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Synthesis of derivatives of Naphtol AS containing polar groups and modification used for C.I. Pigment Red 57

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Abstract

The synthesis of derivatives of Naphtol AS containing polar groups (–COOH, –SO_3H) and factors affecting the reaction have been studied. Four derivatives of Naphtol AS containing –COOH or –SO_3H groups in the 3- or 4-position of the phenyl ring were synthesized. Derivatives of Naphtol AS as the second coupling component were used in mixed coupling and the effect of its added amount on the colour strength, hue, flowability and dispersing extent (in water) of pigments was studied. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: C.I. Pigment Red 57; Naphtol AS derivative; Modifier; Mixed coupling

1. Introduction

Derivatives of Naphtol AS are important intermediates which can be used in the preparation of various insoluble azo pigments and as a modifier used for modification of mixed coupling methods for azo pigments [1,2]. Little information about the synthesis of Naphtol AS containing –COOH or –SO_3H groups in the 3- or 4- position of the phenyl ring has been reported [4]. In this paper, four derivatives of Naphtol AS are prepared and major factors affecting the reaction discussed.

The application properties of pigments, such as shade, colour strength, dispersibility and flowability depend on their chemical constitution and physical properties such as crystal phase and polarity of the particle surface. Mixed coupling with derivatives of the coupling component is one effective process for improving the physical properties of pigments [4–6]. C.I. Pigment Red 57 was modified by mixed coupling with derivatives containing polar groups as the second coupling component. The dispersing extent in aqueous medium, flowability, colour strength and shade of the modified pigment were studied.

2. Experimental

2.1. Preparation of N-(p-carboxylphenyl)-2-hydroxy-3-naphthylamide (I) and N-(m-carboxylphenyl)-2-hydroxy-3-naphthylamide (II)

A mixture of BON-acid(2-hydroxy-3-naphthoic acid) 0.01 mol, *p*(*m*)-amino benzoic acid 0.01 mol and O-dichlorobenzene 5 cm^3 was heated to 70–80°C, then PCl_3 0.015mol was added dropwise to

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the mixture in the presence of small amount of DMF at 140°C and the mixture refluxed 2 h. Solvent was removed under reduced pressure, water (20 cm^3) added and the mixture stirred 20 min, and then allowed it to stand overnight. It was then filtered and the residue washed and dried. The yields of (I) and (II) were 92 and 94%, respectively. ((I): Found C 70.25; H 4.23; N 4.53; Calc. C 70.30; H 4.23; N 4.56; (II): Found C 70.28; H 4.20; N 4.60; Calc. C 70.30; H 4.22; N 4.53).

*2.2. Preparation of N-(*p*-sulfonic-phenyl)-2-hydroxy-3-naphthylamide (III) and N-(*m*-sulfonic-phenyl)-2-hydroxy-3-naphthylamide (IV)*

A mixture of BON-acid 0.01 mol, solvent (see Table 3) 8 cm^3 and the appropriate anilinesulfonic acid 0.01 mol was heated to 70°C; PCl_3 (0.015 mol) was added dropwise and the mixture refluxed 2 h, then treated according to section 2.1. ((III): Found C 59.41; H 3.80; N 4.08; S 9.30; Calc. C 59.38; H 3.78; N 4.06; S 9.31; (IV): Found C 59.40; H 3.82; N 4.08; S 9.34; Calc. C 59.38; H 3.78; N 4.06; S 9.31).

2.3. Modification of C.I. Pigment Red 57

BON-acid (2.97×10^{-2}, 2.95×10^{-2}, 2.93×10^{-2}, 2.90×10^{-2} mol) was coupled with the equivalent of the diazonium salt of 4B acid (4-chloro-5-methyl-2-anilinesulfonic acid), respectively. At the same time, the derivatives of Naphtol AS (3.00×10^{-4}, 5.00×10^{-4}, 7.00×10^{-4}, 10.00×10^{-4} mol) containing polar groups in aqueous sodium hydroxide were added and, after coupling was complete, the liquors were stirred for a further 30 min, filtered, and the residues washed and dried at 60°C.

2.4. Determination of properties of pigments modified

The shade, flowability and colour strength of the pigments were determined according to Chinese National Standard GB1864-80, 1719-79, 1708-79, respectively. The measurement of the dispersing extent (D.E.) of pigments was effected by literature procedures [7]. Elemental analysis and MS were made by means of a PE-2400 (made by Perkin–Elmer) and MAT-312/SS200 (made by Finnegan), respectively.

3. Results and discussion

3.1. Synthesis of Naphtol AS derivatives

Derivatives of Naphtol AS containing polar groups (–SO_3H and –COOH) in the phenyl ring were obtained by heating BON-acid and the appropriate aminobenzoic acid or anilinesulfonic acid in the presence of PCl_3 catalyst and solvent (o-dichlorobenzene).

3.1.1. Syntheses of Naphtol AS derivatives containing a –COOH group

The effect of the amount of PCl_3 on the condensation reaction was investigated; the results are shown in Table 1.

The results show that reaction yield tends to increase with increasing amount of PCl_3. When the mole ratios of BON-acid and PCl_3 are between 1:0.5 and 1:1.5, the yields are very high; with a yield of about 92% for the ratio 1:1. Under the optimum reactants ratio, the change of reaction yields at various times were studied using

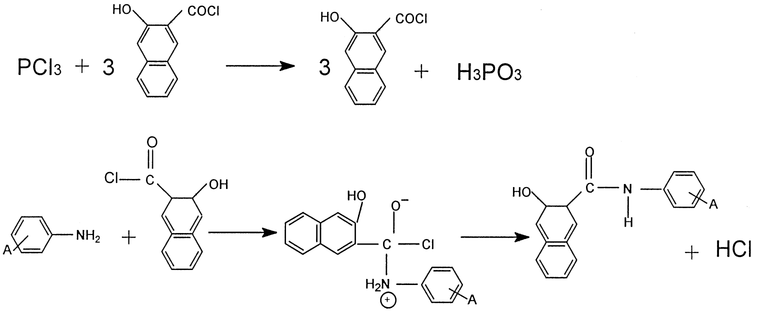


Table 1
Yields and TLC of intermediate (I) at various concentrations of PCl_3[a]

No.	BON-acid (mol)	BON-acid/PCl_3	Yield (%)
M-1	0.01	1:0.5	87
M-2	0.01	1:1	92
M-3	0.01	1:1.5	80
M-4	0.01	1:2	55

[a] p-$NH_2C_6H_4COOH$, 0.01 mol; DMF, 0.01 mol; o-dichlorobenzine, 5 ml; 140°C, 2 h; TLC; mobile phase benzene:*iso*-propanol:aqueous ammonia = 8:18:9 (vol.). R_f 0.66 (BON-acid), R_f 0.60((I)).

dichlorobenzene as solvent and in the presence of DMF; relevant data is shown in Table 2.

Within the reaction times used, the longer the reaction time, the higher was the condensation yield. When the reaction time was within 1 h, the yield reached 80%, and the yield was 87% within 2 h. When the reaction time was further prolonged, reaction yields were not increased.

On the basis of the above experimental conditions, condensation reaction was carried out in which *p*-amino benzoic acid was replaced by *m*-amino benzoic acid, and the yield was 94%. The MS of the intermediates prepared were measured and the appropriate molecular ion peaks at m/e = 307 were clearly evident.

3.1.2. Preparation of Naphtol AS derivatives containing an $-SO_3H$ group

In the presence of phosphorous trichloride , BON-acid was condensed with the appropriate anilinesulfonic acid and the effect of different kinds of solvents on the yield is shown in Table 3.

Table 2
Effect of reaction time on the condensation reaction of intermediate [I]

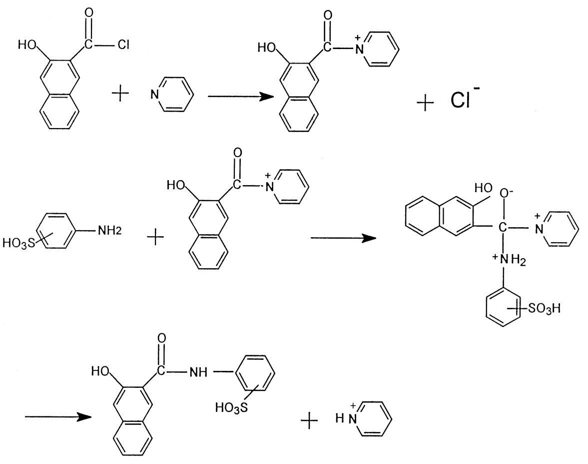
No.	BON-acid (mol)	PCl_3 (mol)	Amino-benzoic acid (mol)	Reaction time (h)	Yield (%)
M-5	0.01	0.5	0.01	0.5	60
M-6	0.01	0.5	0.01	1.0	80
M-7	0.01	0.5	0.01	2.0	87
M-8	0.01	0.5	0.01	3.0	87
M-9	0.01	0.5	0.01	5.0	85

Table 3
Yield of intermediate (III) using various solvents[a]

No.	Solvent	ϵ (25°C)	μ (D)	$E_T(30)$ (kcal/mol)	Yield (%)
N-1	Pyridine	12.4	2.37	3.0	87.4
N-2	o-Dichlorobenzine	9.93	2.27	2.57	75.1
N-3	PhCl	5.62	1.54	2.30	67.2
N-4	DMF	2.38	—	1.90	55.3

[a] BON-acid, p-sulfonilic acid, 0.01 mol; DMF, 0.01 ml; PCl_3, 0.005 mol; solvent 5 ml; 70°C, TLC: mobile phase, benzene:*iso*-propanol:aqeous ammonia = 1:18:9(vol.); R_f 0.57.

According to the Hughes–Lngolol rule, the initial reactants are transformed into an active complex compound and on increasing the solvent polarity, the reaction rate increases. Data in Table 3 show that with decreasing solvent parameters $E_T(30)$ and ϵ value, the condensation yields also reduce. When pyridine is used as solvent, the reaction yield is the highest because pyridine acts both as an acid binding agent and as a catalyst for the nucleaphilic reagent in the reaction.



The basicity of pyridine is much higher than that of the anilinesulfonic acid, so the reaction activity of pyridine attacking the acyl chloride is higher than that of the anilinesulfonic acid, and the acyl pyridine ammonium ion then more easily reacts with the anilinesulfonic acid. This means that the reaction is catalysized by pyridine. When this condensation reaction was carried out aniline *p*-sulfonic acid instead of aniline-*m*-sulfonic acid, the yield of the intermediate IV is 92% (R_f 0.62). It is concluded from the above results that the alkalinity of aniline-*m*-sulfonic acid is slightly stronger than that of aniline-*p*-sulfonic acid, and the former reagent gives the higher yield.

3.2. Modification of C.I. Pigment Red 57

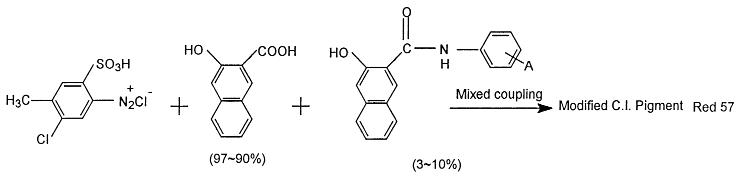
Derivatives of Naphtol AS (I)–(IV) were used as the second coupling component of modification for the C.I. Pigment Red 57 (Carmine 6B).

3.2.1. Effect of the second coupling component on properties of pigments

The shade, colour strength and flowability of pigment modified with the intermediates I–IV were studied and some of the results are shown in Table 4.

With addition of the second coupling, the colour strength and transparency of the pigment are obviously increased and the shade of the modified pigments is slightly bluish red. This is advantageous to the rapid production of the crystal core of the pigment and restrains crystalline growth. Under the experimental condition, the producing rate of the crystal core is faster than the growing rate. In this case , the particle size of the modified pigment becomes smaller and the specific surface becomes larger. The oil absorption is enhanced and flowability is also decreased, with increase in the colour strength. Because of the increased conjugation chain of the lake pigment, the modified pigment is more bluish red in here, but when the amount of the second coupling component is too high (10%), the pigments become a strong bluish red.

Colour measurement parameters of pigment modified with intermediate II were determined and the results are shown in Table 5. It is apparent that ΔE (chromatic difference) is between 7.8 and 9.83 and that the modified pigments have an obvious difference compared with the standard sample. The ΔH of modified pigments A and B show a negative value. The modified pigments have a bluish hue compared with the standard sample, and the shade becomes gradually bluer with amount of modifier from 3 to 5%. The Δ*C*



A: -SO$_3$H or -COOH

Table 4
The properties of the modified Carmine 6B

No.	Modifier	Amount (%)	Shade[a]	Flowability (mm)	Transparency[b]	Colour strength
Carmine 6B	–	–	B	34	+	100
P-1	(II)	3	B	38	+	105
P-2	(II)	5	B	34	+ + +	110
P-3	(II)	7	B B	33	+ + +	115
P-4	(II)	10	B B B	27	+ +	Strong bluish red
P-5	(IV)	3	B B	37	+	105
P-6	(IV)	5	B B	33	+	110
P-7	(IV)	7	B B	31	+ + +	115
P-8	(IV)	10	B B B	31	+ +	Strong bluish red

[a] B: slightly blue; BB: fairly blue; BBB: strong bluish red.

[b] +: slightly transparent; + +: fairly transparent; + + +: strongly transparent.

Table 5
CIELAB values of modified pigments

Product	Modifier	Amount (%)	x	y	ΔE	ΔL	ΔC	ΔH
Carmine 6B	–	–	18.49	10.79	–	–	–	–
Modified pigment A	(II)	3	23.24	13.32	7.80	4.01	6.56	−1.5
Modified pigment B	(II)	5	24.79	14.31	9.83	5.45	7.71	−2.7

data of the modified pigments A and B have a positive value and these modified pigments are more brightly coloured than the unmodified pigments. From these results, it is concluded that when the intermediate II is used as the second coupling component in the mixed coupling, the shade of the modified pigment is more brightly coloured and bluer.

3.2.2. Dispersing extent of modified pigments in aqueous medium

The surface of the modified pigment has a lot of polar groups, such as carboxyl and sulfonic acid groups, which are present in the intermediates I–IV. The phenyl ring of intermediates containing these polar groups can freely rotate and the polar groups can stretch out of the pigment surface. Figs. 1 and 2 show that the dispersing extent (D. E.) of the pigments modified with intermediate II (3–7%) and intermediate IV (7%) is excellent. The D. E. of pigments modified with I and III is also improved. The modified pigments would thus provide outstanding compatibility in aqueous medium and are preferably employed as water based inks or paints.

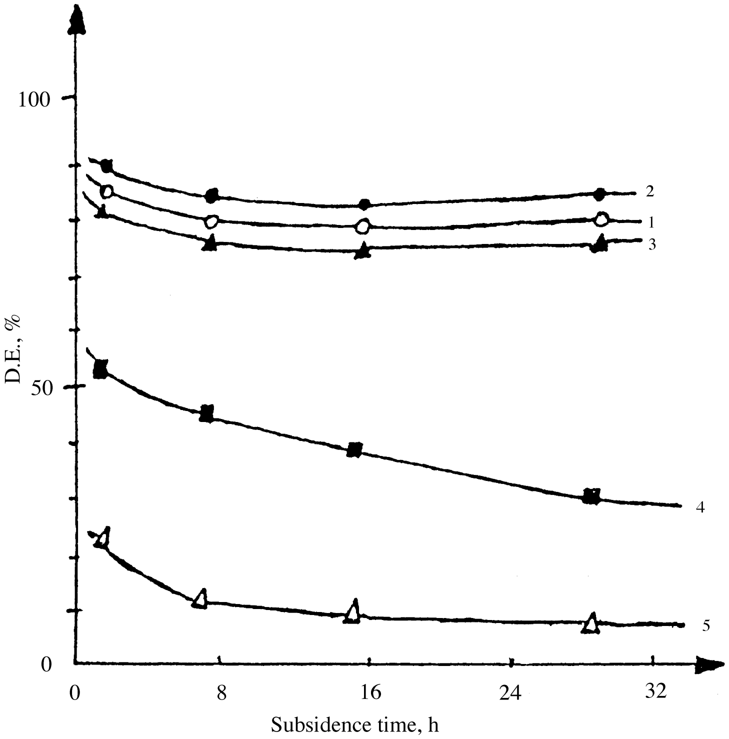


Fig. 1. Dispersion curves of mixed coupling pigments with intermediate (II) in water. Curves 1–5 represent added amount of 3, 5, 7, 10% and Carmine 6B, respectively.

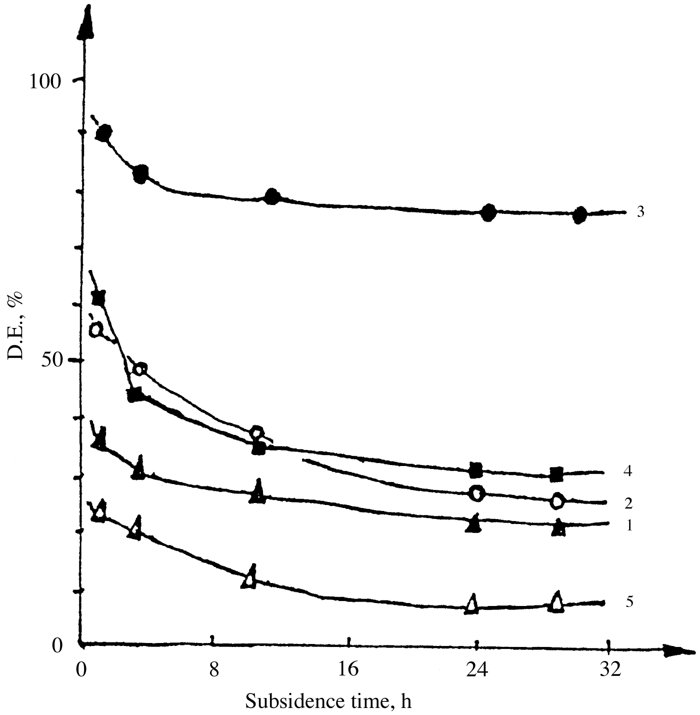


Fig. 2. Dispersion curves of mixed coupling pigments with intermediate (IV) in water. Curves 1–5 represent added amount of 3, 5, 7, 10% and Carmine 6B, respectively.

4. Conclusion

The intermediates I and II can be obtained by heating BON-acid and an aminobenzoic acid together with PCl_3 in the presence of DMF at 140°C in good yields, 92 and 94%, respectively. Similarly, the intermediates III and IV can be obtained by heating BON-acid and an aniline-sulfonic acid together with PCl_3 in the presence of pyridine at 70°C in good yields of 87 and 92%, respectively. Derivatives of Naphtol AS containing –COOH and –SO_3H groups can be used for modification of C.I. Pigment Red 57 by means of mixed coupling. The added amount of both intermediates II and IV is 7%, and the colour strength and transparency is increased and the shade is bluish-red. When the amount of modified II is between 3 and 7% and that of IV is 7%, the dispersing extent of the modified pigments in water medium is excellent.

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