Pigment Yellow 1 – a Viable Inkjet Alternative to Pigment Yellow 74

Alex Shakhnovich; Cabot Corporation Research and Technology Center; Billerica MA, USA

Abstract:

Polymer-free inkjet dispersions, based on Pigment Yellow 74, cocrystallized with ionic synergists, allow for high pigment loading and formulation flexibility. However they suffer from sensitivity to various ink cosolvents and surfactants. Structural factors, responsible for such instability originate from the substitution pattern in the aromatic rings of PY74. This pattern can be changed by using Pigment Yellow 1 and its analogs instead. The dispersions based on PY1 family show remarkable stability of particle size in presence of surfactants and micelle-forming solvents even at very high loadings. The color shade of these pigments can be changed from greenish-yellow to orange by cocrystallization. The prints, obtained with PY1-based inks have much better lightfastness than PY74 prints.

Background

Deficiencies of Pigment Yellow 74, the most widely used yellow inkjet pigment, include limited colloidal stability in presence of organic cosolvents due to ripening/recrystallization, poor lightfastness and problems with chemical surface modification.

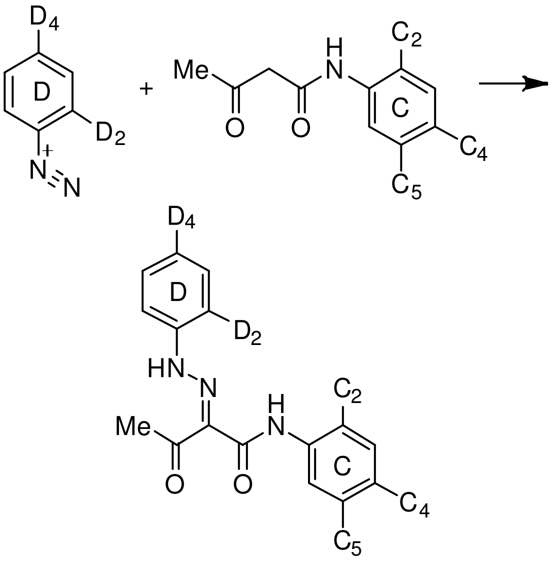
Cabot Corporation developed the preparation of inkjet dispersions of color pigments by surface diazonium treatment of color pigments, such as PB15, PR122 and PY74. This method (in case of PB15 and PR122) results in attachment of charged species to the surface molecules of the pigment particles and provides dispersions with excellent application properties. These do not require additional dispersants and therefore have very good formulation flexibility. Pigment Yellow 74, however, interacts with diazonium salts differently[1] – residual PY74 coupler (acetoacet-o-anisidide) playing important role in the product(s) formation. Affinity of the formed products to the PY74 surface is reasonably poor, which leads to their desorption and to decreased dispersion stability. Furthermore, PY74, which is currently a standard yellow for inkjet applications, is a considerably less lightfast pigment than PB15 or PR122.

It was very desirable, therefore, to investigate alternatives to PY74, which, being coloristically close, may be sufficiently free of above deficiencies.

Results and Discussion

We will call a compound with strong affinity to the pigment surface *and* bearing a charge an Ionic Synergist (IS). Often high affinity of IS comes from structural similarity to the pigment, although it is not possible to predict how similar these two molecules should be to deliver the performance necessary in applications. It is clear that not all regions of the molecules are equal in this respect. The dispersions, described in this article, are generated by high-shear mixing of pigments with corresponding IS in water, followed by particle size reduction and cleanup if needed. Order of mixing usually does not play any role, although ‘ripening’ of the dispersion (heating to 50-80 °C for 15 – 120 minutes) sometimes influences the performance.

Many of commercial monoazo pigments are made by coupling of a diazotized substituted aniline (D-ring) with acetoacetarylide (C-ring):



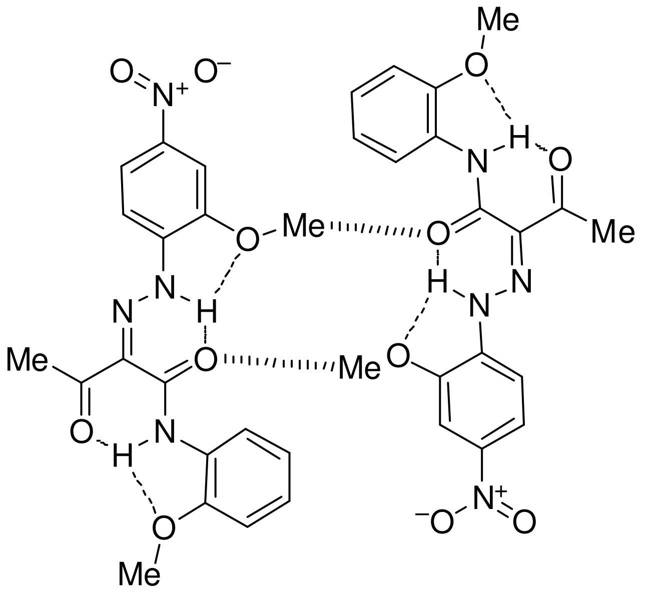
Color Index lists about 2 dozen of these compounds, with PY74 being by far the most commercially important. *It is important to notice that the molecules of these colorants are almost flat, due to multi-centered hydrogen bonds, involving hydrazone nitrogens, carbonyls, aromatic iminogroup and substituents at C_2 and D_2 (if these are capable of H-bonding)* . We have synthesized several IS with structures similar to PY74 having charged groups in C- or in D-ring, which are shown in Table 1.

Table 1 – PY74 and Ionic Synergists for It

Compound	D_2	D_4	C_2	C_4	C_5
PY74	OMe	NO_2	OMe	H	H
1	H	SO_3Na	OMe	H	H
2	NO_2	SO_3Na	OMe	H	H
3	OMe	NO_2	OMe	H	SO_3Na
4	OMe	NO_2	H	SO_3Na	H

Compounds 1-4 readily disperse PY74 in water. Dispersions were evaluated by heat aging in presence of such micelle-forming solvents as 1,2-Hexanediol (12HD) or Triethylene Glycol Monobutyl Ether (TEGMBE). Although the affinity of IS #3,4 with charged groups in D-ring was somewhat better, than the ones with charged groups in C-rings, **all of PY74 based dispersions failed the heat aging test** – particle size growth was in all cases unacceptable (from 150-180 nm to over 1 micron; gelation or large increase in viscosity was also always observed).

It became increasingly clear that the root cause of instability of the dispersions is somehow determined by molecular structure of PY74 itself. Reviewing the X-ray data obtained by Whitaker[2] indicated that in PY74 crystals there are very unusual polycentric hydrogen bonds between methoxy groups of adjacent molecules:



This somehow translates into packing of PY74 molecules as puckered columns, and, finally into high affinity of the surface to micelle-forming solvents (hydrophobic areas on surface is one possible explanation).

Our initial hypothesis was to remove methoxy groups from D_2 and C_2 positions, so that the pattern of this hydrogen bonding will be destroyed or altered. There are 13 commercial pigments, meeting these structure requirements, first and foremost, Pigments Yellow 1, 6 and 1:1 because they do not have methoxy groups in both C- and D-rings. Pigments Yellow 65 and 203 have similar D-ring substitution pattern ($D_2 = NO_2$), but methoxy at C_2 is present.

Table 2 – Commercial Yellow Pigments With C_2 /D_2 Substitution Patterns Different From PY74:

Color Index #	D_2	D_4	C_2
Pigment Yellow 1	NO_2	Me	H
Pigment Yellow 6	NO_2	Cl	H
Pigment Yellow 1:1	NO_2	OMe	H
Pigment Yellow 65	NO_2	OMe	OMe
Pigment Yellow 203	NO_2	Me	OMe

The common feature of these pigments is the presence of nitrogroup (instead of methoxy group) in D_2 position. It could be expected that the color strength of the chromophore will be reduced as the nitro group is moved from position D_4 to D_2. Comparison of visible spectra of PY74 and PY1 in chloroform confirms this suggestion (Figure 1). Whereas PY74 produces one sharp absorption peak at 420 nm with $\varepsilon = 39{,}800$; PY1 has two smaller peaks, centered at 349 and 415 nm ($\varepsilon_{415} = 21{,}380$). This transmission data, by the way, does not necessary mean, that PY1 prints at equal pigment loading will be 50% weaker than PY74. Print color strength is measured in reflectance mode, so scattering may play a very significant role. Some IS for PY1, PY6, PY1:1 and PY65/203 with charged groups at different locations were prepared, some of them (#5-10) are shown in Table 3.

Table 3 – Ionic Synergists for Pigments Listed in Table 2

Compound	D_2	D_4	C_2	C_4	SS*)
5 (for PY1)	NO_2	Me	H	SO_3Na	OK
5a (for PY1)	NO_2	CO_2Na	H	H	Fair
5b (for PY1)	NO_2	SO_3Na	H	H	Fair
6 (for PY6)	NO_2	Cl	H	SO_3Na	OK
7 (for PY1:1)	NO_2	OMe	H	SO_3Na	OK
8 (for PY1)	NO_2	Me	H	PIG**)	OK
9 (for PY203)	NO_2	Me	OMe	SO_3Na	Fail
10 (for PY65)	NO_2	OMe	OMe	SO_3Na	Fail

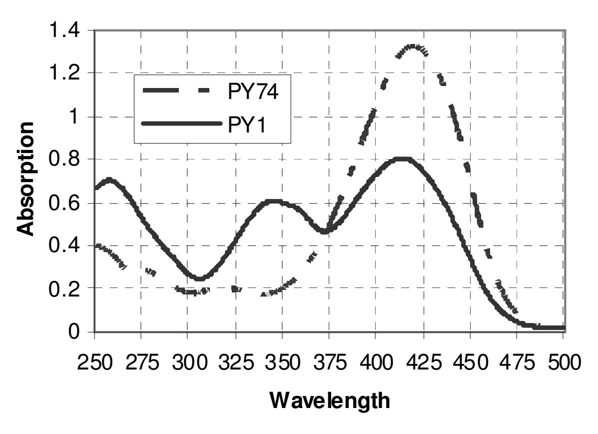
*) SS = stability to solvents during heat aging (see text); **) PIG = Proprietary Ionic Group with affinity to paper components

The dispersions of the pigments were generated as described above and heat aging performance of these dispersions had been evaluated.

The very first attempt to use an IS #5 with charged group in ring C as a dispersant for PY1 was very successful; a stable dispersion resulted. This dispersion, contrary to the ones, obtained from PY74, had outstanding heat aging stability in presence of 12HD, TEGMBE or surfactants, used in inkjet ink formulations (such as Surfynol ® 465 for example). No viscosity increase over the course of heat aging was observed, even at very high pigment loadings. For PY6 and PY1:1, which both have nitro group in D_2 and hydrogen atom in C_2 the IS #6,7, containing charged groups in C ring, were also very suitable and provided dispersions with outstanding stability.

Furthermore, the charged group does not have necessarily to be a sulfonate or carboxylate; using a proprietary Ca-binding group[3] instead (IS #8) provides a dispersion with as good stability as #5, but giving much higher print OD.

Figure 1



Electronic spectra of PY1 and PY74 in chloroform at 86 mg/l (1 mm layer)

When the charged group, however, was located at D_4, the stability of the dispersions, generated from PY1 using IS #5a,b somewhat decreased (although these were still much better than any of PY74-based dispersions).

Finally, if a C_2 methoxy group is present, affinity of IS #9,10 to PY65 or PY203 falls to unacceptable level and no stable dispersion can be obtained from these two pigments.

All dispersions, based on PY1, PY6 and PY1:1 were formulated into inkjet inks and a number of printing tests had been conducted, using both piezo and thermal printing platforms. It was found, that PY6 and PY1:1 are hardly acceptable as PY74 replacement; both are weaker than PY74; in addition PY6 is objectionably greenish and PY1:1 prints are in fact orange.

It is interesting to notice, that we evaluated cocrystallization of PY1, PY6 and PY1:1, when these pigments are formed simultaneously by mixed coupling and later converted into dispersions using IS #5-8; it is possible to tune up the shade of the colorant by varying the ratio of components. Affinity properties of IS in this cases remain pretty much intact. Some of the prints color data are given in Table 4. (XEROX 4200 plain paper; 4% pigment loading; piezo platform, 100% duty)

Table 4 – Color data for various PY1, PY6 and PY1:1 prints

Pigment	IS	Chroma	Hue
PY1	5	75.2	98.7º
PY6	6	68.2	101.5º
PY1	8	89.1	98.0º
PY1-PY6 (1:1)	5+6	79.0	97.9º
PY1- PY1:1 (4:1)	5+7	68.8	82.5º
PY74	IS w/PIG	85.9	95.8º

On the other hand, PY1 on plain and photographic papers looks visually remarkably close to PY74, although the PY1 prints, as expected, sometimes look ~10% weaker. This can be easily compensated by small pigment loading adjustment, so that strong saturated prints of PY1 were obtained, which had very similar appearance to PY74. Very low viscosity of PY1 dispersions allows for wide formulation space.

In order to compare the lightfastness of PY1 to PY74 and to PY155 a series of prints was generated, each of them consisting of 6 patterns with progressively decreasing optical density. The prints were irradiated in the Xenon Ark Weather-o-Meter® (Intensity 0.35 W/m^2 at 340 nm; 3 weeks, 100% light duty cycle). Evaluation was conducted numerically and visually; some of lower density patterns were completely bleached and, therefore, considered as *completely failed*. In this test, PY1 appears to be much more lightfast than PY74, being closer to such a lightfast pigment as PY155. The comparison of light stability is given in Table 5.

Table 5 – Xenon Arc Lightfastness data

Pigment	Chromaticity $^{*)}$		Completely Failed Patterns
	Initial	Delta	
PY1	102	15.6	2 out of 6
PY1-PY1:1 (97:3)	101	15.9	2 out of 6
PY74	101	67.6	4 out of 6
PY155	90.4	6.4	1 out of 6

$^{*)}$ Highest density pattern

Conclusions

Although it is difficult to make general predictions on affinity of IS to azopigments, examples given in this work clearly demonstrate that it is possible to design IS for commercial yellow pigments and to prepare yellow inkjet dispersions with much improved properties by the careful combination of a pigment and IS structure. Particularly, for the PY1 family, two structure factors were found to be critical, and both have to be present together – nitro group in D_2 position and hydrogen in C_2. PY1, an inexpensive commercial yellow colorant seems to be a much improved alternative to PY74 in terms of coloristic properties, printing performance and, last but not least, lightfastness.

References

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Author Biography

Alex Shakhnovich received his MS in Chemistry in 1972 from Moscow State University and his PhD in Heterocyclic Chemistry (1979) from Institute of Dyes and Intermediates (Moscow, Russia). He had been working in different academic and industrial institutions in Russia and US, including Clariant and General Electric. Since 2002 he is a Principal Scientist at Billerica, MA R&D center of Cabot Corporation. His research interests include synthesis, surface modification and application of organic colorants.