Color InkJet Dispersions Utilizing Synergists as Dispersants

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Abstract

Polymer-free colorant dispersions, based on yellow and red azo pigments as well as copper phthalocyanine, cocrystallized or mixed with ionic synergists, enable high pigment loadings and formulation flexibility in inkjet inks. Careful selection of synergist structure allows to significantly improve dispersion stability towards various ink cosolvents and surfactants. Structural factors, responsible for synergist performance depend on the substitution pattern in both azo pigment and synergist. It was shown that for optimal affinity to the pigment surface and for the stability of the final dispersion the synergist structure does not have to exactly match the structure of parent pigment. The yellow dispersions are obtained from two most common organic pigments, based on Acetoacetanilide chemistry – Pigment Yellow 1 and Pigment Yellow 74. For both of these colorants the dispersions with up to 30% solid contents and very low viscosity were prepared. Crystal structure differences between PY1 and PY74 dictates the synergist choice and explains variations in stability. Magenta (Red) dispersions were obtained from Pigment Red 8, Pigment Red 23, Pigment Red 269 and a few others, all based on Naphtol AS chemistry. These pigments provide an alternative for quinacridones, traditionally used as M component of digital CMY triade. Although their color is generally less bluish, than that of quinacridone, Naphthol AS pigments are a lot stronger and certainly less expensive, than quinacridones. It was also possible to generate cyan dispersions, based on PB15, using modified copper phthalocyanines as synergists.The technology of dispersion with synergists can be designed as a simple mixing process, without using additional chemicals. The process generates minimal amount of effluents, most of which can be recycled. All dispersions demonstrate good stability of particle size in presence of surfactants and cosolvents/humectants even at high loadings.

Introduction

There is limited number of approaches to making of color pigment dispersions for inkjet application. The most common method is using a polymeric dispersant, custom or commercial. Obvious advantage of this method is process simplicity and relative versatility, as the same dispersant can be used for a variety of pigment chemistries. There are some challenges in this approach. Polymer loading should be at least 20% of the pigment loading, increasing the solid content and making formulation space more restricted. Polymer affinity to the pigment surface is based on Van der Waals forces and to some extent on hydrogen bonding and is, therefore, non-specific. Modern ink systems, especially the ones designed for coated stock, contain other polymers and surfactants, which compete for the pigment surface. As a result, viscosity and thermal stability issues are not uncommon for polymeric dispersions. The polymer shell can be crosslinked to improve stability, but this is an extra step, influencing process complexity and, sometimes, some of dispersion properties.

An alternative is the surface treatment of pigments, usually with electrophilic reagents. A most common example is diazonium treatment, conducted at Cabot[1]. This chemistry was designed first for Carbon Black and later translated to many color pigments. This process generates very robust charged Carbon Black particles with variety of surface chemistries. The charge is covalently attached to the surface and this bond is virtually undestructable.

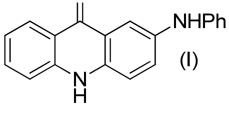
When this chemistry is applied to color pigments, there are drawbacks – low reactivity and need of purification. Especially for azo pigments, which generally have low reactivity towards electrophilic agents, traditional diazonium treatments are not very effective[2]. More reactive diazonium salts, based on heterocyclic amines open the space to treat a broader class of pigments and increase the amount of surface modification, but they are quite expensive[3].

Pigment synergists, also called crystal growth inhibitors, are small molecules, having certain degree of structural similarity to the parent pigment and having either a charged group or a bulky substituent to disrupt crystal growth of pigment. Due to structural similarity the synergists have strong and specific affinity to pigment surface. This affinity can be fine tuned to the application requirements by structure modification. The most common examples of synergists are phthalimidomethylated derivatives of PB15 and PV19, which are being used in pigment industry for decades[4]. Ionic synergists offer another way to get color pigment dispersions wth high robustness and at low cost. Dispersion is generated by mixing a pigment, a synergist and a liquid vehicle, followed by particle size reduction. No additional steps are necessary. Synergists also can be combined with a pigment by cocrystallization or co-synthesis[5]. A very important advantage of synergists is coloristic identity or close similarity to base pigment. This means that adding synergist does not 'dilute' the color, i.e. 100g of pigment and 5 g of synergist is equivalent to 105 g of pigment!

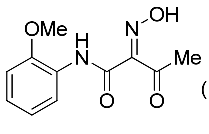
Design of Synergist structures

Unfortunately, for complex systems like modern inks, the structure of an optimal synergist cannot be predicted by molecular modeling.

Principle of structural similarity is a good guide; however there are examples when effective synergists are not too similar to the parent structures. Two examples of this are the anilinoacridone (I), which is a very strong synergist for quinacridone pigments[6], and nitrosocompound (II), which inhibits the crystal growth of PY74 very effectively[7]:

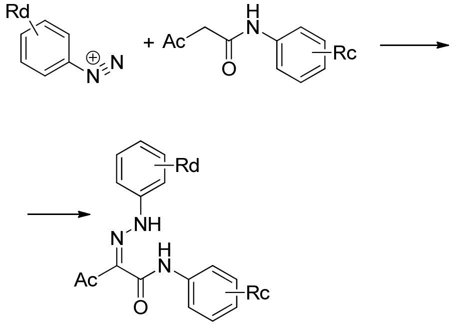


(I)



(II)

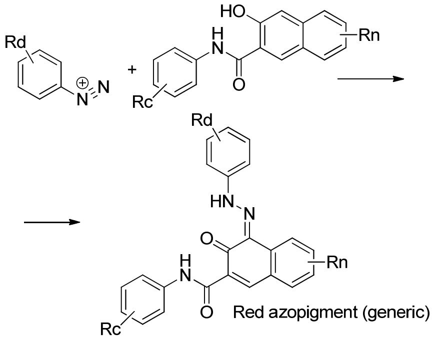
Common sense and availability of starting materials are gudes to obtain a good synergist-based system. Yellow azo pigments generally are prepared from an aromatic diazonium salt and an acetoacetanilide coupler:


Yellow azopigment (generic)

Here preparation of synergist by modifications of both Rd and Rc is possible, however Rd modifications are technically easier to conduct, because in case of Rc modifications use of diketene (banned from use in most of the countries) is required. For simplicity we can classify 4 types of molecular modifications:

A. An ionic group is ADDED, the rest of the structure NOT CHANGED
B. An ionic group is ADDED, other substituent(s) are removed or moved in different position(s)
C. An ionic group is ADDED and the structure of the molecule is significantly CHANGED (example – aromatic diazonium is replaced by heterocyclic diazonium)
D. An ionic group is ADDED and a significant part of a molecule (~50-100 amu) is REMOVED (example – removal of a PhCONH- group, which is often used as an element, improving solvent resistance)

The only difference of red azopigments is a Naphtol AS coupler:


Red azopigment (generic)

In the case of red azopigments modifications on Rn are technically very difficult to conduct; Rc are possible, and for Rd all 4 types of modification (A-B-C-D) are easy to do. For carbo- and heterocyclic pigments, like quinacridones or phthalocyanines, only type A modifications are possible and practical (phthalimidomethylated phthalocyanines and quinacridones - see above)

Process Description and Testing

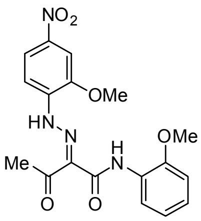
For proprietory reasons the exact structures of prepared synergists cannot be disclosed. Only the modification site (Rd, Rc, Rn) or the type of modification (A-B-C-D) will be mentioned. All pigments were used in presscake form; powder form often works too, but the yields are generally lower and large particle content may be elevated.

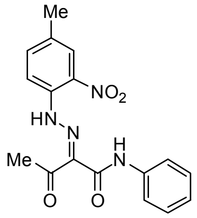
Laboratory preparation of synergists was conducted in such a way that final content of inorganic salts was below 5%. This allowed in many cases to exclude purification of the final dispersion.

A general procedure included mixing a pigment, a synergist (usually at 3-8% level over the weight of pigment) and water in such a way that solids content was 18-20%. The mixture was homogenized in high speed rotor-stator mixer (Silverson) for 30-60 min, followed by sonication in a flow-through or a batch sonicator. The dispersion was centrifuged to bring particle size and LPC content to specifications and subjected to accelerated heat aging tests in various ink or proxy ink systems.

Colorants Used in This Study

Historically, many attempts had been made to select a yellow pigment, other than PY74. Earlier it was happening because of its inferior lightfasness, later on – because the stability of PY74 dispersions often needed improvement. This study was focused on two yellow azopigments – Pigment Yellow 74 and Pigment Yellow 1.


PY74


PY1

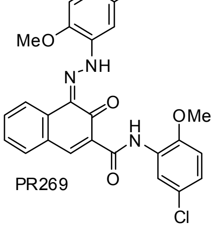
Synergists were designed for both pigments and we were able to clearly demonstrate differences between these colorants:

Table 1 – PY1 vs. PY74

Colorant	Lightfastness	Color Strength	Max. Solids
PY74	Lower	Higher	Up to 22%
PY1	Higher	Lower	Up to 31%

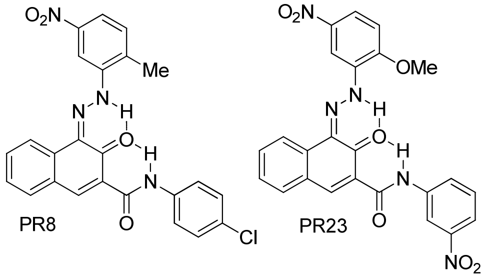
Some advantages of PY1 do not justify in most cases a switch from PY74 to PY1; still such a choice now exists.

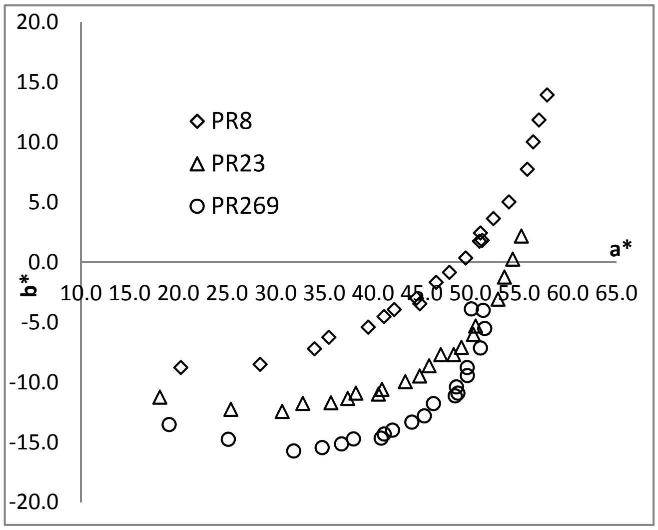
Situation with a magenta component is different; as of now all IJ ink manufacturers use quinacridone pigments, such as red shade PV19, PR122 or a solid solution of PR202+PV19. All of these pigments are weak and expensive; contrary to azopigments their manufacturing is rather complex. For quite a long time we heard requests from the industry to design an alternative magenta dispersion, specifically based on PR269. It is a strong and bright red pigment; its shade does not match the color of a quinacridone, such as PR122 – it is more yellow. This pigment, according to Herbst and Hunger[8], belongs to Group II Naphthol AS pigments, which were designed for improved solvent fastness by introduction of strong hydrogen-bonding groups such as –CONH-. We were able to design synergists of D-type for PR269 and


PR269

disperse this pigment. Unfortunately, because of mentioned strong hydrogen bonding it is very difficult to prepare stable dispersions of PR269. They usually do not survive heat aging even in the absence of cosolvents. This is why our attention was focused on less complex Group I Naphthol AS pigments, specifically on PR8 and PR23:

These pigments are also strong and inexpensive. They are used in printing and packaging[9], so it was worthwhile to explore the synergist solutions for them. We were able to design a matrix of synergists of A and B types for PR8 and PR23.





Picture 1. a* - b* plot of PR8, PR23 and PR269 prints as a function of print density (increases to the right)

The dispersions were remarkably stable in heat aging. Coloristically these pigments, especially PR23 may be a better choice for InkJet than PR269.

Assuming the same K/S value in Kubelka-Munk equation the relative strength of these colorants at equal loading (3%) in inkjet inks was found to be: PR8 = 100%; PR23 = 94%; PR269 = 79%. The a*-b* plot illustrates the color properties further.

In our view, for commercial inkjet printing, PR23 is an attractive opportunity. It should be noted here, that the lightfastness of PR269, PR23, PR8 and other Naphthol AS pigments is on par with PY74 lightfastness, so in many cases low lightfastness may not be a show-stopper.

Finally, for cyan colorant there is no available choices outside of copper phthalocyanine pigments PB15:3 and PB15:4. We were able to design group A synergists for these pigments and demonstrate excellent dispersion and ink stability.

Heat Aging Summary

The typical model system for heat aging is formulated at 5-7% pigment, 10-15% aggressive micelle-forming cosolvent, such as 1,2-hexanediol or triethylene glycol monobuthyl ether and the balance of water. The heat aging was conducted at 60 ^{o}C for 6 weeks; more than 10% growth in particle size or viscosity was considered unacceptable. We do not show printing results here, but all dispersions were printed using generic ink formulas in both thermal and piezo systems without any problems. Results of heat aging are summarized in Table 1:

Table 2: Heat aging summary

Pigment	Synergist type	Modification site	Number of synergists	Results (# passed)
PY1	B	Rd	3	Pass (2)
PY74	A,B,C	Rd	12	Pass (4)
PY74	A	Rc	1	Pass (1)
PR269	D	Rd	2	Fail
PR8	A,B	Rd	5	Pass (3)
PR23	A,B	Rd	5	Pass (3)
PB15:4	A	n/a	4	Pass (3)

Conclusions

A wide range of stable synergist based dispersions was designed for several pigments, used in InkJet printing. Process includes mixing and particle size reduction with virtually no effluents. An inexpensive and strong red pigment – PR23 was evaluated as an alternative to quinacridone pigments PR122, PV19 and PR202.

References

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[6] US 4,258,190; US 4,544,746
[7] E.E. Jaffe, private communication
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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 (since 1991) in US, including Clariant and General Electric. Since 2002 he is working at R&D center of Cabot Corporation in Billerica MA. Dr. Shakhnovich holds a position of Cabot Research Fellow in Industrial Organic Chemistry. His research interests include synthesis, surface modification and application of organic colorants.