“Tweaking” the Pigment Color for Advanced Printing Applications

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Abstract

The color of organic pigments for commercial printing applications, commonly considered as invariable, can be “tweaked” by adjusting chemical environments surrounding the pigment particles. The extend of color change, though small, is frequently noticeable with a naked eye. This phenomenon is due to subtle interactions between the surface molecules of the pigment and surrounding polar moieties either chemisorbed or vicinal to the pigment surface. Detailed understanding of this effect may allow avoiding undesirable color changes degrading the printed color quality. It may also be used in development of advanced inks for various printing applications.

Introduction

High throughput digital commercial printing technologies are known to consume a significant amount of pigmented inks. Sustaining rapid analog-to-digital printing transformation requires reduction of the cost of consumables while simultaneously providing or increasing the color gamut. A majority of the commercial printing solutions relies on a selected set of mass-produced organic pigments to achieve the desired color gamut. Since commercial introduction of novel organic pigments would invariably cause a significant increase of the ink cost, other ways of expanding the printed color quality and gamut need to be found.

Some of our recent findings [1,2] suggest that color appearance of the commonly used organic pigments can be altered within some ranges by a simple pigment chemical treatment, and that this color alteration could be advantageously used in expanding the printed color gamut. Although color alteration of a dye molecule by changing polarity of its aqueous solution is a well-known phenomenon (solvatochromism [3]), there has been no report describing a corresponding effect in a solid pigment powder.

This report presents several examples of pigment color modification and provides explanation for the color “color tweaking” phenomenon supported by experimental results and molecular modeling. Color shift data has also been used to evaluate how much color gamut of an exemplary digital printing solution could be expanded by modifying some of its pigments.

Pigment color “tweaking” concept

The possibility of advantageously adjusting the color of an organic pigment particle can be derived from a detailed understanding of the color creation mechanism. Since organic pigments exhibit a very high absorption coefficient within a specific color region, the color impression imparted by a pigment particle results from the structural and electronic properties of the pigment region within which most of the light absorption occurs.

Detailed modeling of the light absorption and reflection by an assembly of submicron pigment particles shows that a significant portion of the light absorption takes place within a shallow region of the particle reaching no further than few tens of nm below its surface. In this region the absorption properties are defined by the fundamental electronic structure of the molecular chromophore, and also by the interactions between the surface molecules and the physico-chemical environment surrounding the pigment particle. Since the fundamental chromophore properties are invariant under the normal conditions, one can modify the particle environment in order to change its color appearance. This modification may involve removing some of the functional molecular moieties chemisorbed to the surface of a pigment particle, introducing new surface functionalization, surrounding particle with vicinal polar moieties electrostatically and electrodynamically interacting with the pigment surface molecules or removing such moieties.

Experimental

In the present work, we investigated two organic pigments: Cyan (P.C.15:3) and Yellow (P.Y.74). Both pigments are mostly crystalline with presence of amorphous phase. In addition, selected study was conducted for several other organic pigments (P.Gr.7, P.Y.185, P.Y.139, and P.R.146). For all pigments used in the study the particle size was of the order of few hundred nm. All pigments were received from leading pigment manufacturers and are readily available as major commercial products. Pigment structure is described by its C.I. (Color Index) identifier, for example P.C.15:3 = β-phase copper phthalocyanine (CuPc) with no halogen atoms.

The aforementioned color “tweaking” effect can be accomplished by a chemical process targeting specific functional groups attached to the surface of a pigment particle. This technique can be effective when population of the pigment particles has homogeneous properties that are well understood. However, in most cases, commercial organic pigments used in printing applications can be relatively heterogeneous with a significant amount of poorly understood impurities, and they may require a simpler processing modifying interaction between the pigment surface molecules and their surroundings. Some of the processes used in our experiments involved pigment washing/centrifuging, soaking in aqueous solutions of inorganic acids and bases having pH from 3 up to 11, extraction (Soxhlet) using organic solvents with various polarities, and encapsulation which placed aliphatic carbonyl compounds in direct vicinity of the pigment particle’s surface.

Processed pigment particles were dried and monitored with SEM to evaluate the treatment effect on pigment agglomeration. Processes causing formation of excessive particle agglomerates were rejected. Pigment’s color expressed in terms of the a*b* coordinates (CIE L*a*b* color coordinate system, CIE = Commission International de l’Eclairage) was determined by measuring uv/vis diffuse reflectance of a continuous layer of pigment particles on a flat surface using either a commercial color measurement setup (Elrepho unit) or Cary 6000 spectrometer with “Praying Mantis” optics (Cary data translated into L*a*b* coordinates assuming a D50 white point).

Structural and chemical changes introduced by selected pigment processing were elucidated with the X-ray photoelectron spectroscopy (XPS) and bulk- or surface-sensitive IR measurement (IR transmission and Attenuated Total Reflectance – ATR). Our previous work [1,4] has shown that the described pigment processing aimed at “tweaking” its color did not introduced any new phases both in bulk and at the surfaces of pigment particles, and it only caused occasional, minor stress changes resulting in minute shifts of some X-ray diffraction peaks.

Results and Discussion

Figure 1 demonstrates example of chemical modification of the vicinity of yellow pigment particles (P.Y.74) introduced by Soxhlet extraction using hexane. The decrease of the low energy component of C1s signal is due to removal of some hydrocarbon-like molecular species surrounding the pigment nanocrystals. Similar results confirming extraction of molecular moieties vicinal to the pigment particle were obtained for other similarly treated pigments.

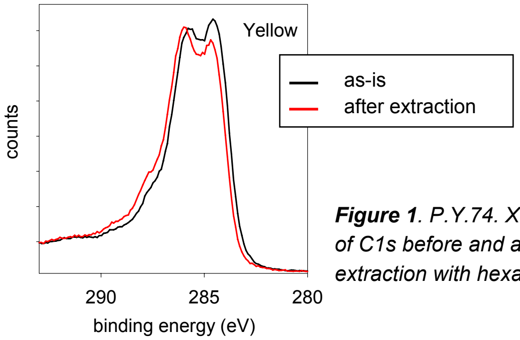

***Figure 1**. P.Y.74. XPS spectrum of C1s before and after Soxhlet extraction with hexane.*

Figure 2 shows another effect of changing the interactions between the pigment surface molecules and polar molecular moieties vicinal to the pigment particle. As previously described [2,4], extraction of sulfonate groups terminating surface of the P.C.15:3 pigment particles caused shift of the vibrational frequency (730 cm^{-1} C-H out-of-plane bending) of the peripheral benzene C-H bond of CuPc molecules which reside at the surface of pigment nanocrystal. This frequency shift, confirmed by molecular modeling [4] of interactions between the CuPc molecule and polar groups either chemisorbed or present in a vicinity of the pigment particle’s surface, is due to bond deformation within the CuPc surface molecules. It also results in color change of the pigment particles, as shown in Table 1. Similar color “tweaking” was observed for other pigments. Table 2 shows color shift of the P.C.15:3 pigment after multiple centrifuging using aqueous solvent, while Table 3 demonstrates results of solvent extractions for selected pigments.

Table 1. Color change and out-of-plane vibration of the peripheral benzene (approx.730 cm^{-1}, IR surface component only [2]) as a function of extracted sulfonate moieties.

CuPc pigment	SO_3 (%)	IR peak (cm^{-1})	Color coordinate	
			a*	b*
as-is	1.4	728.7	25.08	-43.48
extracted (toluene/ 3hrs)	0.4	730.4	23.15	-38.05

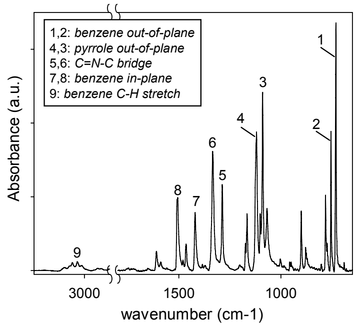

***Figure 2A.** IR absorption spectrum of P.C.15:3.*

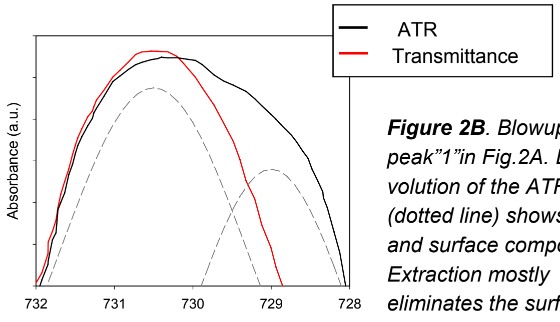

***Figure 2B**. Blowup of the peak”1”in Fig.2A. Deconvolution of the ATR signal (dotted line) shows bulk and surface components. Extraction mostly eliminates the surface signal [2].*

Although presented data cannot offer a single recipe for desired color “tweaking” of all commercial organic pigments, they provide several generic observations that can be summarized as follows: (1) in all cases color changes are relatively small but frequently visible with a naked eye (several a*, b* units), (2) it appears that in most cases magnitude of color shift depends on the polarity of solvent (when solvent used to extract moieties interacting with pigment surface molecules), (3) effect of color modification depends on the composition of commercial pigment, and particularly on intentional pigment modifiers and unintentional impurities present within the pigment powder. Therefore, color “tweaking” process must be tailored to a specific pigment, and (4) preliminary results show that further processing of color-modified pigments, analogous to ink formulation, appears in most cases to retain the achieved color change, though this may depend on details of ink production. This effect needs to be further investigated for specific color “tweaked” pigments.

Table 2. Color shift due to a high speed (60K RPM) centrifuging of the P.C.15:3 pigment using aqueous solvent.

Cyan 15:3	a*	b*
as-is	25.09	-43.48
10X centrifuged	25.01	-34.57

The value of potential color “tweaking” can be evaluated by projecting observed changes of color coordinates on a printer color gamut map. Figure 3 shows an imaginary color gamut, based on CMYK pigmented inks, similar to some of the commercial printing solutions. Simple calculations assuming shift of the C color coordinates corresponding to data obtained for CuPc pigment show a considerable extension of the printed color gamut that may provide a potential color quality advantage.

Table 3. Color modification (ex. $\Delta a^*=a^*_{\text{after extraction}} - a^*_{\text{original}}$, shown as $\Delta a^* \& \Delta b^*$) introduced by Soxhlet extraction (3 hrs) using solvents with different polarities. The original pigment color coordinates {a*&b*} are also provided. DCM = dichloromethane. The a*,b* error is approx. 0.02.

pigment	hexane	toluene	DCM	H_2O
P.C.15:3 {25.09&-43.48}	2.09&-2.20	2.03&3.40	0.86&0.8	-0.72 &1.59
P.Gr.7 {-32.24&-5.85}	-5.16&0.44	-3.55&0.84	-4.9&1.0	-0.46&0.94
P.Y.185 {2.82&109.97}	-0.36&-1.42	0.35&-3.20	0.80&-3.28	0.21&1.83
P.R.146 {58.04&34.63}	0.92&1.02	-3.68&-0.89	-9.24&-3.94	-8.51&-2.79
P.R.122 {46.81&4.71}	-1.32&-0.04	0.12&0.22	-0.01&0.19	-0.70&-0.43

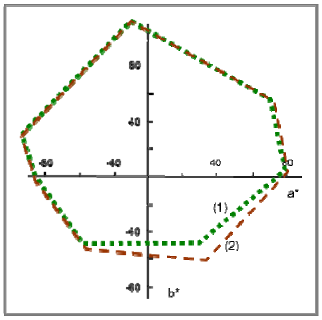

***Figure 3**. Calculated expansion of the color gamut for a hypothetical CMYK printing setup assuming the largest observed color shift of the Cyan pigment. (1) – original color gamut, (2) – color gamut including potential modification of the Cyan pigment.*

Conclusion

It is shown that a simple chemical processing of solid organic pigments may "tweak" their color. This phenomenon has been demonstrated for a number of commercial pigments, and it was explained in term of modifying intricate interactions between the pigment surface molecules and vicinal polar moieties present in pigment powder (somewhat analogous to solvatochromism of selected dye molecules in a liquid solvent). Although the present work does not provide a generic recipe of any organic pigment, it provides some color guidelines for selected pigments. Understanding of the color "tweaking" phenomenon may help to avoid situation when unexpected color change would adversely impact color print quality, and it may also provide for advantageous expansion of the printed color gamut in some printing solutions.

Acknowledgements

The authors are grateful for fruitful discussion with Yan Zhao, and support from Omer Gila and Eric Hanson. We acknowledge the generous support of pigment samples by commercial pigment vendors.

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Author Biography

Dr. Krzysztof (Chris) Nauka received MS in solid state physics and PhD in materials science from MIT. Since then he has worked at Hewlett-Packard Laboratories in Palo Alto, CA on a variety of topics ranging from the optoelectronic and IC devices to nano- and quantum structures. More recently he has been involved in research focused on the materials for printing applications.

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