New Inkjet Yellow Pigments – Halogenated Quinolonoquinolones

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Abstract

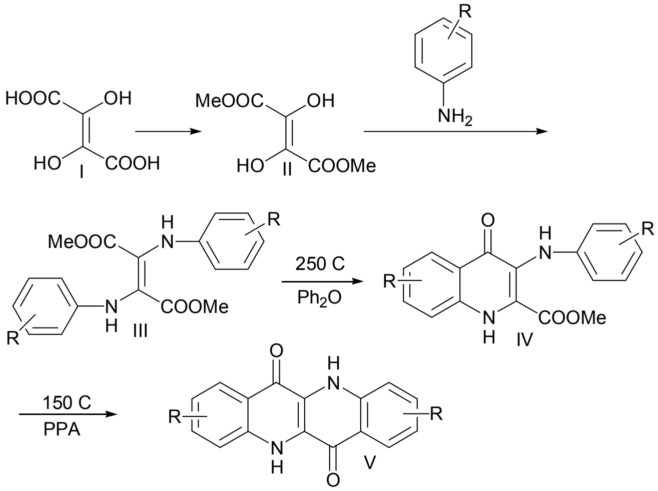
Deficiencies of Pigment Yellow 74, the most widely used yellow inkjet pigment, include poor lightfastness, limited colloidal stability in presence of organic cosolvents due to ripening/recrystallization processes and problems with chemical surface modification. This promotes a search for better yellow pigments for inkjet applications. The known class of quinolonoquinolone (QQ) pigments had been studied at Cabot as one of the possible alternatives to PY74. Specifically, several new asymmetric monohalogenated QQ's had been prepared, characterized and evaluated. Pigment Yellow 218 (3-Fluoro-QQ), Pigment Yellow 220 (2-Fluoro-QQ) and Pigment Yellow 221 (3-Chloro-QQ) were found to be especially suitable for surface modification by using Cabot's diazonium chemistry methods and had been succesfully converted into stable nanosized inkjet dispersions. These three pigments, being of comparable strength and shade with PY74, demonstrate outstanding lightfastness of prints, matching that of copper phthalocyanine and quinacridones. Dispersions of these QQ's have very high colloidal stability and are not sensitive to cosolvents or humectants. QQ synthesis had been studied and the key step was significantly improved to maximize the yield of asymmetrically substituted component by preventing randomization in the course of preparation.

Background

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 results in attachment of charged species onto a surface of the pigment and provides dispersions with excellent application properties. These do not require additional dispersants and therefore have very good formulation flexibility. Dispersions of phtalocyanines and quinacridones deliver cyan and magenta prints with excellent lightfastness. Pigment Yellow 74, however, which is currently a standard yellow for inkjet applications is a considerably less lightfast pigment than PB15 or PR122. We were interested in a new yellow pigment with the lightfastness matching that of phthalocyanines and quinacridones and which would be capable of diazonium surface treatment. Our fundamental studies of the mechanism of diazonium treatment of quinacridones lead us to heterocyclic pigments as possible candidates. These are generally considered to be more lightfast than simple azopigments. After screening the candidates for ability to be treated by diazonium salts, we quickly focused on quinolonoquinolones (QQ).

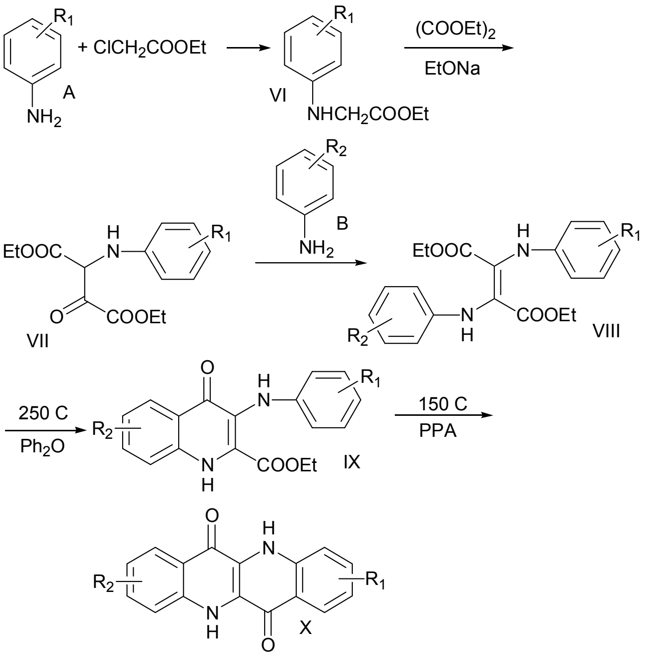
Preparation of Pigments

In 1967-79[1,2,3] quinolonoquinolones in pigmentary form were prepared by several methods. They never were commercialized, although their application properties were very promising.



(1)

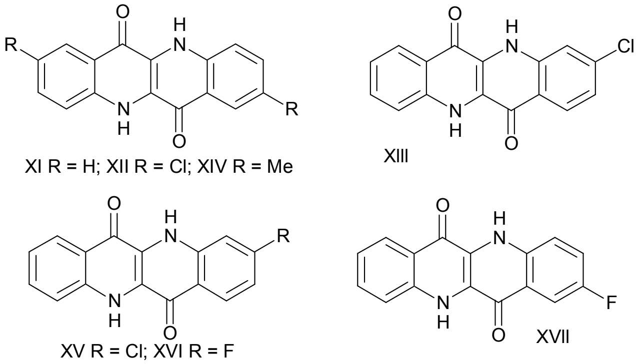
There are two methods of preparation, described in the literature. The first method[1,3] (Eq. 1) starts with dihydroxyfumaric acid (I),



(2)

which is converted first into the dimethyl ester (II), which in turn reacts readily with 2 mols of aromatic amine giving enamine (III). This enamine is cyclized into quinolone (IV) by heating to 250-270 °C in an inert solvent, such as phenyl ether or Dowtherm ® A. The second cyclization of (IV) into QQ (V) is conducted by heating with polyphosphoric acid (PPA). It is interesting to notice here, that cyclizations can be conducted only stepwise – neither thermal nor acid cyclization can be used to directly convert III into V. It is also important, that only unsubstituted or symmetrically substituted QQ can be obtained by this method. The second method[3] (Eq. 2) differs from the first one in the way of preparation of enamine. In this case aromatic amine A reacts with ethyl chloroacetate forming N-arylglycine ethyl ester (VI). This reacts with diethyl oxalate in presence of base, forming aryl-oxalacetate (VII). Reaction of VII with same or different aromatic amine (A or B) gives enamine (VIII) which further undergoes thermal cyclization into quinolone (IX) and acid cyclization into QQ (X). Both para- and meta-substituted anilines can be used in these synthetic protocols. Cyclization of an enamine, based on p-substituted anilines results in a single isomer, whereas meta-substituted anilines could potentially lead to several QQ isomers, the ratio of which will depend on both electronic and steric properties of substituents.

Using the first method an unsubstituted QQ (XI) as well as 2,9-dichloro-QQ (XII), 3,8-dichloro-QQ (XIII) and 2,9-dimethyl-QQ (XIV) had been prepared and appropriately characterized. The second method had been applied to the synthesis of 3-chloro-QQ (XV), 3-fluoro-QQ (XVI) and 2-fluoro-QQ (XVII). (Eq. 3) We have discovered, that contrary to the literature data, the synthesis of asymmetric QQ, based on N-arylglycine ethyl ester leads to a statistical mixture of ~50% of monosubstituted QQ, ~25% of unsubstituted QQ and ~25% of disubstituted QQ[4]. We have proved that this is caused by the equilibrium at the enamine formation step (Eq. 4). We have consderably improved the content of monosubstituted isomer by replacing ethyl esters with much less soluble methyl esters and by conducting the enamine formation in methanol under controlled conditions. This allowed us to enrich the content of monosubstituted species in XV, XVI and XVII to >80% and correspondingly decrease the share of unsubstituted and disubstituted QQ's[4].



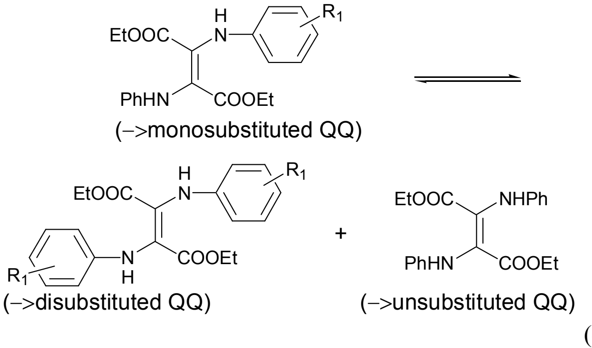
XI R = H; XII R = Cl; XIV R = Me

XIII

XV R = Cl; XVI R = F

XVII

(3)



(–>monosubstituted QQ)

(–>disubstituted QQ)

(–>unsubstituted QQ)

(4)

Diazonium Treatment and Properties of Dispersions

All of the synthesized pigments were subjected to surface treatment with diazotized sulfanilic acid. Well described in Cabot patents and articles, this method attaches 4-sulphonatophenyl groups onto a surface of pigment and renders the pigment self-dispersible. We have found that more electron-rich compounds XI, XIV-XVII react with diazonium, forming stable dispersions[5]. Contrary to this, electron-poor dichlorinated XII and XIII do not provide dispersions with acceptable quality. This confirms our early observations that polyhalogenated phthalocyanines and quinacridones treat with diazonium with very low yield.

Obtained dispersions are stable against the action of all humectants and surfactants, used in inkjet inks. Specifically, stability towards 1,2-hexanediol and triethylene glycol monobutyl ether is outstanding. These two cosolvents are very aggressive and destroy virtually any PY74 dispersion. We have formulated the prepared dispersions into inkjet inks and printed these material using both thermal and piezo platform. There was no printing issues. It turned out that both unsubstituted (XI) and dimethylated (XIV) QQ have unacceptable hue angle – they are too red. Additionally, they are considerably weaker than PY74. Not surprisingly, monosubstituted compounds XV-XVII presented a good combination of color hue and strength. 3-Fluoro-QQ (XVI) is very similar in color and strength to PY74; 3-Chloro-QQ (XV) is close, albeit a bit weaker. The third representative of this group – 2-fluoro-QQ (XVII) provides a warmer skin-tone hue.

Lightfastness

The prints were exposed to UV-A lamps using QUV weatherometer up to 1,000 hours. They demonstrated excellent fading resistance, matching and even surpassing copper phthalocyanines and quinacridones. Therefore, obtained pigments provide a unique opportunity to be a part of a CMY triade useful for outdoor printing application.

Colour Index Registration

Pigments XV-XVII had been registered in Colour Index under the following names: 3- Fluoro-QQ – Pigment Yellow 218; 2-Fluoro-QQ – Pigment Yellow 220; 3-Chloro-QQ – Pigment Yellow 221.

Conclusions

New monohalogenated QQ yellow pigments are free from the deficiencies of simple azo pigments. Due to their excellent coloristic and fastness properties QQ provide a 'missing link' for a CMY pigment triade, suitable for outdoor printing or for archival purposes. Surface treatment of these pigments had been accomplished using diazonium method, providing a path to robust yellow inkjet dispersions with very good formulation space.

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.