

## Colorimetric investigation of the reaction between *p*-phenylenediamine and *meta*-substituted derivatives of benzene on a model support

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### Synopsis

The aim of this work was the employment of colorimetric techniques in the analysis of the color formed, on a proteic substrate, by the reaction between *p*-phenylenediamine and some *meta*-substituted benzene derivatives in the presence of hydrogen peroxide and in media at different pH values. In particular we investigated the chromatic variations that take place on the substrate in dependence on different reaction conditions. The obtained results show that for each couple of reagents the colorimetric data, namely the reflectance of the formed color, change considerably with the pH of the reaction medium and demonstrate how this parameter can be considered a good descriptor of the composition of the formed pigment.

### INTRODUCTION

The reaction of *p*-phenylenediamine (PPD, precursor) with *meta*-derivatives of benzene, having amino and/or hydroxy groups as substituents (couplers), is widely applied in oxidative hair dyeing. The general pathway of these reactions has been explained by Corbett (1–7) (Figure 1), who has pointed out that it is not unique, is affected by the reagents' concentration, and is strongly sensitive to the pH of the solution.

The *p*-quinone di-imine 1, or rather its conjugated acid 2, is the key species of the whole process of dye formation. According to Corbett, at pH > 8 and using ferricyanide as oxidant, the oxidation of *p*-phenylenediamine (PPD) to the di-imine 1 is quantitative and very fast (1). Even if the reaction kinetics may vary with different couplers, the indo dye 3 is the main product because in these conditions the self coupling of *p*-phenylenediamine, which yields the Bandrowski's base 4, may be considered negligible. In contrast, with hydrogen peroxide, the rate of formation of the di-imine 1 is slow and the indo dye 3 can react with the unoxidized *p*-phenylenediamine, leading to molecule 5, which is considered

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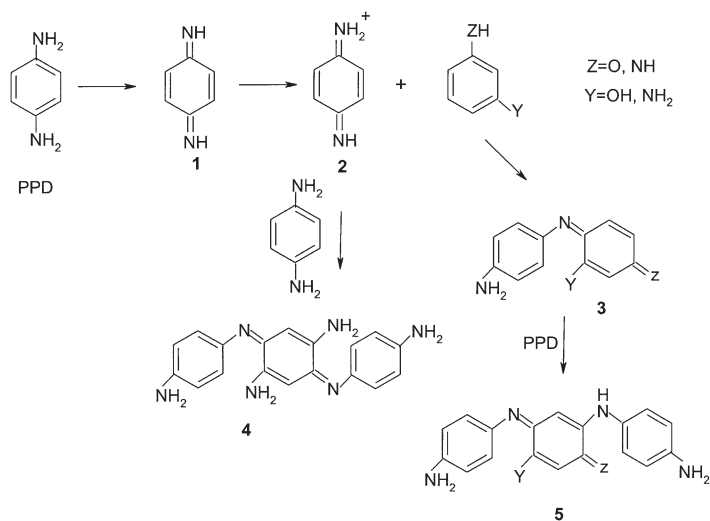


Figure 1. General pathway of reactions of *p*-phenylenediamine with *meta*-derivatives of benzene.

the major colored species formed through the process (6). Because the rate of formation of the Bandrowski's base 4 is slower than that of the reaction of *p*-phenylenediamine with the couplers, the literature data exclude the fact that in these conditions, even if more favorable, this compound could be formed (2–5).

The permanent hair-coloring process employs hydrogen peroxide as an oxidant and involves the in-fiber formation of indo dyes. According to Corbett, the hair could influence the relative diffusion rates of the reagents inside the fiber (7). For this reason it has been concluded that knowledge of the kind of colored molecules produced by these reactions in aqueous solution could not be easily extended to hair dyeing (7). On the other hand, the quantization of the colored species formed in the hair appears difficult because of the complexity of the reactions. In fact, in some cases the species 3 and 5 may also be transformed to high-molecular-weight colored molecules (6,8). For these reasons, the prediction of the chromatic outcome performed by a mixture of precursors and couplers in the hair dyeing process is, at present, an unsolved question.

Since the solution of this problem is related to the overall characteristics of the color obtained at the end of the dyeing process, colorimetric analysis could be a useful tool in this investigation. In fact, the reflectance of the dyed support can be considered a useful indication of the colored pigments produced in the dyeing process. In this respect, investigation of the color reflectance variations produced on a support by a couple precursor–coupler under different reaction conditions could be a new and useful approach to the problem.

Our study on the color and on the color variations induced on a model substrate by the reaction of *p*-phenylenediamine with different couplers at different pH values in the presence of hydrogen peroxide constitutes a first step in this direction. Virgin wool, being of a proteic nature, was considered suitable as a model substrate for human hair. Some differences exist between hair and wool, but we consider this aspect subordinate to providing homogeneous samples without complicating pigments. In addition, wool fabric has been used by others as a model support for human hair for predicting the tanning reaction of dyes (9). Resorcinol, 2-methylresorcinol, 3-aminophenol, and 2-amino-4-(2-hydroxyethylamino)

anisole sulfate, employed in current hair dye formulations, were chosen as model couplers. Seven pH values in the range of 7.5–10.5 were investigated.

## MATERIALS AND METHODS

### MATERIALS

Technical grade *p*-phenylenediamine (PPD), resorcinol (RES), 2-methylresorcinol (MeRES), 3-aminophenol (AP), 2-amino-4-(2-hydroxyethyl-amino)anisole sulphate (AHA), and perhydrol were kindly provided as a gift by Tocco Magico (Italy) and utilized without further purification. Perhydrol, stabilized with phosphoric acid, was opportunely diluted to obtain hydrogen peroxide at 20 volumes. TLC was performed on preparative 20 × 20-cm, 1-mm, Silica gel 60 F<sub>254</sub> plates from Merck (Germany).

### METHODS

The commercial virgin wool tissue, cut in 5 × 20-cm strips, was washed with a non-ionic detergent aqueous solution, rinsed with water, and dried before the coloration. Each strip was dipped in 100 ml of a solution formed by 50 ml of hydrogen peroxide (20 volumes, 6%) and 50 ml of a solution containing the *p*-phenylenediamine-coupler (1:1 ratio) and the ammonium hydroxide needed to obtain the final required pH value. After 30 minutes the strip was removed, carefully rinsed with tap water, and dried at 45°C. In each experiment the reagents' concentration (precursor and coupler) was  $2 \times 10^{-2}$  M. Experiments were carried out at pH 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, and 10.5. pH values were monitored at room temperature with a Metrohm pH-meter 744. The colorimetric measurements were performed with a colorimeter X-Rite SP62 model, with an integration sphere to determine the color reflectance. The L, a\*, and b\* values reported are related to the illuminant D65 at 10 degrees. Each reported value is the mean of ten measurements, performed randomly on the surface of the colored strips, with standard deviation never exceeding 1.2%. In these conditions the colorimetric data of virgin wool were: L = 95.12, a\* = 0.05, and b\* = 6.73.

TLC experiments were carried out by spotting about 0.5 ml of the aqueous solution of the performed reaction on a strip of 5 cm and eluting with CHCl<sub>3</sub>:EtOAc:EtOH 7:2:1. For the weathering experiments, two wool strips were colored with the color mixture obtained with each couple of reagents at the stated pH. One of these was directly exposed to atmospheric agents; the other one was weathered, avoiding a direct exposure to sunlight in order to distinguish the color degradation induced in the presence or in the absence of direct sunlight. The weathering experiments were carried out for 24 days. At days 0, 4, 7, 11, 14, 18, and 24 the color of each strip was measured. All the experiments were performed in duplicate.

## RESULTS AND DISCUSSION

Preliminary experiments showed that for each pair of precursor-coupler, the color reflectance produced on the wool strips was constant ( $R_{\infty}$ ) when the reagents' concentration was  $\geq 1 \times 10^{-2}$  M. As a consequence, a  $2 \times 10^{-2}$  M concentration of the two reagents was employed in all the reported experiments. The values of the colorimetric parameters (L, a\*, b\*), from each pair of *p*-phenylenediamine-coupler at different pH values, are reported in Table I.

**Table I**  
L, a\*, b\* of the Colors Due to the Reaction of *p*-Phenylenediamine with Different Couplers as a Function of pH

Colorimetric Parameters	pH						
	7.5	8	8.5	9	9.5	10	10.5
	RES						
L	17.31	16.08	17.04	28.61	36.78	41.4	45.13
a*	1.24	1.03	1.43	3.64	3.49	2.52	2.12
b*	2.72	1.96	2.99	11.91	15.44	18.04	17.56
	MeRES						
L	17.51	18.18	20.51	30.28	43.15	49.01	48.41
a*	5.21	5.5	6.8	9.24	8.98	8.8	9.1
b*	5.39	5.97	8.02	12.7	13.36	16.85	18.49
	AP						
L	17.22	20.47	20.72	21.74	28.05	28.08	27.05
a*	1.24	1.22	1.32	2.36	5.39	7.77	8.48
b*	3.74	5.3	5.39	5.77	4.44	1.67	0.78
	AHA						
L	24.77	23.09	19.63	18.39	13.36	13.8	15.86
a*	5.43	5.44	5.39	6.61	4.46	3.95	3.82
b*	-11.65	-11.58	-11.36	-14.38	-9.13	-9.98	-11

The colorimetric data for each coupler, even if in different way, show that by increasing the pH of the medium, in the pH range of 8.5–9.0 a considerable color variation takes place. In order to achieve an estimate of the presumably different distributions of colored pigment formed by these reactions above and below this pH range, the reaction solutions of PPD both alone and with each coupler at pH 7.5 and 9.5 were analyzed by preparative thin-layer chromatography. In the absence of a coupler and at pH 7.5, the best conditions for the Bandrowski's base formation (2), the TLC from PPD alone shows the presence of several colored bands. The main band contains an intense dark brown component ( $R_f = 0$ ) that, according to the literature, is a high-molecular-weight material, and an intense dark blue band ( $R_f = 0.15$ ) that the literature data assign to Bandrowski's base (10). The L, a\*, and b\* values of the color formed on wool by PPD under the same conditions are 15.98, 1.24, and -4.04, respectively, and may be considered in agreement with the TLC data.

The reaction between resorcinol (RES) and PPD, according to Corbett (6), gives a very unstable magenta hydroxyindoaniline 3 that may lead to a brown polymer (polymeric hydroxyindoaniline) and to a dark green molecule 5 that, furthermore, may be transformed to low-molecular-weight brownish intermediates (8). From the data reported in Table I, in the pH range of 7.5–8.5, the pigment formed on the wool shows a small L value, with values of a\* and b\* very near to zero (very dark brown color). For pH values >9.0 a strong increase of b\* takes place, while the value of a\* even if positive, is always small. The pigment formed in the range of pH 9.0–10.5 is a brown that moves to light brown. TLC of the system PPD-RES at pH 7.5 shows many other minor products having  $R_f > 0.5$ , a strong dark brown component with  $R_f = 0$ , a trace of a narrow dark blue band (Bandrowski's base), and a large moderate brown/light greenish band with  $R_f = 0.2$ –0.3. At pH 9.5 the brown/light greenish band is more intense, while the component with  $R_f = 0$  has almost disappeared. The colorimetric data appear consistent with the

chromatographic data. Indeed, at lower pH, the recognized L,  $a^*$ , and  $b^*$  values agree with the strong prevalence of a dark brown pigment formed by reaction between PPD and RES or by PPD with itself. When the pH is increased, the colorimetric values show that the formation of the dark brown pigment falls in the pH range of 8.5–9.0. At pH > 9.0 the increase in  $b^*$  value is consistent with the prevalence of moderate brown components of probably low molecular weight, while the moderate increase in  $a^*$  could be due to the presence of the dark green molecule 5 (in the CIELab space the green color is characterized by positive  $b^*$  and negative  $a^*$  values, while for the brown color  $a^*$  and  $b^*$  are always positive).

As regards 2-methylresorcinol (MeRES), the pigment formed is always a brown color (from dark to medium brown) that is different from RES and is characterized by some reddish shade when the pH value is increased (see Table I). The TLC of the mixture of the reaction carried out at pH 7.5 shows a moderate-intensity dark brown band with  $R_f = 0$ , a dark blue small band with  $R_f$  identical to that of the Bandrowski's base, and a moderate brown band followed by a large reddish one ( $R_f = 0.2$ – $0.3$ ). At pH 9.5 the component with  $R_f = 0$  is at a low concentration and the brown/reddish band is very intense, indicating that the formation of this pigment is favored by the higher pH. This reddish band could be due to the presence of the indoaniline 3. In the case of RES this species is not detectable and, according to Corbett, is highly unstable. After prolonged exposure to the daylight of the TLC plate, the reddish band turns to brown.

In order to obtain further information about the features of the colored pigments derived from these two couplers, weathering experiments were performed as described in the Methods section. The only significant data were those obtained from direct sunlight exposure of the colored wool samples. The pigments obtained at pH  $\leq 8.5$  from both couplers faded moderately after sunlight exposure, and the relative L,  $a^*$ , and  $b^*$  values are not reported. The data related to the weathering of the pigments obtained at pH  $\geq 9.0$  appear particularly interesting and are reported in Table II and III.

It is evident that the brown colors from resorcinol fade moderately while the colors from MeRES fade with a progressive reduction of the redness converging to a brown color. These results suggest that the products deriving from RES and MeRES by sunlight may be similar. The colorimetric data related to the couple 3-aminophenol (AP) and PPD (see Table I) provide a dark brown color that moves to a dark red-purple at pH > 9.5. Starting from pH 9.0 the value of  $b^*$  rapidly decreases while  $a^*$  increases. These data are in agreement with TLC results. In fact, TLC of the reaction performed at pH 7.5 shows a grey-brown pigment with  $R_f = 0$ , and a large brown band followed by a red-purple band. At pH 9.5 the compounds with  $R_f = 0$  are identical but the red-purple band is much more intense. On exposure to daylight, the red-purple band turns to brown. According to Corbett (5), with ferricyanide the magenta aminoindoaniline 3 may be considered the only product, while with hydrogen peroxide the formation of the brown molecule 5 should be preferred. Our results, on the contrary, show that hydrogen peroxide also supports the formation of aminoindoaniline 3. The progressive lowering of the  $b^*$  value when the pH is rising agrees with an increase of the red-purple pigment.

Weathering experiments carried out on wool strips colored at pH 10.5 (see Table IV), the best approach to obtaining the compound 3, show that also without the direct sunlight, four days are enough to realize a strong variation from a dark red to a brown color. These results point out that the aminoindoaniline 3 is very unstable, leading, like RES and MeRES, to a brown color.

**Table II**  
Weathering Effect on Color Fastness of PPD-RES with Direct Sunlight Exposure

Colorimetric Parameters	Days						
	0	4	7	11	14	18	24
	pH 9.0						
L	28.61	26.73	27.68	28.91	30.1	31.43	32.41
a*	3.64	3.78	3.98	4.29	4.61	4.46	4.57
b*	11.91	11.08	11.37	11.79	12.16	12.64	13.02
	pH 9.5						
L	36.78	33.69	35.57	38.18	39.04	40.36	43.5
a*	3.49	3.95	4.18	4.45	4.63	4.43	4.45
b*	15.44	14	14.11	14.43	14.4	14.64	15.43
	pH 10.0						
L	41.4	40.17	42.34	44.69	46.4	47.82	49.47
a*	2.52	3.46	3.59	3.68	3.81	3.54	3.67
b*	18.04	16.36	15.93	15.47	15.34	15.42	15.74
	pH 10.5						
L	45.13	45.82	47.68	50.13	52.02	53.39	54.97
a*	2.12	2.94	3.07	3.16	3.16	2.93	2.94
b*	17.56	15.95	15.45	14.98	14.8	14.83	15.02

**Table III**  
Weathering Effect on Color Fastness of PPD-MeRES with Direct Sunlight Exposure

Colorimetric Parameters	Days						
	0	4	7	11	14	18	24
	pH 9.0						
L	30.28	29.43	30.93	32.65	33.27	36.01	35.52
a*	9.24	9.07	8.49	7.73	7.51	6.98	6.71
b*	12.7	12.56	12.4	12.41	12.39	12.72	13.07
	pH 9.5						
L	43.15	42.28	44.2	45.51	47.5	48.05	50.9
a*	8.98	8.77	7.78	7.1	6.61	6.03	5.35
b*	13.36	13.57	13.09	13.06	12.68	13.16	13.31
	pH 10.0						
L	49.01	48.37	50.91	52.36	54.5	55.39	56.89
a*	8.8	8.62	7.48	6.75	6	5.48	4.97
b*	16.85	16.37	15.39	15.12	14.8	14.95	14.86
	pH 10.5						
L	48.41	48.16	51.11	52.89	54.76	56.64	58.92
a*	9.1	8.68	7.49	6.66	6.05	5.28	4.62
b*	18.49	17.22	16.08	15.43	15.05	14.91	15.03

Table IV  
Weathering Effect on Color Fastness of PPD-AP at pH 10 without Direct Sunlight Exposure

Colorimetric Parameters	Days						
	0	4	7	11	14	18	24
L	27.59	28.56	29.04	29.26	29.4	29.89	30.29
a*	8.31	7.15	6.75	6.36	6.36	5.88	5.93
b*	1	2.54	3.15	3.62	3.75	4.3	4.43

Table V  
Weathering Effect on Color Fastness of PPD-AHA without Direct Sunlight Exposure

Colorimetric Parameters	Days						
	0	4	7	11	14	18	24
pH 9.0							
L	18.39	18.72	21	24.25	26.13	28.34	31.05
a*	6.61	4.8	4.05	3.44	3.03	3	2.58
b*	-14.38	-10.04	-6.91	-3.77	-2.08	-0.55	-1.32
pH 9.5							
L	13.36	13.66	14.36	15.41	16.65	18.11	20.24
a*	4.46	3.97	3.75	3.53	3.38	3.44	3.18
b*	-9.13	-8.1	-7.08	-5.84	-4.8	-3.68	-2.25
pH 10.0							
L	13.8	14.46	15.59	17.27	18.89	20.83	23.66
a*	3.95	2.78	2.13	1.74	1.56	1.77	1.68
b*	-9.98	-7.85	-5.88	-3.71	-2.09	-0.52	1.31
pH 10.5							
L	15.86	17.11	19.46	22.25	24.2	27.19	30.92
a*	3.82	2.1	1.23	0.9	0.74	0.86	0.71
b*	-12	-8.41	-5.19	-1.87	0.21	2.1	3.9

The colorimetric data of the pigment deriving from the couple 2-amino-4-(2-hydroxyethylamino)anisole sulfate (AHA) and PPD (see Table I) show that, in all the range of pH values under study, L, a\*, and b\* values are typical of the purple-blue color. TLC shows at pH 7.5 the presence of a strong dark brown pigment, with  $R_f = 0$ , and a large and strong blue band, with  $R_f = 0.1-0.25$ . At pH 9.5 the band with  $R_f = 0$  is light (yellow brown) while the blue band is very strong. Furthermore, the blue band turns slowly to brown by exposure to daylight (Table V).

Corbett states that the reaction rate between PPD and aromatic *m*-diamines is very high. The analysis of the color formed in the tested pH range really suggests that the blue aminoindamine 3 or the trinuclear derivative 5 are always the main products of the reaction. In spite of this, the pigment formed is very sensible to weathering also in the absence of the direct action of sunlight. The color fades and turns from blue to a purple shade and finally to dark brown or dark red (Table V).

## CONCLUSIONS

The whole of the experimental data show how it is possible to follow satisfactorily the variation of the pigment composition obtained from the reactions under a study carried out at different pH values by colorimetric analyses. In fact, if the colorimetric data can be considered a good descriptor of the formed pigment, our hypothesis of using the reflectance as an innovative parameter for the prevision of the color yielded by such reactions can be asserted. Furthermore, the obtained data show that the color formed on the wool may be considered a good expression of the whole of the chromatic features of the major components present in the reaction solution. The results agree with the hypothesis that the wool fiber does not interact chemically with the colored molecules.

The weathering experiments show that, for all the couplers, the color decay, near to the destruction of the colored molecules, displays color alterations similar to those shown by the same colored molecules on an inert support like the silica gel used for the TLC. Since the color fastness on the wool is greater than that on TLC plates, we can assume that the colored molecules reside in the interior of the wool fiber. The data seem to exclude any chemical interaction between the support and the dye formation, and as a consequence, wool seems to be an ideal substrate for a preliminary study of the application of colorimetry as a new base of inspection in color prediction.

## ACKNOWLEDGMENTS

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