Pigments for Inkjet Applications

INTRODUCTION

The inkjet (IJ) method of non-impact printing has been used commercially since the 1980s. Originally the inks contained colorants that were soluble in the ink vehicle, i.e. dyes. Later on, however, deficiencies of the dyes, such as mediocre image permanence (light- and weatherfastness, ozone resistance) and poor waterfastness became obvious. Industry requirements for better colorants for outdoor or photo printing were becoming more and more demanding. It is well known that in applications such as paint, plastics and coatings, the use of pigments instead of dyes increases the performance characteristics of the color package dramatically. The same turned out to be true for IJ. The use of carbon black instead of weaker black azo dyes totally revolutionized the IJ industry, bringing text printing close to laser printer quality regarding speed, edge acquity and durability. In fact, deficiencies in black were the main driving force for considering pigmented inks. By the late 90's all major players were using black pigment because of carbon black's desirable image permanence, high color strength and flat spectral absorption. Epson and Kodak now broadly use color pigmented inks in their IJ products, while HP, Canon and Lexmark still use color dyes and limit pigment use to high end photo and office applications.

Pigments by definition are not soluble in the media of application, so the waterfastness of pigment-based prints is generally much better than that of dye-based prints. As expected, the light- and ozone fastness of pigmented prints turned out also to be much improved vs. dyes. However, a number of significantly improved IJ dyes with high light- and ozone fastness have been discovered and developed recently.

In order for the pigments to be formulated into inkjet inks they have to be dispersed to small particle sizes (roughly between 50 and 200 nm, depending on the application) and this dispersion needs to be made colloidally stable. The colloidal stability can be achieved either by using pigment surface modification to form an adequate surface charge, or by adsorption of certain compounds on the surface of pigment particles. These compounds may be low-molecular weight pigment derivatives or they may be polymeric dispersants, stabilizing the particles by steric repulsion or by charge repulsion. The details of these methods will be described later in this chapter.

These improved properties often come at a cost. Replacing a colorant solution by a colorant dispersion raises several issues.

1. The colloidal stability of the dispersion is a critical property, as the inkjet ink should not settle for months or longer, depending on the application. Although all pigmented inks will eventually settle, their resistance to settling depends on their size, density, surface chemistry and the dispersants used. As the settling rate is proportional to the square of the diameter and to the density difference vs. the solvent, large particles are problematical. Reducing the particle size of pigments below 100 nm is usually technically challenging and costly. Some pigments such as Pigment Green 36 have high densities due to their metal and/or halogen content and are extremely hard to maintain in a colloidally stable state.

2. Second, ejecting particulates through the micro jets (may be 10-30 microns in diameter) at high velocity puts many restrictions on the ink properties. The viscosity and surface tension of the ink should be carefully controlled, which may be difficult in a system that contains both nanoparticulates at high loading and dispersants. Of utmost importance is the large particle content (usually expressed as number of particles larger than 0.5 or 1 micron per 1 ml of ink). Large particles may plug the jets and channels and cause irreversible damage to the printhead.

3. In the case of thermal IJ printheads, where the surface of the firing resistor is briefly heated to a very high temperature, no deposition on the resistor should take place. Such a deposit is thermally insulating and usually damages the resistor irreversibly. Preventing this phenomenon adds additional requirements to the ink purity and composition.

4. Depositing pigment particles on the paper surface creates many problems related to the penetration, adhesion and cohesion of these particles, and sometimes results in poor highligter smear resistance, gloss inconsistency of photo prints and the like.

5. Inks with high solids contents are required for some lightfast pigments that have low color strength compared to dyes. This problem, however, seems to be limited mainly to quinacridones.

Most of the named problems are technical, rather than fundamental in nature. They can be solved or alleviated by carefully choosing the surface treatment, by ink formulation work and/or by selecting appropriate printing algorithms. Pigments are continuing to replace dyes for many non-impact printing applications, particularly IJ. IJ grades of pigments, IJ pigment dispersions or both are now commercially available from multiple global manufacturers, such as Cabot Corporation, Clariant, Ciba, DuPont, Dainippon Ink, Daicolor-Pope, Toyo Ink , Dainichiseika, Degussa, Sensient, Kao, Mikuni and others.

CARBON BLACK

Carbon black is produced by the partial combustion or thermal decomposition of hydrocarbons. Several methods are used, including the furnace black, thermal black, lamp black and acetylene black processes[1,2,3]. The furnace black process is the most common. In this process, natural gas (or another fuel) is burned to form a hot gas stream that is directed into a tunnel. An aromatic oil is sprayed in and the black forms as the gas moves down the tunnel. The reaction is quenched with the addition of water, and the product is collected as a low density powder (fluffy black) or is further processed into millimeter sized pellets.

Morphology

Carbon black aggregates consist of primary particles that are fused together to form fractal like structures. The aggregates associate with each other because of van der Waals forces to form agglomerates and can be formed into millimeter sized pellets during manufacturing. The primary particles are typically 10 – 75 nm in diameter and the aggregates are typically 50-300 nm in diameter. The surface area of carbon blacks is largely determined by the size of the primary particles and is usually in the range of 30 –200 m^2/g, but there are some outside these ranges with some exceeding 500 m^2/g. The aggregates have significant internal void space because of their fractal nature or "structure". The dibutyl phthalate absorption (DBP) number or oil absorption number (OAN) is used to characterize commercial carbon blacks and is a measure of the combination of the internal void volume and the volume between closely packed aggregates. These values normally range from 40-130 mL/100g of carbon black.

The primary particles of the carbon black are made up of amorphous carbon and small graphitic crystallites roughly 15-25A in size. TEM work has shown that the crystallites near the surface are parallel to it and the ones in the center are randomly arranged. There are different models of the actual surface[4]. In one, there are graphitic basal planes separated by regions of amorphous carbon. In another, the edges of graphitic crystallites are exposed at the surface with the basal planes buried inside the particle.

The morphological characteristics of carbon black affect its ease of use in a variety of applications and the properties of materials containing carbon black. For example, carbon blacks with low surface areas and high DBP values are more easily dispersed into inks and other media than blacks with high surface areas and low DBP values. The pigmentation properties also depend on morphology, with high surface area materials giving the greatest jetness (blackness), provided that the blacks are well dispersed. The undertone color depends on the primary particle size and the application.

Surface chemistry of carbon black

Extensive efforts have been made to characterize the surface chemistry of carbon blacks[1,5]. Although carbon blacks are nearly all carbon, impurities of oxygen, sulfur, nitrogen and small amounts of other elements are present. Most of the work has centered around the identification and quantification of oxygen containing functional groups. Some approaches are based on titrations, while others use pyrolysis/MS[6], FTIR[7], Raman[8], ESCA[9] or combinations of wet chemical and spectroscopic methods[10,11]. Through this work, a number of functional groups have been identified as being present on the surface of carbon black including carboxylic acids, ketones, phenols, anhydrides, aldehydes, quinones, lactones, lactols and pyrones[5,12]. Carbon blacks have a mixture of these groups on their surfaces. The quantification of the groups remains
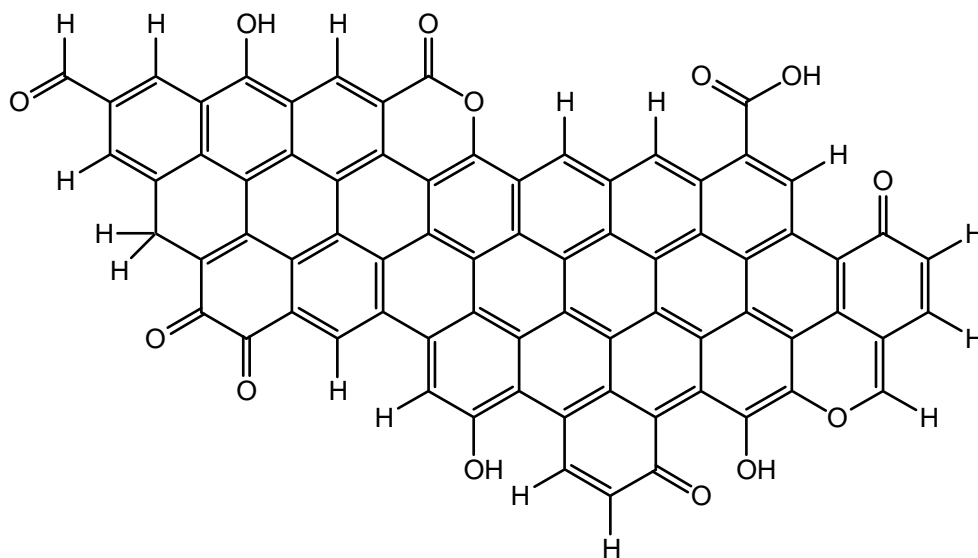
challenging, though.

Figure 1, Functional groups on the surface of carbon black

ORGANIC PIGMENTS

It is well known that a robust composite color match can be built from a white, a black and from two colorants (A and B) which have hue angles correspondingly smaller and larger than the required colors. The closer the hues of A and B are to the required color, the better the match. This is why the industrial color palettes for paints and plastics applications usually consist of 12 – 20 colorants, more or less evenly spaced by hue angle. Because of limited number of jets available, such a large palette is not practical for most of IJ applications.

The most widely used pigment set for IJ consists of a cyan (C), a magenta (M) and a yellow (Y) pigment. Together with a black pigment (K) that makes a 4-color set, commonly designated as CMYK. All composite colors are built by superposition of these four primaries (paper serves as a scattering white). That means that color reproduction may not be adequate for some demanding applications, such as photo prints. Therefore, some photo printers may have additional color cartridges such as green, orange, red, blue or, otherwise, two cartridges with the same colorants, but at different dilutions (light magenta, light cyan or grey). That approach may increase the number of cartridges to 8-12, which may add to the cost of the system considerably. Some typical a*-b* curves for a CMY inkjet pigment triade (PB15 – PR122 – PY74) are shown on the plot below as a function of print density.
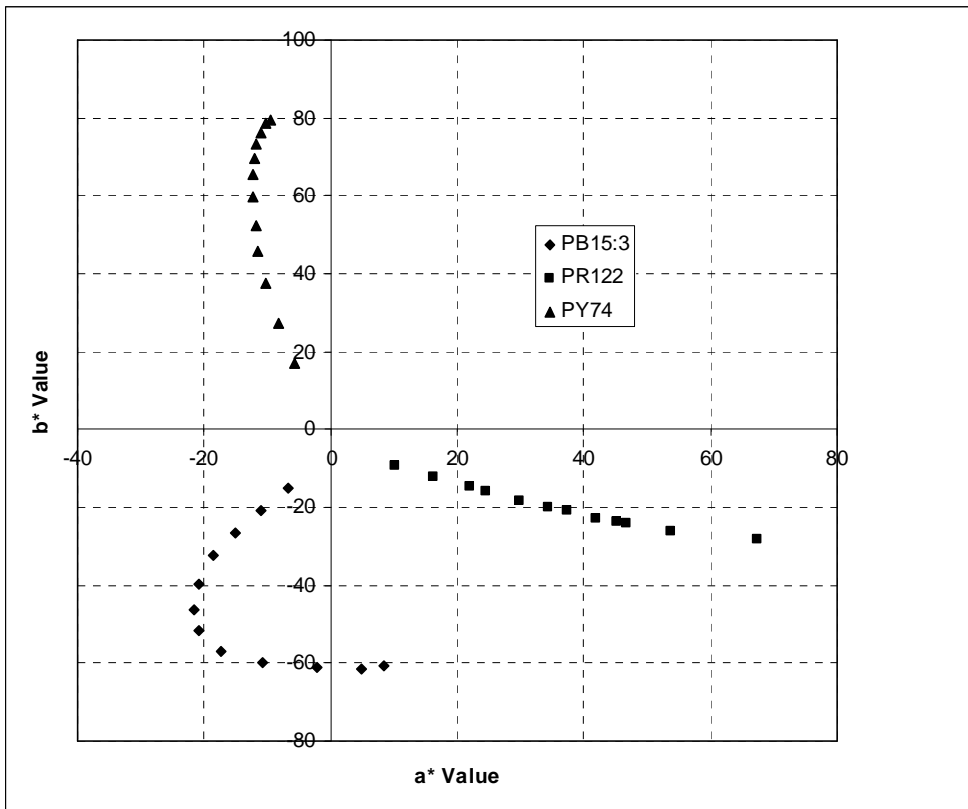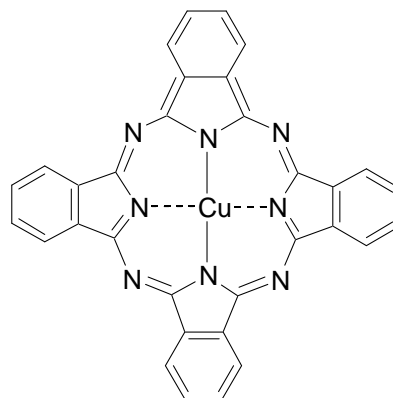
Figure 2. Typical color values for 12-step monochromatic ramps printed on Epson Premium Glossy Photo Paper

The 3-color CMY set is well defined; for a cyan color almost all ink manufacturers are using

green shade copper phthalocyanine – Pigment Blue 15:3 or 15:4. This pigment is

coloristically very strong, extremely lightfast and weatherable. Its hue angle is generally between

240° and 280°. The only fundamental problem with PB15 is its strong reflection in the red area[13],

which shows itself as bronzing (the reddish shade luster of a print when viewed at an angle).

Although there are many inventions targeted to mitigate bronzing, it is a fundamental problem

and can not be eliminated completely.

Quinacridone pigments are the main class of colorants used as IJ magentas. Their permanence and clean color are responsible for the choice. Quinacridones, however, are relatively weak colorants. Their pink color is detemined not by molecular structure, but rather by association of molecules in the crystal and by intramolecular electron transfer. Therefore, the pigment loading in magenta ink is usually higher than in cyan or yellow inks.


PR122 R = Me
PV19   R = H
PR202 R = Cl
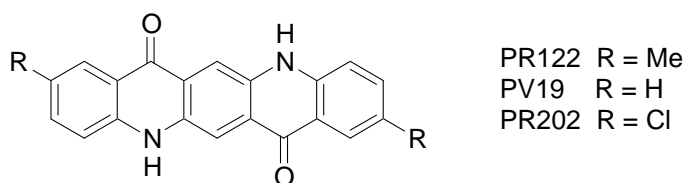
Many ink manufacturers use bluish red Pigment Red 122 (dimethylquinacridone). Pigment Red 122 has only one crystalline modification and its hue angle is generally between 315° and 340°. A recent trend, however is the replacement of PR122 with red shade (RS) PV19 (γ-modification of quinacridone). The reason for this is the difference in hue angles between these pigments - RS PV19 has a hue angle of between 355° and 10°. Because RS PV19 is much yellower than PR122, it makes much cleaner composite reds and oranges. Another pigment, that may be used in this group is PR202 (2,9-dichloroquinacridone). It usually looks stronger and yellower than PR122. Several attempts had been made to use red Naphtol AS pigments as magentas. However their lightfastness is so inferior to quinacridones, that this approach is now practically abandoned. The widest variety of pigments used in IJ is certainly in the area of yellow. That can be explained by the fact, that as of today, there is no single yellow pigment which would meet all of the stringent IJ requirements. By far the most widely used IJ yellow pigment is Pigment Yellow 74. It is very strong and clean yellow colorant, widely available from many manufacturers. Its hue angle is slightly over 90° at full strength, making it a good choice for a neutral yellow. PY74 has two major drawbacks, though.
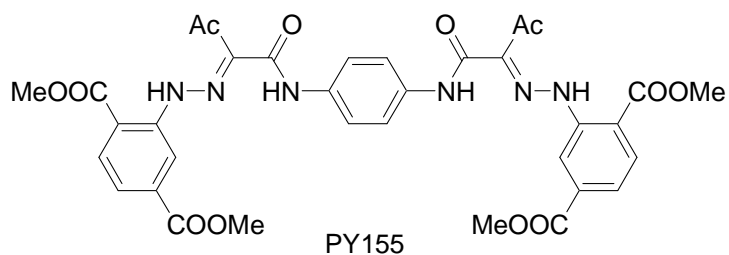
PY74
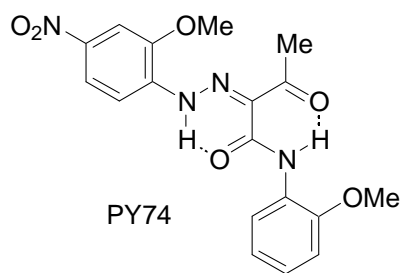
One of them is its poor lightfastness, which is especially noticeable when the pigment is dispersed to particle sizes below 100 nm. Another one is the slight solubility of this pigment in some components of ink vehicles, which makes formulation work more difficult and sometimes compromises the long-term colloidal stability of the inks.

There are several other azo pigments, which can be used to improve the properties of yellow ink dispersions.

PY180

PY120 R_1= H, R_2 = COOMe
PY175 R_1 = COOMe, R_2 = H
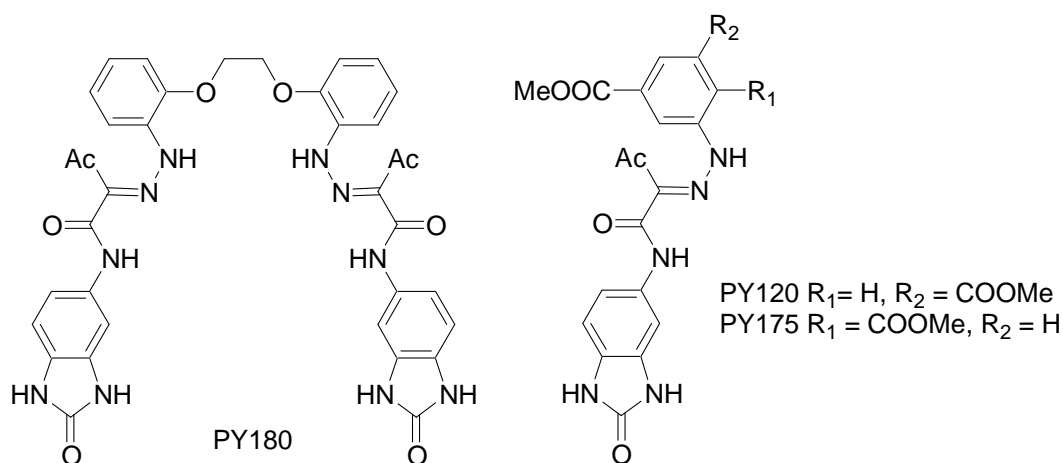
Many attempts had been made to use benzimidazolone pigments, such as PY180, PY120 and PY175. They have much improved solvent resistance and higher lightfastness than PY74. Colorwise, PY180 is very close to PY74 and is almost as strong. However, the colloidal stability of these three pigments in dispersions is much more difficult to achieve because of the strong self-assembling action of the surface benzimidazolone groups. Inks based on benzimidazolone yellows are not commercially avialable. Another choice of a yellow azo-pigment is represented by dimeric PY155.

PY155

Being a little greener and weaker than PY74, this pigment has an improved lightfastness and is used in some commercial inks. Obviously enough, strong and inexpensive diarylide yellows such as PY12 are rarely mentioned in the IJ literature due to potential benzidine release,
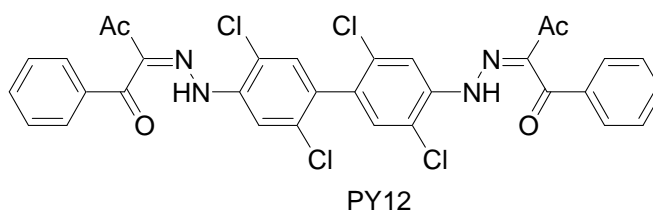
PY12

especially in thermal IJ systems. The most lightfast pigment in the azo yellow group is disazocondensation yellow PY128.

PY128
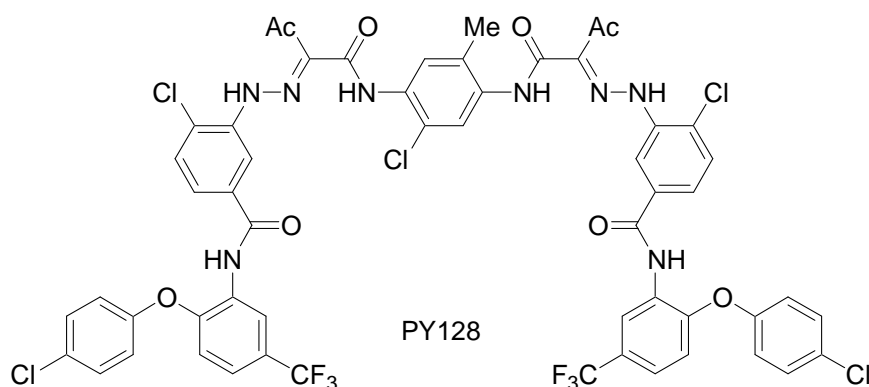
This pigment is weaker (per weight unit) than other azo pigments due to the presence of heavy side groups. It has limited use in some commercial lightfast inks. There are also some references to several heterocyclic yellow pigments, such as PY138, PY139 or PY185 as well as PY150 (metallized). One group of yellow heterocyclic pigments deserves special mention. These are quinolonoquinolones (QQ), mentioned in several Japanese and US patent documents[14,15]. These pigments have been known since the 1930s, and commercially viable preparation routes have been disclosed in 1967-68 and later improved in 2002-2007[16].

PY220

PY218 R = F
PY221 R = Cl
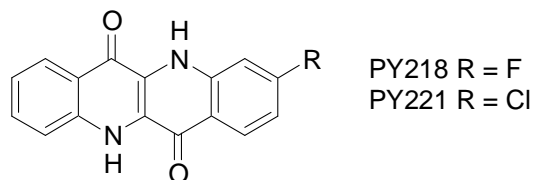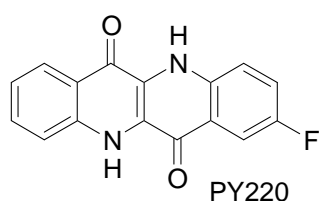
Structurally, QQs are very similar to quinacridones. Their shades range from reddish yellow (2-Fluoro-QQ or PY220) to neutral yellow (3-Fluoro-QQ, or PY218 as well as 3-Chloro-QQ, or PY221). These pigments have outstanding lightfastness and solvent resistance, which are on par with phthalocyanines and quinacridones. Using them as a yellow component of a CMY triade allows the creation of an ink set for outdoor applications[17].

DISPERSION METHODS FOR INKJET PIGMENTS (NANOSIZED DISPERSIONS)

Earlier in this chapter we outlined several strict requirements for IJ pigment dispersions. First and foremost, these are colloidal stability and particle size distribution. Generally the particle size has to be reduced to 80-150 nm, which is often challenging.

Particle size reduction may be achieved with different kinds of milling equipment such as media mills[18]. Alternatively, flow impingment or ultrasound methods can be used for dispersion. Some of the pigments can also be dissolved in certain solvents and reprecipitated as extremely fine particles[19]. All of these processes generate a considerable amount of fresh surface. If unstabilized, these surfaces collapse back together and particle size reduction may not happen. To prevent this collapse, different methods of stabilization of these surfaces are employed. The easiest way is to use commercially available pigment dispersants, which are widely available. These are either polyelectrolytes with affinity to the pigment surface, or polymers with bulky groups providing steric stabilization. Generally they are non-selective, so they work better with some pigments than with others. Their major advantage is their commercial availability and relatively low price. It is possible to 'encapsulate' the pigment with polymer by changing solvent environment and/or pH to 'crash' the polymeric dispersant onto the surface of pigment particles. In this case the polymeric dispersant is associated with the pigment by means of physical adsorption, so this process is reversible and the dispersion stability is extremely sensitive to components of inks. If

these components are good solvents for the encapsulating polymer, the dispersion stability may be compromised, especially in the long-term. In general, the use of conventional dispersants makes the job of ink formulation difficult. Many examples of inkjet dispersions obtained by encapsulation are described in patents and applications by DIC. The polymeric dispersant used here is a copolymer of styrene-acrylic acid-methacrylic acid with an acid number around 150. According to the inventors, this material is equally well suited for dispersing carbon black and color pigments[20].

A custom polymeric dispersant is an improvement – the polymer molecule is tailored to the pigment and to the application. There are dozens of patents from companies such as Canon, Epson, KAO, DIC, DuPont and others describing the synthesis and use of custom pigment dispersants for IJ. Some of them are very complex, involving such techniques as grafting and block copolymerization.   For example, some DuPont patents describe a dispersant based on a diblock copolymer A-B or triblock copolymer A-B-A where block B has an affinity for the pigment, whereas block A is responsible for colloidal stabilization[21].

A further improvement in the polymer dispersant area is possible with the appropriate design of a polymer-attached anchoring group, which has specific affinity for pigment surface. In several examples, chromophores such as AmDMQA, were synthesized and attached to a styrene-maleic acid or styrene-acrylic polymer.

AmDMQA + styrene-maleic anhydride copolymer →

Dispersant with anchoring group
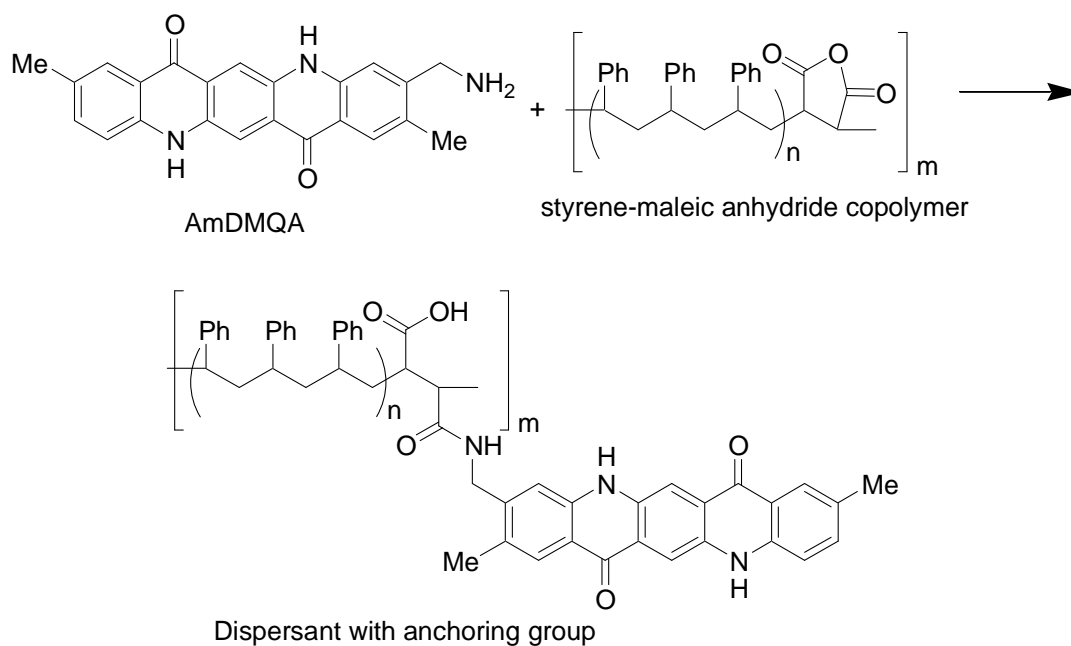
This custom dispersant is very effective in dispersing various quinacridones. In this case, the cooperative action of multiple anchoring groups within one polymer chain is beneficial for dispersion stability[22].

Another method for colloidal stabilization makes use of low molecular weight pigment derivatives. Pigment derivatives are molecules which have structures that are similar to the corresponding pigments but contain bulky or ionizable groups. The rationale for pigment derivative use is the following: due to the similarity to the corresponding pigment structures, they adsorb well on the surface and therefore control the crystal growth. They are also called crystal growth inhibitors. Some examples are given below:

PMQ
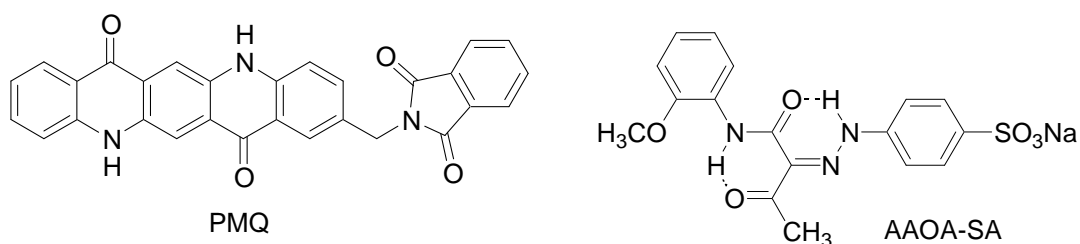
AAOA-SA

The use of PMQ for dispersing quinacridones is quite common and well documented. AAOA-SA is one of many similar compounds that can be prepared from acetoacetanilides and aromatic amines which contain ionic or ionizable groups. Some of them are good dispersants for PY74 and related azo pigments. Several stable IJ dispersions have been generated; they gave images

with good color saturation. A dispersant similar to AAOA-SA can be either generated in the presence of a pre-synthetized azo pigment to form an inkjet dispersion or, conversely, both the azopigment and a dispersant can be formed simultaneously in a mixed synthesis of PY74 or another azo pigment providing a self-dispersible IJ grade[23]. The dispersion properties can be fine-tuned by optimizing the diazonium salt structures, ratios and other conditions.

SURFACE MODIFICATION

The most robust method for changing the surface properties of pigments is to attach functional groups to the surface directly or through linking groups. The modifications can be chosen to improve the dispersion stability of IJ inks containing the pigments as well as to improve the printing properties of the inks.

Carbon black

The oldest method for the modification of carbon black surface chemistry is oxidation[5]. Common oxidants include air, hydrogen peroxide, hypochlorites, nitric acid, nitrogen dioxide, ozone and persulfates. Each reagent produces a mixture of oxygen functional groups on the surface, with the distribution depending on the oxidant. Materials that disperse in water can be produced with sufficient oxidation, and hypochlorites[24] and persulfates[25] have been used to make water dispersible carbon blacks for inkjet inks.

Attached organic groups

The surface can also be modified via a reaction with organic molecules or intermediates to introduce specific functional groups. One approach is to use the native oxygen groups as a reagent and site of attachment[26]. Usually, only one kind of group can be used for the reaction. As a result, only part of the surface is available for reaction, even when oxidized blacks are used. Another approach is to use the most abundant part of the surface, carbon, for the reaction. Several methods of this type have been explored including those based on diazonium chemistry[27],

azo chemistry[28], peroxide chemistry[28], sulfonation[29], cycloaddition chemistry[30] and other methods[31,32].

The reaction of carbon[27,33,34] with the diazonium salts is the most widely used method for surface modification of carbon blacks for inkjet inks[35]. The organic groups are attached directly to the carbon surface, and the surface coverage is not limited by the availability of specific oxygenated groups. The diazonium salt enables the introduction of a variety of functional groups onto the surface. A phenyl group is typically used as a spacer between the carbon surface and the functional group, but other spacers are possible. Simple functional groups such as sulfonate or carboxylate can be used to make treated carbon

$$\text{[C]}-\text{C}_6\text{H}_4-\text{SO}_3^-\ \text{Na+} \qquad \text{[C]}-\text{C}_6\text{H}_4-\text{CO}_2^-\ \text{Na+}$$
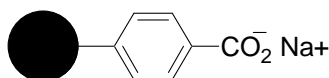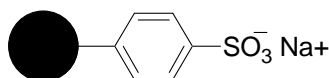
blacks with excellent dispersion stability and low surface tension in water and IJ inks.   Because of the flexibility of the chemistry, other properties can be controlled by adjusting the number, position or type of groups on the phenyl ring. For example, the optical density of prints made from inks containing the modified pigments can be improved when calcium binding groups are attached to the surface[36]. The groups may complex with calcium in paper under certain conditions, destabilizing the pigment and giving darker prints. One possible calcium binding group is the bisphosphonate group:

$$\text{[C]}-\text{C}_6\text{H}_4-\text{CH}\begin{cases}\text{PO}_3\text{NaH}\\ \text{PO}_3\text{Na}_2\end{cases}$$
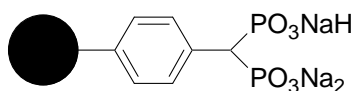
More complex groups can be attached to the carbon surface via secondary reactions with groups already attached through diazonium chemistry[37]. Polymers can be bonded to the pigment surface

either via a direct diazonium reaction[38] or by a secondary reaction. The attached polymers can give improved durability to printed inks.

Organic pigments

There are significant differences between organic pigments and carbon black that affect the ability to bond to their surfaces. First, organic pigments are molecular crystals. The molecules of the organic pigments are bound together with relatively weak bonds compared to the covalent bonds in carbon black particles. Consequently, the individual pigments have specific, well defined compositions. Further, most organic pigments are not good electron donors, as is carbon black.

There are several methods for modifying the surface of organic pigments. Some are effective for a limited range of pigments, while others are more general. An example of the former is the reaction of Pigment Green 36 with thiolates to form sulfide links to the surface [39].

Pigment Green 36
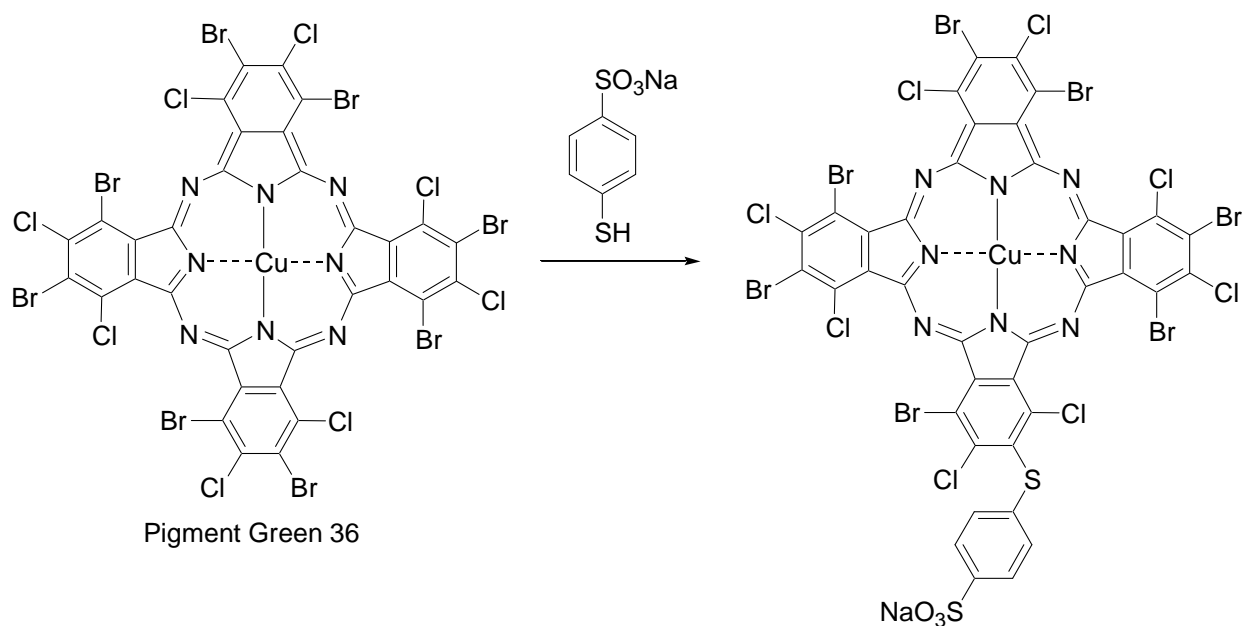
Another example is the hydrolysis of an ester group in PY155[40].

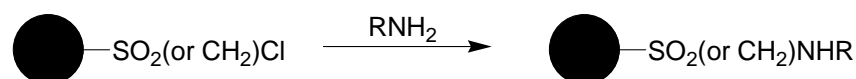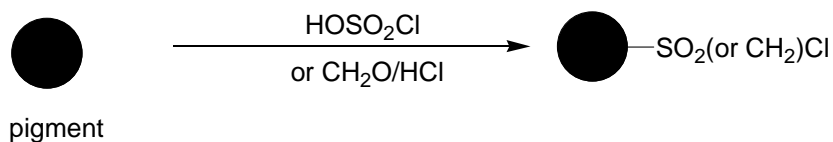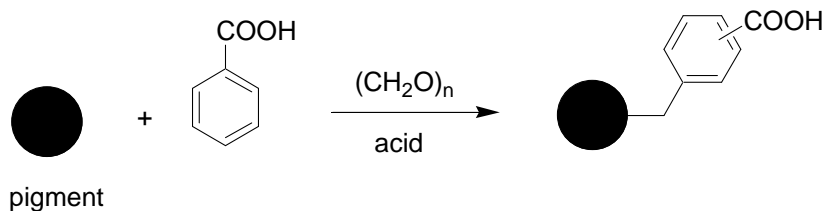PY155

NaOH

Modified PY155
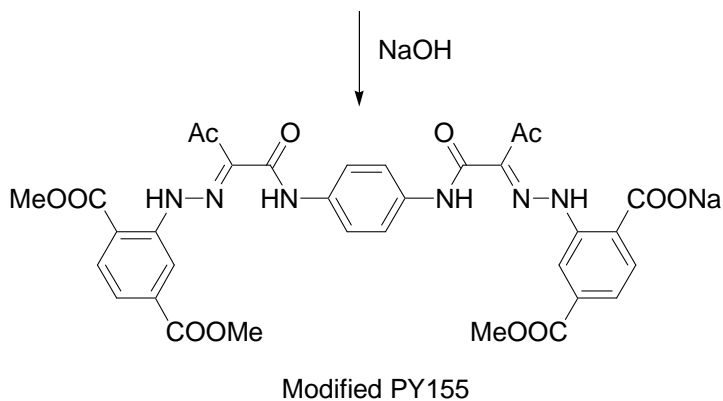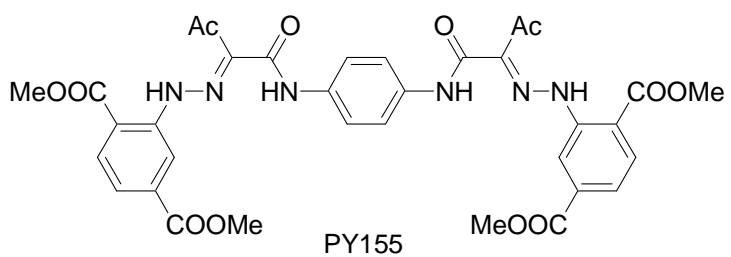
Examples of more general reactions are sulfonation[41],

chlorosulfonation or halomethylation followed by amidation[42,43],

and aralkylation using formaldehyde[44].

Pigment modification with diazonium salts is also possible. Cabot successfully expanded the diazonium treatment method of carbon black, described above, to several color pigments[45].

In an effort to elucidate the mechanism of diazonium treatment of the color pigments, the quinacridone PV19 was reacted with the carboxyphenyldiazonium ion. Nitrogen was evolved. Extraction of the product with dimethylformamide yielded seven red dyes with UV-VIS spectra very close to that of the parent PV19, which means that no change of chromophore had taken place. Three of the dyes were positively identified by MS as product of mono-and bis-arylation of PV19. Two of the structures are shown below and are examples of the expected structures.
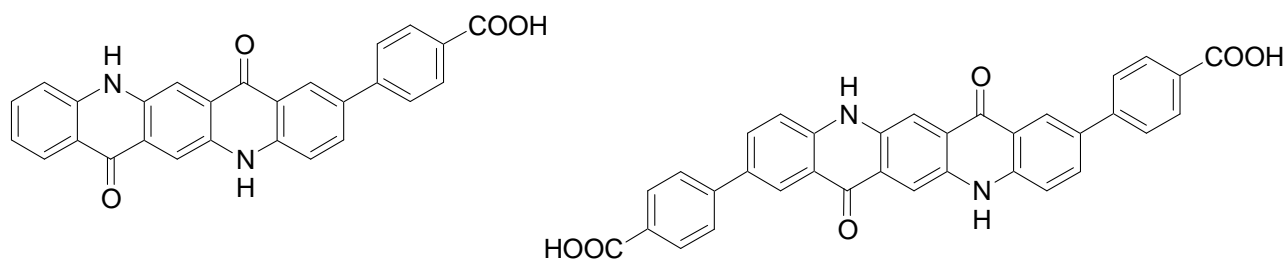
In the case of the reaction of the sulfophenyldiazonium ion with the quinacridone PR122, many products were again found. Among them was the azo dye shown below, indicating that some azo coupling can also occur to some extent.
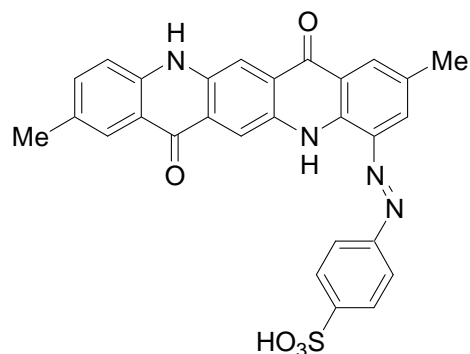
It should be noted that *soluble* acridone and quinacridone derivatives, such as ASA, QSA or DMQSA do not react with diazonium salts. This important finding indicates that the reactivity of the PR122/PV19 surface depends on the solid state nature of the pigments[46].

R = H; QSA
R = Me; DMQSA
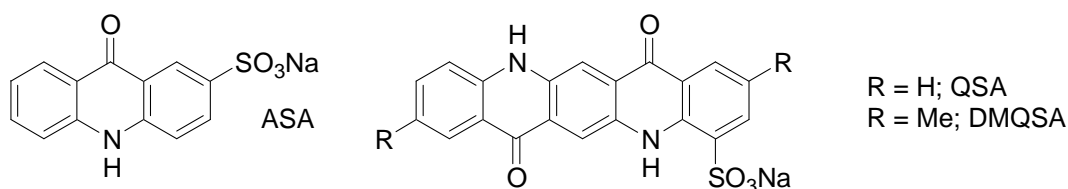
Dispersions of Pigment Yellow 74 (azo pigment), Pigment Red 122 or Pigment Violet 19 (quinacridones) and Pigment Blue 15:3/4 (phthalocyanines), available under the trade name of Cab-O-Jet®, are now used as sources of CMY pigments by the inkjet industry.

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