Synthesis and evaluation of novel photochromic disazo condensation pigments

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Photochromic disazo condensation pigments have been synthesized by the condensation of 1-azaphenyl mercuric acetate-2-hydroxy-3-naphthoic acid with various benzidine derivatives and subsequent treatment with dithizone. The photochromic disazo condensation pigments have been characterized by their IR spectra and elemental analysis. The kinetic study of photochromic behaviour has been investigated by preparing films of the pigment. The pigment film on exposure to sunlight or tungsten light source of suitable wavelength showed very good photochromic effect. The film regained its original colour on removal from sunlight. The duration for return of the colour depends upon the intensity of incident light, ambient temperature, moisture content and thermal treatment of the film.

Metal dithizonate dyes are one of the earliest organic dyes that were found to exhibit photochromism. In spite of the fact that several modern day dyes have dominated the world of photochromism, the interest in metal dithizonate is still alive.

Disazo condensation pigments are commonly referred to as high-grade organic pigments indicating mainly that they offer a desirable combination of good to excellent resistance to light, heat, bleeding and chemical attack. Disazo condensation pigments have found considerable application in both plastics and organic coatings. The high fastness properties of the disazo condensation pigments combined with their low density and fine particle size have also promoted their substantial use in the spin colouration of miscellaneous synthetic fibres and in the pigmentation of printing inks.

The literature survey of photochromic compounds and disazo condensation pigments, reveals that not a single photochromic disazo condensation pigment is reported. Hence, it was thought worthwhile to synthesize photochromic disazo condensation pigments. The photochromic behaviour of one of these pigment blended with PMMA have been studied.

Experimental Procedure

Synthesis of p-aminophenyl mercuric acetate [I]
The title compound was synthesized by following the procedure described in literature.

Synthesis of 1-azaphenyl mercuric acetate-2-hydroxy-3-naphthoic acid [II]
The synthesis of title compound comprises two steps

(a) Diazotization of p-aminophenyl mercuric acetate
The title compound was diazotized by following the procedure described in literature.

(b) Coupling of diazo solution with 2-hydroxy-3-naphthoic acid
2-Hydroxy-3-naphthoic acid (1.88 g, 0.01 mol) was dispersed with wetting agent, tween 20 (few drops). To this hot water (25 mL) containing sodium hydroxide (4 mL, 10% w/v) and sodium acetate (3.0 g) was slowly added. The mixture was then slowly heated till a clear solution was obtained. The solution was cooled to 0-5°C in an ice bath and a freshly prepared diazo solution was added dropwise over a period of 2 h keeping temperature below 5°C. The pH of the reaction mass was adjusted to 7.5-8.0 by addition of 10%
sodium carbonate solution. The reaction mixture was further stirred for 2 h at 0-5°C and then heated up to 60°C, diluted with water (100 mL) and further stirred for 1 h. The red coloured precipitates were filtered, washed several times with water and finally dried at room temperature, yield (75%). Crystallized in acetic acid, m.p. 218°C IR (KBr): 3300-3450 cm\(^{-1}\) (OH), 2920 cm\(^{-1}\) (C-H of caCH), 1600, 1520, 1450 cm\(^{-1}\) (phenyl ring), 1560 cm\(^{-1}\) (N=N).

Analysis: Calculated for C\(_{19}\)H\(_{14}\)N\(_2\)O\(_5\)Hg. C, 41.4%; H, 2.6%; N, 14.6%; Hg, 36.4%.

Found: C, 41.3%; H, 2.4%; N, 14.5%; Hg, 36.1%.

**Synthesis of disazo condensation pigments [III]**

A cleaned dry flask was charged with 1-azaphenyl mercuric acetate-2-hydroxy-3-naphthoic acid (18.15 g, 0.033 mol) and dry benzene (17 mL) with 2 drops of N,N-dimethyl formamide and was cooled to about 10°C in an icebath. To this thionyl chloride (2.7 mL, 0.37 mol) was added and kept overnight. The reaction mixture was refluxed at 80°C for 4 h cooled to room temperature and dry air was passed through the reaction liquid for 15 min. Excess thionyl chloride was distilled out under reduced pressure at 50°C at 5 mm of Hg. The reaction flask was cooled to room temperature and dry benzene (20 mL) was added. To this benzidine (5.8 g, 0.017 mol) in dry benzene (50 mL) was added with good stirring. The contents were refluxed at 90°C for 6 h, and the excess benzene was distilled out. The solid was filtered and washed thoroughly with water and finally dried at room temperature, yield (79%). Crystallized in acetic acid, m.p. 268-271°C.

Following the above procedure all the other disazo condensation pigments were prepared. The characterization data of all the disazo condensation pigments are presented in Table 1.
Synthesis of diphenyl thiocarbazone (Dithizone)

The title compound was synthesized by following the procedure described in literature.

Synthesis of photochromic disazo condensation pigments [IVa]

Disazo condensation pigment (IIIa) (0.01 mol), dithizone (0.01 mol) and sodium bicarbonate (0.035 mol) were mixed and then added to a vigorously stirred mixture of water (100 mL) and chloroform (150 mL) at room temperature. The mixture was stirred vigorously for 3 h and the resulting reddish pink coloured solution was evaporated under vacuum to obtain a reddish pink coloured solid. The solid product was filtered, washed with water and dried. The same procedure was used to prepare all the photochromic disazo condensation pigments. The characterization data of all the photochromic disazo condensation pigments are presented in Table 2.

Measurements

A Nicolet-400D FT-IR Spectrophotometer was used for infrared spectra of the sample in KBr pellets. The photochromic behaviour was carried out using Beckman DK-2A, Ratio Recording Spectrophotometer using sunlight as an irradiation source.

Film (0.05 mm) of photochromic disazo condensation pigment blend was prepared by blending photochromic disazo condensation pigment sample IVa (0.020 g) with polymethylmethacrylate (2.5 g) in dry chloroform (30 mL) and spreading it over a glass plate followed by evaporation of the solvent at room temperature. The film was elapsed for at least overnight before measurement of photochromism. The film was exposed to natural bright sunlight in the summer season for 0.5 to 20 min and immediately placed in a Beckman DK-2A, Ratio Recording Spectrophotometer. The change of absorbance was recorded by scanning a spectrum at various time intervals at 37°C. Absorption spectra of infinite time was taken after several days.

Results and Discussion

The reaction scheme represent the synthesis of photochromic disazo condensation pigments. All the photochromic disazo condensation pigments were characterized by infrared spectra and elemental analysis.

Fig. 1 shows the infrared spectra of some photochromic diazo condensation pigments.

Table I—Characterization data of disazo condensation pigments (IIIa)

| No. | Diamino component (R) | Molecular formula | Mol. wt | Yield (%) | m.p. (°C) | Found (%) | Calcd. (%) | H | N | R² | Value 
|-----|----------------------|-------------------|--------|-----------|-----------|-----------|-----------|----|----|----|--------
| a   | Benzidine            | C₁₀H₁₀N₂O₄Hg₂     | 1248.0 | 79        | 268-71    | 48.0      | 2.8       | 6.6 | 31.8| 0.72|
| b   | o-Tolidine           | C₁₀H₁₀N₂O₄Hg₂     | 1276.0 | 71        | 235-37    | 48.8      | 3.0       | 6.5 | 31.1| 0.69|
| c   | α-Dianisidine        | C₁₂H₁₀N₂O₄Hg₂     | 1308.0 | 75        | 260-64    | 47.5      | 2.9       | 6.3 | 30.5| 0.70|
| d   | Fast Black B         | C₁₀H₁₀N₂O₄Hg₂     | 1263.0 | 79        | 262-65    | 47.3      | 2.8       | 7.7 | 31.5| 0.65|
| e   | DDS                  | C₁₅H₁₅N₅O₅Hg₅S   | 1312.0 | 76        | 255-57    | 45.6      | 2.6       | 6.2 | 30.3| 0.74|
| f   | DDS                  | C₁₅H₁₅N₅O₅Hg₅S   | 1312.0 | 76        | 255-57    | 45.6      | 2.6       | 6.2 | 30.3| 0.74|
| g   | p-Phenylene diamine  | C₁₅H₁₅N₅O₅Hg₅S   | 1172.0 | 79        | 248-51    | 45.0      | 2.8       | 7.0 | 34.0| 0.78|

* Melting points carried out by open capillary method.

Determinations on the using chloroform:xylene (3:1) solvent system.
Table 2—Characterization data of photochromic condensation pigments (IVa-g)

<table>
<thead>
<tr>
<th>No.</th>
<th>Diamino component (R)</th>
<th>Molecular formula</th>
<th>Mol. wt. (g/mol)</th>
<th>Yield (%)</th>
<th>m.p.°C</th>
<th>Found (%)</th>
<th>Calcd. (%)</th>
<th>Hg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Benzidine</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1564.0</td>
<td>74</td>
<td>225-30</td>
<td>52.6</td>
<td>3.1</td>
<td>11.8</td>
</tr>
<tr>
<td>b</td>
<td>1-Toluidine</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1668.0</td>
<td>72</td>
<td>203-05</td>
<td>53.1</td>
<td>3.2</td>
<td>11.6</td>
</tr>
<tr>
<td>c</td>
<td>α-Dianisidine</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1700.0</td>
<td>74</td>
<td>220-23</td>
<td>52.0</td>
<td>3.1</td>
<td>11.4</td>
</tr>
<tr>
<td>d</td>
<td>Fast Black B base</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1657.0</td>
<td>77</td>
<td>198-99</td>
<td>52.0</td>
<td>3.2</td>
<td>12.5</td>
</tr>
<tr>
<td>e</td>
<td>DDM</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1654.0</td>
<td>80</td>
<td>215-17</td>
<td>52.8</td>
<td>3.2</td>
<td>11.6</td>
</tr>
<tr>
<td>f</td>
<td>DDS</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1704.0</td>
<td>77</td>
<td>192-94</td>
<td>50.6</td>
<td>3.1</td>
<td>11.3</td>
</tr>
<tr>
<td>g</td>
<td>p-Phenylenediamine</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;Hg&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1566.0</td>
<td>78</td>
<td>168-70</td>
<td>50.5</td>
<td>3.1</td>
<td>12.3</td>
</tr>
</tbody>
</table>

* Melting points carried out by open capillary method.
* Determined on tlc using pyridine-ammonia:water (12:7:2) solvent system.

Fig. 1—Infrared spectra of (a-g) photochromic disazo condensation pigments IV.<sub>a</sub>-IV.<sub>g</sub> respectively

N=N-stretching vibration. Bands around 1190-1200 cm<sup>-1</sup>, 1152 cm<sup>-1</sup> are due to N-C-S vibrations and around 690-725 cm<sup>-1</sup> (C-S) stretching and 560 cm<sup>-1</sup> are due to N-M<sup>+</sup> stretching which clearly indicates the presence of mercury dithizonate moiety<sup>10</sup>.

Other characteristic bands observed for a particular sample are as follows: 2860 cm<sup>-1</sup> due to C-H bending vibration of -OCH<sub>3</sub> group (α-Dianisidine), 1260 and 1020 cm<sup>-1</sup> due to =C-O-C stretching vibration (α-Dianisidine), 1160-1250 and 1020-1080 cm<sup>-1</sup> are due to symmetric and asymmetric S=O stretching vibration (DDS).

Spectral change during irradiation

The photochromic disazo condensation pigment PMMA-films on exposure to bright sunlight or a light source of suitable wavelength (500-W) tungsten lamp or 150-W Xenon lamp<sup>11</sup> showed very good photochromic effect. Fig. 2 indicates the spectral change of a photochromic disazo condensation pigment PMMA film for different irradiation time at 37°C. A single peak at 465 nm is observed before irradiation due to yellow orange colour. On exposure to bright sunlight a new peak appears at longer wavelength (580 nm) due to greyish blue colour, presumably because of photoinduced isomerization<sup>12</sup>. It is observed that increasing the exposure time the intensity of the original peak decreased while that of the new peak increases and finally reaches an equilibrium. Table 3 summarizes the results of the change in rate at different time intervals of the photochromic
The first order rate constants $k_1$ and $k_2$ were determined by using the equation,

$$k_1 = \frac{2.303}{t} \log \frac{D_o}{D}$$

$$k_2 = \frac{2.303}{t} \log \frac{D}{D_o}$$  \hspace{1cm} (1)

where $D_o$ and $D$ denote absorbances before and during irradiation respectively, and $t$ is an irradiation time.

**Spectral recovery in the dark**

The spectral recovery in the dark is of thermal nature, the reverse process takes place rather slowly in the solid state such as film, at ordinary temperatures. The rate of return to the original spectrum in the dark was measured by exposing the film to a bright sunlight for a fixed time (5 min) and recording the spectra after keeping for different time intervals in dark (1 min ...45 min ...infinite). Typical spectral for film of sample (IVa) are depicted in Fig. 3. Compared to Fig. 2 the reverse trend is observed i.e. the intensity of peak I (465 nm) increases and peak II (580 nm) decreases with recovery time in the dark. A single isobestic point (Fig. 3) was observed between active and normal forms indicates the absence of other reaction intermediates.

Fig. 4 show the plots of absorbance versus returning time for different exposure time of peak

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**Table 3—Photochromic behaviour of polymeric blend of PMMA and photochromic disazo condensation pigment (IVa)**

<table>
<thead>
<tr>
<th>Irradiation time (s)</th>
<th>Absorbance ratio light to dark</th>
<th>Peak-I</th>
<th>Peak-II</th>
<th>Isobestic point absorbance at 513 nm</th>
<th>$k_1 \times 10^{-3}$</th>
<th>$k_2 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.7852</td>
<td>2.7122</td>
<td>0.286</td>
<td>8.65</td>
<td>33.25</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.7768</td>
<td>2.8755</td>
<td>0.278</td>
<td>4.20</td>
<td>17.60</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.7500</td>
<td>2.9981</td>
<td>0.262</td>
<td>2.39</td>
<td>9.15</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.6913</td>
<td>3.2404</td>
<td>0.255</td>
<td>1.22</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>420</td>
<td>0.6781</td>
<td>3.5872</td>
<td>0.247</td>
<td>0.924</td>
<td>3.04</td>
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<tr>
<td>600</td>
<td>0.6517</td>
<td>3.7285</td>
<td>0.243</td>
<td>0.724</td>
<td>2.19</td>
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<tr>
<td>900</td>
<td>0.6176</td>
<td>3.8361</td>
<td>0.239</td>
<td>0.535</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.5782</td>
<td>3.9195</td>
<td>0.231</td>
<td>0.456</td>
<td>1.13</td>
<td></td>
</tr>
</tbody>
</table>

a—First order rate constant at peak I (465 nm).
b—First order rate constant at peak II (580 nm).

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Fig. 2—Spectral change of photochromic disazo condensation pigment (IVa)-PMMA film irradiated at 37°C [(1) 30 s (2) 60 s (3) 120 s (4) 300 s (5) 420 s (6) 600 s (7) 900 s (8) 1200 s and (a) before irradiation]

Fig. 3—Visible spectrum of return reaction of the photochromic disazo condensation pigment (IVa)-PMMA film exposed to sunlight for 5 min, [(a) infinite time; (1) isobestic point, curve 1-12 shows 0, 1, 2, 3, 5, 7, 10, 20, 25, 30 min after irradiation]

Fig. 4—Relationship between the absorbance at peak II (580 nm) with return reaction time in the dark at 37°C for the photochromic disazo condensation pigment (IVa)-PMMA film at different irradiation time [(a) 30 s (b) 60 s (c) 120 s (d) 300 s (e) 420 s (f) 600 s (g) 900 s and (h) 1200 s]
It is readily recognized that the return rate is rapid in the beginning which slows down after 5 min.

The first order rate constant for the recovery of the photochromic disazo condensation pigment (IVJ)-PMMA film was obtained from the expression\(^2\),

\[ k_{\text{obsd}} = \frac{2.303 \log \frac{D_o}{D_t - D_o}}{t} \]

where \( D_o \), \( D_t \) and \( D_a \) refer to the absorbance at peak II, at the beginning of the run, at time \( t \) and after complete return respectively, and the corresponding expression\(^2\),

\[ k_{\text{obsd}} = \frac{2.303 \log \frac{D_o - D_a}{D_a - D_t}}{t} \]

Table 4—Recovery in the dark, rate constant \( k_1 \) and \( k_2 \) for different irradiation time

<table>
<thead>
<tr>
<th>Irradiation time</th>
<th>50% recovery</th>
<th>( k_1 \times 10^{-3} )</th>
<th>( k_2 \times 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s )</td>
<td>time at peak II</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>4.66</td>
<td>5.00</td>
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<td>60</td>
<td>8</td>
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<tr>
<td>120</td>
<td>8</td>
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<td>4.16</td>
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<tr>
<td>300</td>
<td>12</td>
<td>1.94</td>
<td>3.00</td>
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<tr>
<td>420</td>
<td>13</td>
<td>1.66</td>
<td>2.66</td>
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<tr>
<td>600</td>
<td>17</td>
<td>2.00</td>
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<tr>
<td>900</td>
<td>20</td>
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<tr>
<td>1200</td>
<td>22</td>
<td>1.01</td>
<td>1.20</td>
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</table>

a—First order rate constant at peak I (465 nm).
b—First order rate constant at peak II (580 nm).

\[ \text{Fig. 5—Relationship between } \ln \left( \frac{D_o}{D_t - D_a} \right) \text{ vs } t, \text{ time of returning in the dark at peak II (580 nm) for the photochromic disazo condensation pigment (IVJ)-PMMA film at different irradiation time [(a) 30 s (b) 60 s (c) 120 s (d) 300 s (e) 420 s (f) 600 s (g) 900 s and (h) 1200 s]}
\]

\[ \text{Fig. 6—Relationship between } \ln \left( \frac{D_o - D_a}{D_t - D_o} \right) \text{ vs } t, \text{ time of returning in the dark at peak I (465 nm) for the photochromic disazo condensation pigment (IVJ)-PMMA film at different irradiation time [(a) 30 s (b) 60 s (c) 120 s (d) 300 s (e) 420 s (f) 600 s (g) 900 s and (h) 1200 s]}
\]

\[ \text{Fig. 7—A plot of } \left( \frac{D_o}{D_t} \right) \times 100 \text{ vs } t, \text{ where } D_o \text{ and } D_t \text{ denote the absorbance immediately after exposure time and returning in the dark, respectively, } t \text{ is returning time in min [(a) 30 s (b) 60 s (c) 120 s (d) 300 s (e) 420 s (f) 600 s (g) 900 s and (h) 1200 s]}
\]

\[ \text{where } D_o, D_t \text{ and } D_a \text{ now refer to the absorbance measured at peak I. Fig. 5 shows a plot of } \ln \left( \frac{D_o}{D_t - D_a} \right) \text{ vs } t \text{ at peak II and Fig. 6 show a plot of } \ln \left( \frac{D_o - D_a}{D_t - D_o} \right) \text{ vs } t \text{ at peak I for various exposure times. The rate constants } k_1 \text{ and } k_2 \text{ are calculated from the above plots. 50% recovery of the return absorbance in the dark at 580 nm was calculated from the terms } D_o/2D_a \times 100 \text{ (Fig. 7) where } D_o \text{ and } D_t \text{ denote the absorbance immediately after exposure time and returning}
\]
References


Conclusions

All the photochromic disazo condensation pigments were obtained in good yield. The pigment blend with PMMA gives good photochromic effect. The pigment film after repeated exposure reaches a steady-state of equilibrium. The first order rate constants decrease with increasing irradiation time. During recovery in the dark, the first order rate constant $k_2$ is decreased but such trends are not observed in the first order rate constant $k_1$. 

References