Reactions in diazonium treatment differ greatly from one pigment to another.
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Diazonium treatment is a well-established method for making self-dispersible grades of carbon black pigments. The fact that many colour pigments can be similarly treated is surprising, because they have very different surface chemistries. The diazonium reaction for two types of pigments is shown to proceed in quite distinct ways.

In the 1990s, a new method of dispersing carbon black was invented [1]. It had been shown that when carbon black was treated with a solution of diazotised sulfanilic acid, a stable dispersion was formed (see Figure 1) in which the ionised sulfonate group, which is a part of the attached benzensulfonic acid group, provides charge stabilisation of the particle. It is almost impossible for the treating agent to desorb or otherwise leave the surface of the particle and so the carbon black dispersion is very stable. The level of attachment, which is usually expressed in ppm of sodium counterion, may be quite high and is certainly adequate for charge stabilisation of the colloidal particles.

This method was expanded to include many other treating agents and to explore attachment chemistries such as, for example, the attachment of polymers to particles [2]. The new carbon black dispersions have quickly found many applications, including inkjet pigment dispersions and are now manufactured on a large scale.

Diazonium treatment - not only for carbon black pigments
An extension of this diazonium treatment method to include colour pigments for the inkjet industry would clearly be very beneficial. After some time, it was established that many colour pigments can undergo diazonium treatment to form stable dispersions useful for inkjet.

Pigment Yellow 74 (azo), Pigment Red 122 or Pigment Violet 19 (quinacridones) and Pigment Blue 15:3 (phthalocyanine) are now converted into inkjet dispersions on a commercial scale and used as to make a CMY colour pigment set by the inkjet industry [3].

However, the mechanism of the treatment remained unclear. The surface chemistry of colour pigments should be very different from that of carbon black, as the latter is a very strong electron donor and in addition all colour pigments are molecular crystals. The molecules of colour pigments are bound together with bonds that are weaker than those present in carbon black particles. Intramolecular electron transfer should not be common for colour pigments.

So what mechanisms are involved in this stabilisation process? A considerable amount of research has been carried out and is summarised below.

Possible reaction mechanisms in diazonium treatment
The aromatic diazonium ion can react via several pathways:
- Forming an azo bond by reaction with a nucleophilic aromatic or C-H acidic aliphatic carbon (1).
- Elimination of nitrogen with formation of an aryl cation, which further reacts as in (1).
- One-electron transfer and elimination of a nitrogen molecule to form an aryl radical, which can have multiple reaction pathways, including (1). This is usually realised when transition metals ions such as Cu⁺ are present.
- By being reduced, for example to an aromatic hydrazine, and later reacting as hydrazine with any available electrophile, such as a carbonyl bond. For this to occur, a reducing agent should be present in the system.

The reactions of PY74, PR122, PV19 and PB15:3 with diazonium salts have not been described in the literature. However, several other electrophilic substitution reactions are described for quinacridones or phthalocyanines, such as sulfonation, amidomethylation or halomethylation [4, 5, 6].

Analysis of the reaction products
In order to isolate the reaction product of PY74 with diazotised sulfanilic acid, the pigment and water had to be removed from the dispersion, leaving just the treatment products. A method of achieving this was found by applying the dispersion to filter paper, drying the spot at room temperature and extracting all the PY74 with chloroform in a Soxhlet apparatus.

After this extraction was complete, the residue was extracted with water from the filter paper and analysed by high-pressure liquid chromatography (HPLC). In this particular case only one compound (I) is found, which has an absorption spectrum with $\lambda_{\text{max}} = 377$ nm.

As shown in Figure 2, this maximum is shifted to a shorter wavelength in relation to the $\lambda_{\text{max}}$ of 412 nm that the PY74 chromophore should have (the nitro group has a very strong modifying effect on absorption). This suggests that the end product of the treatment is not the PY74 colorant molecule itself, substituted in one of the aromatic rings. It was then established that the treatment product of PY74 is compound (I) as shown on the right hand side of Figure 3. An independent synthesis was conducted as shown in Figure 3 and the assignment of the chemical structure was validated.

Dispersion effect relies on the presence of the residual azo coupler
It is believed that this compound is formed by azo coupling of diazotised sulfanilic acid with the residual azo coupler acetocacet-o-anisidide (AAAO), which is always present in commercial grades of PY74. To prove this conclusively, other possibilities had to be eliminated - to verify, for example, that there was not a diazonium exchange or that the diazotised sulfanilic acid had not been reduced to a hydrazine which could then exchange with PY74 as shown in Figure 4.

A soluble derivative of PY74 (II) was then synthesised in order to follow the reactions by UV-VIS (UV and visible light absorption monitoring) in solution. The introduction of an ionised sulfonic group is known to have minimal if any effect on the reactivity of colorant intermediates toward electrophilic attack.

No reactions were observed when compound (II) was incubated either with phenylhydrazine sulfonate or with diazotised sulfanilic acid. It was concluded that the only remaining way in which the PY74 treatment can take place is the reaction between untreated AAOA and the diazonium salt with the formation of pigment derivative (I).

Understanding of the mechanism leads to new dispersants
Compounds similar to (I) can be prepared from AAOA and different aromatic amines which contain ionic or ionisable groups. Many of them turned out to be dispersants for PY74. Several inkjet dispersions were produced and found to give images with good colour saturation and dispersion stability. Two patent applications [7, 8] have been filed as a result of this work. The first describes the generation, by the
Treatment mechanisms for quinacridone pigments

The next objective in this work was to obtain a better understanding of the treatment mechanism in quinacridone pigments such as PR122 or PV19. From the experience gained in studying the PY74 diazonium treatment, two mechanisms appeared possible:

- Diazonium salt reaction with a component of the pigment;
- Diazonium salt reaction with the pigment itself.

Understanding the treatment mechanism of a quinacridone pigment such as PR122 or PV19 presents certain challenges: quinacridones are very poorly soluble in solvents other than sulfuric and trifluoroacetic acid, so removal of the pigment by extraction is impossible. Another complication is that, due to the complex synthesis of quinacridone, several minor components may be present, most being acridones.

For example, 2-hydroxy-3-carboxyacridones (HCMA/HCA) and their decarboxylated versions (HMA/HA) shown in Figure 5 are formed if the synthesis of bis(arylamine)terephthalic acid - a precursor to quinacridone - is conducted in the presence of oxygen.

Secondly, incomplete cyclisation of bis-arylamine-terephthalic acid leads to formation of carboxy-anilinoacridones (CAA/CMTA), which may decarboxylate to produce anilinoacridones (AA/MTA) as shown in Figure 6. Finally, many quinacridone pigments may contain quinacridonequinone (QAQ).

Since it was expected that complicated mixtures of products would be found, it was decided to evaluate two pigments, PV19 and PR122, and also two treatment agents, sulfanilic acid and p-aminobenzonic acid (PABA), in this study. The chosen method of separation was by HPLC with UV-VIS PDA detection. PV19/PR122 and their substitution products were expected to yield very similar spectra, because the C-methyl groups have little influence on the spectra. Also, because both pigments are prepared by virtually identical methods, the same impurities could be expected in both cases.

On the other hand, the mass spectra of the corresponding PV19 and PR122 derivatives will differ, either by 28 units for quinacridones or acridones such as AA/CAA, or by 14 units for HCMA/HCA. Both treated and untreated PV19 and PR122 were deprotected by heating or by the action of a strong acid.

Diazonium reaction is with quinacridone pigment itself

When PR122 or PV19 was treated with diazotised PABA, the resulting dispersions, in the form of sodium salts, had a sodium content of 5000 to 7000 ppm (based on solids). The treated pigment was obtained in a dry state by acidification, with removal of sodium is observed.

The main minor component present in PV19 is HCA and in PR122 it is HCMA. Both are readily soluble in bases, forming salts, which have a weak affinity for the quinacridone surface. They react slowly with diazonium salts.

No dispersion is formed when PR122 is treated with 10 000 ppm of NaHCO3 - that is, deprotonated HCMA does not act as a dispersant.

- If HCMA is extracted from PR122 with NaOH prior to treatment, only a slight decrease of the total amount of sodium is observed.
- The HCMA 'adduct' with diazo should have even less affinity for the QA surface.
- All pigment components are present in comparable amounts in untreated and treated samples;
- Extensive extraction of pigment components from the treated pigment does not influence dispersibility.

Based on these observations, the pigment components are believed not to play any significant role in the PR122/PV19 treatment. If this is the case, the only remaining possibility is that the quinacridone colorant itself reacts with diazonium.

Structure identification of the surface species

Separation of the treated and untreated pigments presented challenges, because of the low solubility of quinacridone and because of the affinity of treated material for the pigment surface.

The first approach was to influence the solubility of quinacridone by N-derivatisation, which will disrupt intramolecular H-bonding and therefore improve the solubility of any quinacridone present in the system. It is well known from the literature [9], that many pigments which have NH groups can be derivatised by (Boc)2 O (= di-tert-butyl dicarbonate) in the presence of 4-dimethylaminopyridine as a base.

This reaction converts pigments into a so-called 'latent form', which is more soluble in most organic solvents than the parent pigments. The latent pigments can easily be deprotected by heating or by the action of a strong acid.

Both treated and untreated PV19 and PR122 were successfully converted into Boc-protected form, using DMF (dimethylformamide) as a solvent. However, all attempts to separate the Boc-derivatised pigments by HPLC were unsuccessful - the column was quickly poisoned and no separation was observed. Thin layer chromatography (TLC) was even worse - the silica gel, even when reverse phase-coated, catalyses the decomposition of the Boc-derivatives.

After exhausting these approaches, the treated material was separated by extraction. A DMF extract of PR122, treated with sulfanilic acid, was analysed by liquid chromatography / coupled mass spectroscopy (LC-MS) and one major compound with molecular mass =525 was identified. The probable structure of this product is given in Figure 6 (a tentative substitution point is shown).

This structural assignment is based on the fact that the UV-VIS spectrum of the treatment product is very different from the starting quinacridone, in that it has a very strong absorption at 502 nm. This indicates that the chromophore system of the quinacridone is extended with azobenzene. If there had been nitrogen elimination and direct attachment of an aryl group to the quinacridone nucleus, the resulting spectrum would be very close to that of quinacridone. So in this case, unlike PY74, the diazonium treatment of PR122 is
an electrophilic attack of the diazonium cation on the pigment molecule.

**Reactions with PV19 and PR122 are quite different**

Further changes occur when switching from PR122 to PV19. The latter is the parent quinacridone and it is more reactive than dimethylated PR122, because the most reactive ring positions (para to nitrogen) are in this case unsubstituted. Treating PV19 with diazotised sulfanilic acid or PABA proceeds easily and the dispersions obtained have a 10-20% higher sodium content than PR122. This pigment tends to be ‘cleaner’ than PR122 and the methanol extraction of untreated PV19 contains small amounts of only two minor components - HCA and AA.

DMF extraction of PABA-treated PV19 was subjected to LS-mass spectroscopy (LS-MS) analysis. Seven red dyes were identified with UV-VIS spectra very close to that of the parent PV19, which means that no change of chromophore had occurred. This indicates C-arylation, rather than attachment through the -N=N- group. Three of these seven dyes were positively identified by MS as products of mono- and bis-arylation of PV19. So in this case, there is also a reaction between quinacridone and the diazonium ion, although here elimination of nitrogen is observed.

These researches and other findings related to the diazonium reactions of colour pigments allow us to design better treating agents and develop high-performance dispersions for inkjet and other industries.

**REFERENCES**


**Results at a glance**

- Diazonium treatment is a well-established method for making self-dispersible grades of carbon black pigments. The fact that many colour pigments can be similarly treated is surprising, because they have very different surface chemistries from carbon black.
- Knowledge of the diazonium reactions of colour pigments assists in the development of high-performance dispersions, which are particularly valuable for inkjet ink use.
- The reactions of three different pigment types to diazium treatment are shown in this work to be very different.
- In the case of azo yellow, the diazonium reacts with a residual azo coupler rather than the pigment itself.
- Though quinacridone pigments such as PR122 and PV19 contain many different impurities, the diazonium reaction was shown to be with the pigment molecule itself. Some differences between the reactions on these two pigments were noted.

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Figure 1: Reaction schematic of carbon black with diazotised sulfanilic acid
Figure 2: Electronic spectra of unmodified PY 74 compared with that of the chemically modified compound (1), both measured as solutions in ethyl alcohol.
Figure 3: Synthesis of compound (1) from PY 74
Figure 4: Compound (II) - a soluble form of PY74 - is not reacting either with hydrazine or with diazonium salt.
Figure 5: Structure of 2-hydroxy-3-carboxyacridones (left) and their decarboxylated versions (right) in which R represents a methyl group (HCMA and HMA) or hydrogen (HCA and HA)
Figure 6: Structure of carboxy-anilinoacridones (left) and their decarboxylated derivative anilinoacridones (right) in which the radicals R represent a methyl group (in CMTA and MTA) or hydrogen (in CAA and AA)
Figure 7: Probable structure of PR122 derivative after treatment with diazotized sulfanilic acid
Figure 8: Probable structures of PV19 derivatives after treatment with diazotized p-aminobenoic acid