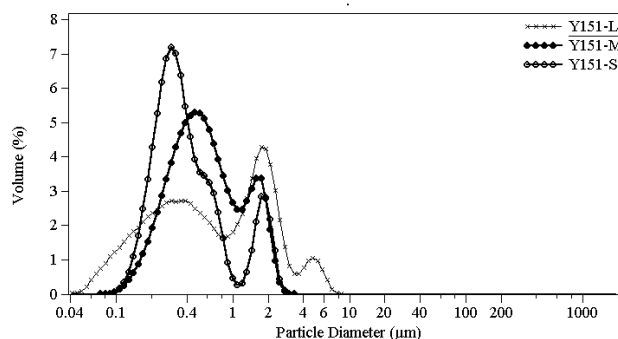


Figure 1. Volume Particle Size Distributions of Y151 Pigments

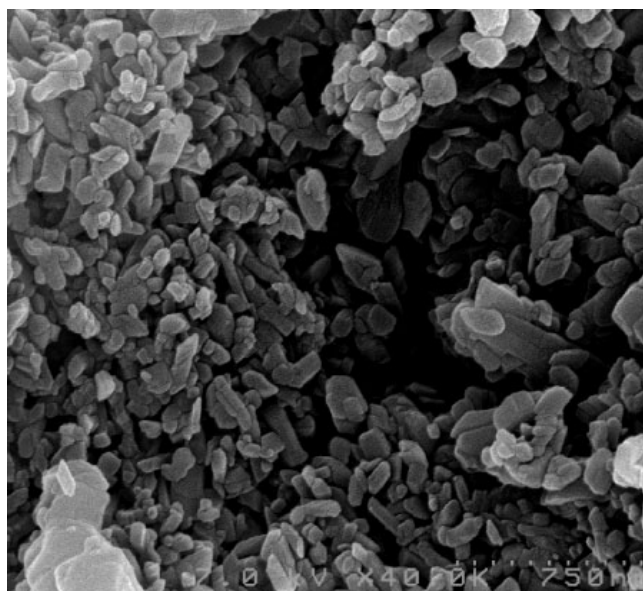


Figure 2. SEM of Y151-S Pigment

Table 1. Volume Particle Size Data

Size	Y151-S	Y151-M	Y151-L
Mean	0.583µm	0.749µm	1.143µm
Mode	0.297µm	0.474µm	1.749µm
Median d <sub>50</sub>	0.359µm	0.554µm	0.635µm

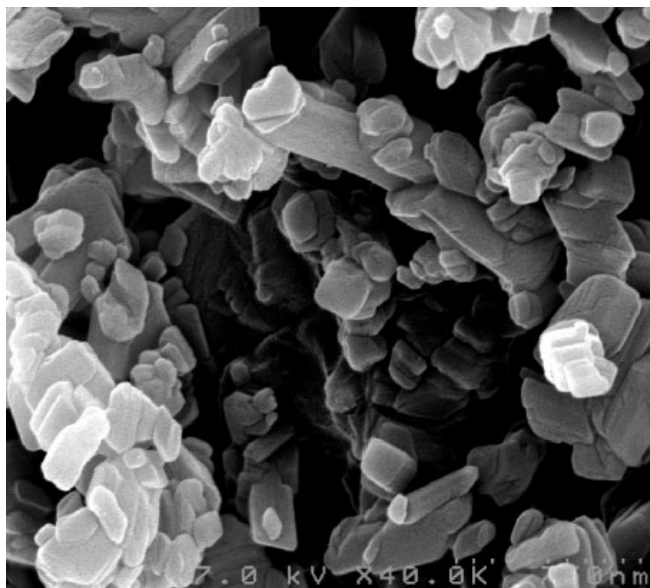


Figure 3. SEM of Y151-M Pigment

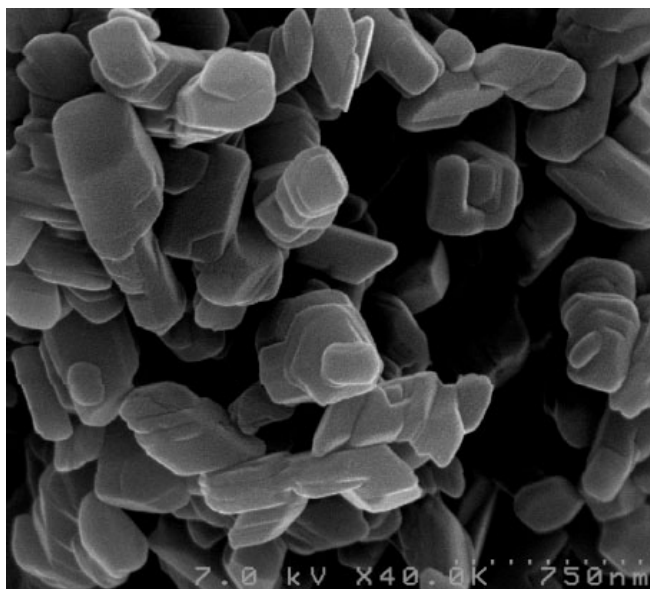


Figure 4. SEM of Y151-L Pigment

The particle size distribution curves and average size values clearly illustrate that the Y151 pigments have been successfully synthesized in small, medium and large particle size forms. Rapid precipitation of the Y151-S pigment gave the smallest particle size with a  $d_{50}$  value of  $0.359\mu\text{m}$  and these particles are illustrated in the SEM image of Figure 2. The Y151-M pigment made using the standard synthesis formulation was found to have a  $d_{50}$  of  $0.554\mu\text{m}$  and the SEM of this pigment is shown in Figure 3, which illustrates a significant increase in the size of the pigment compared to Y151-S. The Y151-L pigment was treated at elevated pressure and temperature in order to grow the pigment crystals. The particle size distribution data and SEM images, illustrated in Figure 4, show that Y151-L has very large

particle size when compared to Y151-S and Y151-M. Manipulation of the reaction speed, quantity and type of additives used and duration of heat treatment have been selectively used to create Y151 pigment powders with controlled particle size distributions.

After the three Y151 pigments were generated in small, medium and large particle size forms, analysis was carried out to investigate the relationship between particle size and pigment properties. The light fastness of the pigments was tested in a water based ink formulation, in both masstone and tint. Colour measurement data of the ink displays made by knife scrape-downs in masstone, before and after light fastness testing are provided in Table 2. The corresponding data for reduced tint formulations are given in Table 3.

Data in Tables 2. and 3. shows that after 432 hours of exposure in the Fade-o-Meter, all of the pigments have changed colour to some extent and that the colour change in masstone is less than that in tint. The small particle size Y151-S exhibited the greatest colour change with a  $\Delta E^* = 4.69$  in masstone and  $\Delta E^* = 5.72$  in tint. This level of colour difference is easily visible to an observer when viewing the ink displays. Conversely, the large particle size pigment Y151-L showed colour changes of less than one colour difference unit when exposed to the same test and this degree of difference is barely visible to an observer. The Y151-M pigment gave colour change values in between those recorded for Y151-S and Y151-L.

Table 2. Colour Data of Y151 Masstone Ink Before and After Fade-o-Meter Exposure

Masstone	L*	a*	b*	C*	h°	$\Delta E^*$
Y151-S	87.95	-5.10	81.51	81.66	93.6	
Y151-S 432 hrs	87.92	-5.39	76.83	77.02	94.0	4.69
Y151-M	88.53	-4.81	77.18	77.33	93.6	
Y151-M 432 hrs	88.81	-5.59	74.87	75.08	94.3	2.46
Y151-L	88.09	-4.46	80.17	80.29	93.2	
Y151-L 432 hrs	87.56	-4.26	79.76	76.88	93.0	0.69

Table 3. Colour Data of Y151 Tint Ink Before and After Fade-o-Meter Exposure

Tint	L*	a*	b*	C*	h°	$\Delta E^*$
Y151-S	93.30	-8.57	38.79	39.73	102.4	
Y151-S 432 hrs	93.53	-8.01	33.11	34.07	103.6	5.72
Y151-M	93.46	-7.14	34.70	35.43	101.6	
Y151-M 432 hrs	93.61	-7.01	31.51	32.28	102.5	3.19
Y151-L	93.73	-6.17	29.77	30.40	101.7	
Y151-L 432 hrs	93.66	-6.19	28.89	29.54	102.1	0.89

Upon closer examination of the  $L^*a^*b^*$  lightfastness data, the colour change is found to be due almost entirely to change in  $b^*$  value. The  $L^*$  and  $a^*$  values of the yellow inks

are generally not changed by exposure, while  $b^*$  is always decreased in value. As fading occurs the Y151 pigment displays become “less yellow” in shade, which has the visual effect of making the inks appear to be dirtier and duller. The colour change due to Fade-o-Meter exposure is illustrated in Figure 5, which shows the  $a^*b^*$  values for Y151 pigments in tint, before and after 432 hours of exposure. The magnitude of change in  $b^*$  is illustrated very clearly and Y151-S exhibits the largest decrease in  $b^*$  while the change of Y151-L is negligible.

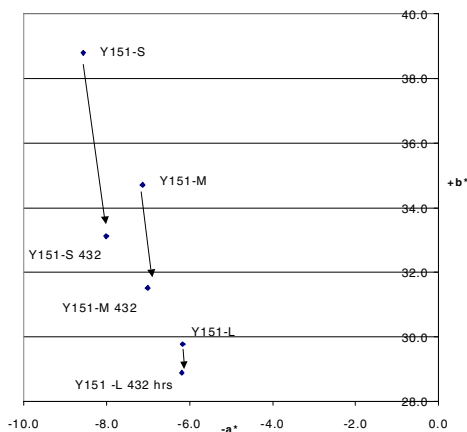


Figure 5.  $a^*b^*$  Colour Change of Y151 Pigment Tint Inks After 432 Hours of Fade-o-Meter Exposure

Side by side drawdowns of the Y151 inks made on Leneta test paper with a #4 Meyer rod, show that Y151-S appears to be very glossy and transparent with high tinting strength. It should be stressed however that all of the Y151 pigments appear to be fairly transparent because of the small film thickness used. Y151-L has the greatest opacity and is correspondingly low in gloss and colour strength, while Y151-M falls in between the gloss, opacity and colour strength of the two pigments. These parameters were measured and are given in Table 4. Colour strength was determined relative to Y151-L because this had the lowest value. Opacity was calculated as the ratio of Y tristimulus values measured over the black and white sections of the Leneta test paper. The numerical values correlate well with

visual observation and reiterate the finding that small particle size results in a high gloss, low opacity, strong pigment in ink dispersions.

Table 4. Gloss, Opacity and Colour Strength Values of Y151 Pigments

	Y151-S	Y151-M	Y151-L
Gloss (60°)	21.5	7.3	3.9
Opacity %	13.5	15.9	16.1
Relative Colour Strength %	149	127	100

## Conclusions

The high performance benzimidazolone pigment, CI Pigment Yellow 151, was successfully synthesized in small, medium and large particle size forms by manipulation of physical reaction conditions. The resulting pigment powders were shown to have average  $d_{50}$  particle sizes of: 0.359 $\mu\text{m}$ , 0.554 $\mu\text{m}$  and 0.635 $\mu\text{m}$ . The results clearly demonstrated that large particle size pigments gave higher light fastness and opacity, but poorer colour strength and gloss. The study demonstrated that it is possible to selectively prepare a pigment with appropriate light fastness for a chosen application, using size-engineering techniques.

## Acknowledgement

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## Biography

Helen Skelton received a degree on Colour Chemistry from the University of Leeds in the UK and then remained in Leeds to gain a Ph.D. in the field of colour measurement using statistical analysis and neural networks. Upon completion of her Ph.D. she worked on a three year project developing inorganic pigments with Elementis Chromium. In January 2001 she moved from the UK, joining Dominion Colour Corporation as a senior chemist in pigment research and now resides in the Toronto area.