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An Investigation of the Thermal Stability of some Yellow and Red Azo Pigments

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ABSTRACT

A series of benzimidazolone and phthalimide derivatives has been synthesized. 2-Amino-5-nitrobenzonitrile was hydrolyzed during its diazotization with nitrosoylsulfuric acid at 70°C to give the diazonium salt of 2-carboamoyl-4-nitroaniline. A series of yellow and red pigments was prepared and their m.p., temperature of color change and TGA determined. The presence of cyano, amide, chloro and methoxy groups improved the thermal stability; methylation of the —NHCONH— and —CONHCO— groups had an adverse effect on the thermal stability, the decomposition temperature being lowered.

1 INTRODUCTION

The thermal stability of organic pigments is an important parameter and studies have been made on the relationship between molecular structure and thermal stability.[1,2] In order to obtain pigments with improved thermal stability, various modifications have been suggested, e.g. increase in the molecular weight, introduction of a halogen substituent and of substituent groups which can form hydrogen bonds.[3]

In this paper, a series of yellow, orange and red pigments (based on acetoacetarylide and benzimidazolone) was prepared. The m.p., temperature of change in color, decomposition temperature and TGA curves were determined. General structure effects, including the influence of intermolecular hydrogen bonds and methylation of the —NH— group in the pigment on thermal stability have been evaluated.

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2 EXPERIMENTAL

2.1 General synthesis of *N*-methylaminobenzimidazolone derivatives (Fig. 1, group A)

5-Nitrobenzimidazolone (5·4 g, 0·03 mol) was methylated with $(CH_3)_2SO_4$ (3 ml) in 20% aqueous NaOH at 100°C for 20 min to give 1·3-dimethyl-5-nitrobenzimidazolone; yield 85%, m.p. 207–209°C (from ethanol). (Found: C 50·73, H 4·34, N 19·79%; calculated: C 51·17, H 4·2, N 20·20%.)

Hydrochloric acid (0·67 ml), water (42 ml) and powdered iron (2 g) were stirred at 85–95°C for 30 min, 5-nitro-1,3-dimethyl-benzimidazolone was added together with iron filings (4 g) and the mixture refluxed for 2 h. After neutralizing to pH 8–9 and filtering, condensation with BON-acid (16·9 g)

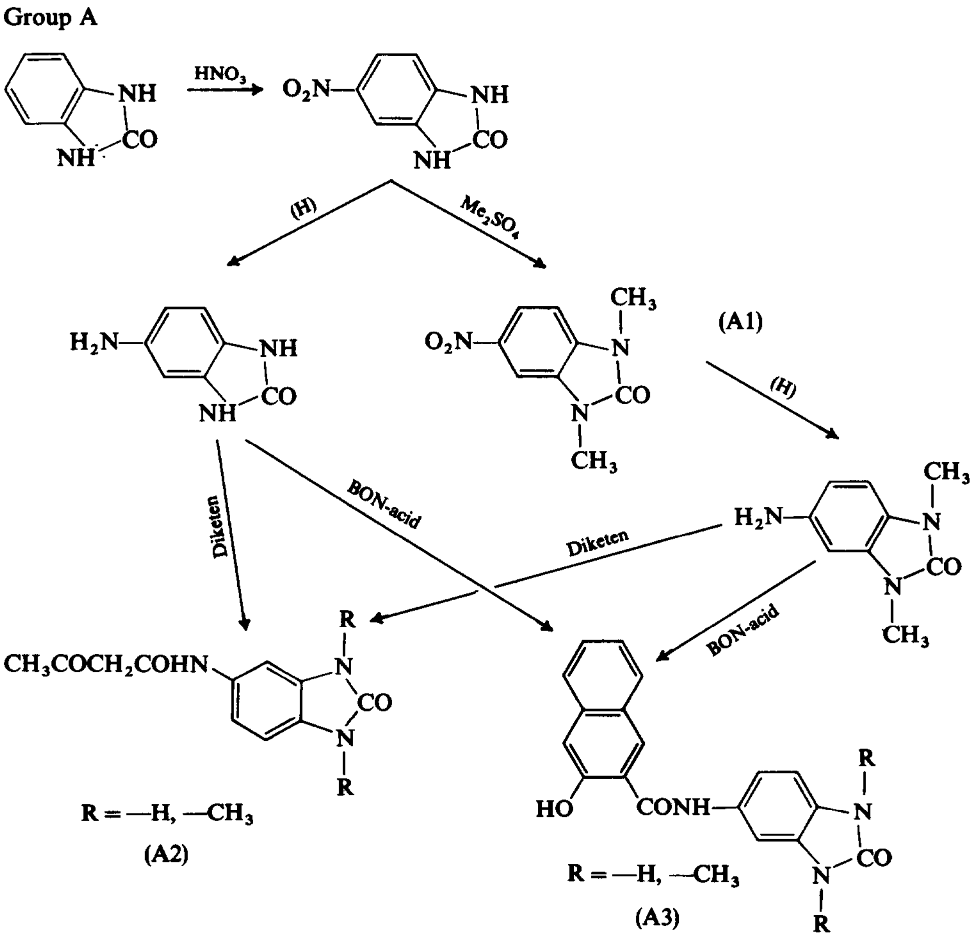
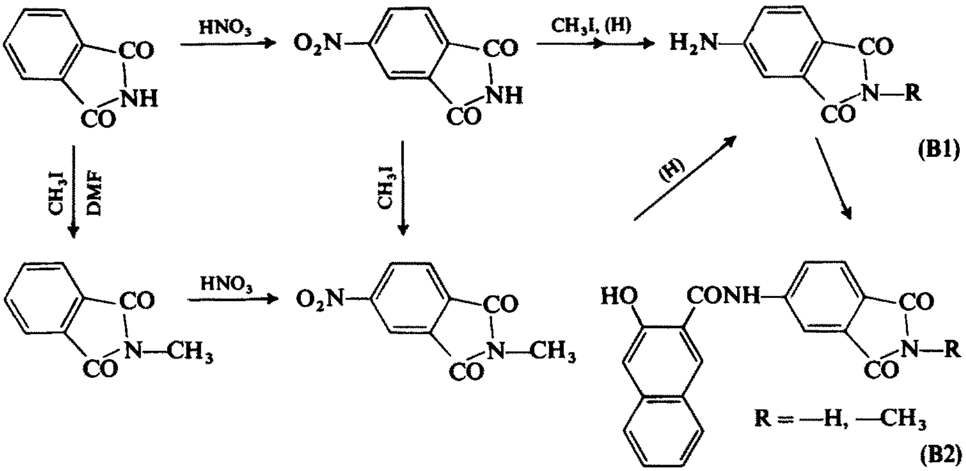


Fig. 1. Reaction scheme of intermediates.

Group B



Group C

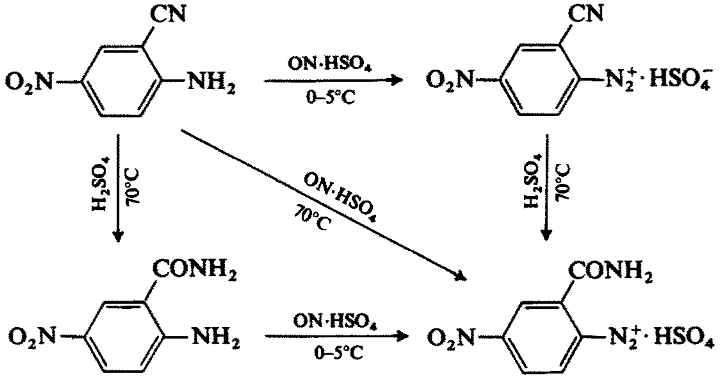
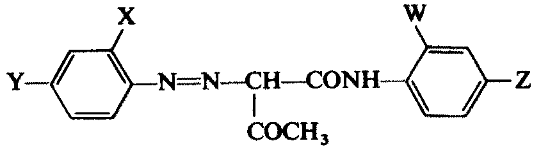


Fig. 1—*Cont.*

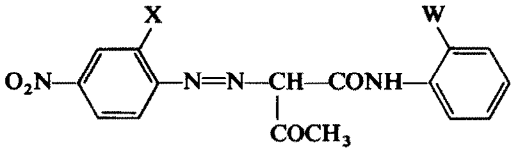
was effected in *o*-dichlorobenzene (100 ml) and PCl_3 (1·8 ml) at 170–180°C for 1 h, and then adjusting to pH 9–10 with aqueous NaOH. The *o*-dichlorobenzene was removed with steam and the residue dissolved in NaOH solution, acidified with HCl, and the precipitate filtered, to give the product A3, m.p. 188–190°C.

2.2 Synthesis of 4-aminophthalimide and *N*-methyl-4-aminophthalimide derivatives (Fig. 1, group B)

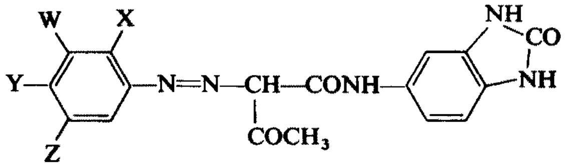
Phthalic anhydride (101 g) and urea were stirred at 100–110°C and the mixture was then heated to 160°C. After cooling, water was added, the mixture heated to 90°C, and filtered; the residue was washed with 30% aqueous Na_2CO_3 and dried to give phthalimide, m.p. 236°C, yield 92%.



X	Y	Z = W = H	W = Cl, Z = H	W = Z = CH₃
H	NO_2	**I.A**	**I.1**	**I.a**
CH_3	NO_2	**I.B**	**I.2**	**I.b**
OCH_3	NO_2	**I.C**	**I.3**	**I.c**
Cl	NO_2	**I.D**	**I.4**	**I.d**
NO_2	CH_3	**I.E**	**I.5**	**I.e**
CN	NO_2	**I.F**	**I.6**	**I.f**

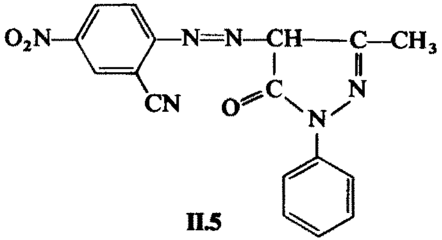


W	X = CN	X = CONH₂
Cl	**II.1**	**II.a**
H	**II.2**	**II.b**
CH_3	**II.3**	**II.c**
OCH_3	**II.4**	**II.d**

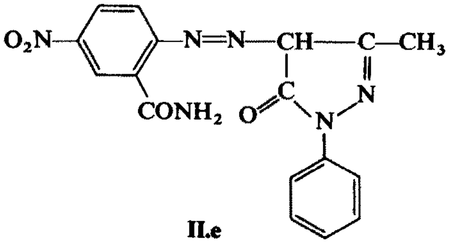


X	Y	Z	W	No.
H	H	Cl	H	**III.1**
H	H	$COOCH_3$	$COOCH_3$	**III.2**
NO_2	Cl	H	H	**III.3**[a]

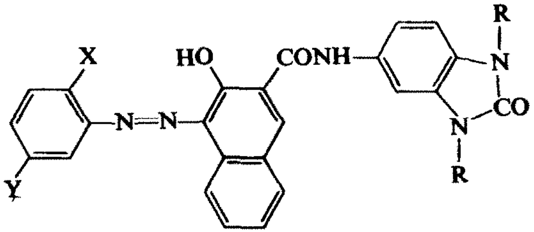
[a] **III.3:** C.I. Pigment Orange 36.



II.5

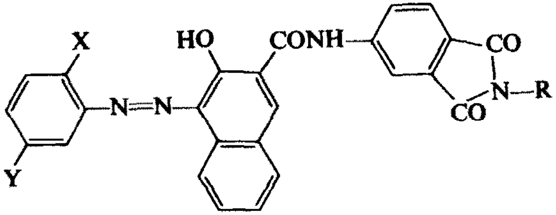


II.e

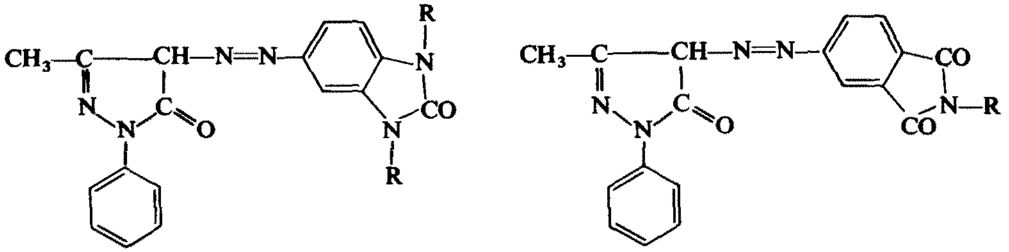


X	*Y*	*R*	*No.*
Cl	Cl	H	**IV.1**[b]
Cl	Cl	CH_3	**IV.2**
OCH_3	PhNHCO	H	**IV.3**[c]
OCH_3	PhNHCO	CH_3	**IV.4**

[b] **IV.1:** C.I. Pigment Brown 25.
[c] **IV.1:** C.I. Pigment Red 176.



X	*Y*	*R*	*No.*
OCH_3	PhNHCO	H	**V.1**
OCH_3	PhNHCO	CH_3	**V.2**
Cl	Cl	H	**V.3**
Cl	Cl	CH_3	**V.4**



R = —H **IV.5**
R = —CH_3 **IV.6**

R = —H **V.5**
R = —CH_3 **V.6**

Fig. 2. Molecular structure of five groups pigments.

Phthalimide (5·6 g) was stirred into sulphuric acid (98%) at 5–10°C, and nitric acid (2·6 ml) was added over 20 min and the mixture stirred for 5 h and then added to ice-water; the resultant precipitate was collected and crystallized from ethanol in colorless needles, m.p. 203–204°C of 4-nitrophthalimide.

4-Nitrophthalimide (12·0 g) was stirred in a mixture of DMF (30 ml) sodium carbonate and methyl iodide (18 ml) at 135–145°C; after 1 h the mixture was added to cold water (50 ml), filtered, and the residue was crystallized from ethanol in colorless needles, m.p. 132–133·5°C of *N*-methyl-4-nitrophthalimide.

Powdered iron (14 g) and water (150 ml) were stirred with hydrochloric acid (20%, 5 ml) at 80–90°C for 30 min, and a paste of *N*-methyl-4-nitrophthalimide (40 g), powdered iron (29·3 g) and a little water was added. The mixture was stirred under reflux for 2 h and neutralized with NaOH to pH 8–9; the resulting product was *N*-methyl-4-aminophthalimide, m.p. 245–246°C.

The preparation of A2, A3, B3 and derived yellow and red pigments have been previously described.[4]

2.3 Determination of properties

Pigment powder (0·2–0·3 g) was treated for 20 min at various temperatures, cooled to room temperature, and the color change temperature was determined. TGA curves and decomposition temperature were measured using an STA-429 Thermal Analyzer (Netzsch Co. Ltd).

3 RESULTS AND DISCUSSION

3.1 Intermediates and pigments

Three groups of intermediates were synthesized as outlined in Fig. 1.

During the synthesis of group C pigments, the 2-amino-5-nitrobenzonitrile was hydrolyzed during the diazotization with nitrosylsulfuric acid at 70°C, giving the diazonium salt of 2-carbamoyl-4-nitroaniline.

Five groups of pigments were synthesized from the above intermediates; these are summarized in Fig. 2.

3.2 Molecular structure and thermal stability

3.2.1 Acetoacetarylide yellow pigments

The m.p. and temperature of decomposition of the pigments synthesized are shown in Table 1.

TABLE 1

M.p. and Temperature of Decomposition of Group I Pigments

No.	*X*	*Y*	*MW*	*M.p.* (°*C*)	*Temperature of:* Decomposition (°*C*)	*Temperature of:* Change in color (°*C*)
I.1	H	NO_2	360	228–230	258	165
I.2	CH_3	NO_2	375	256–258	259	210
I.3	OCH_3	NO_2	390	248–250	261	180
I.4	Cl	NO_2	385	242–243	260	205
I.5	NO_2	CH_3	375	222–223	253	195
I.6	CN	NO_2	380	300–302	286	270

The results show that the pigments which contain a chloro substituent in the coupling component have generally higher m.p. and that the presence of —CH_3, —OCH_3, and, particularly, —CN groups in the *ortho*-position of the diazo component is advantageous in increasing the m.p. of the pigment.

The TGA curves of pigments **I.1–I.6** are shown in Fig. 3; pigment **I.6**, containing the —CN group, is seen to have the highest decomposition temperature, *c.* 290°C.

Similarly, the m.p. and the temperature of change in color of the group **II** pigment are shown in Table 2. The results show that the presence of OCH_3 and Cl substituents in the coupling component increases the thermal stability for similar diazo components, and that the presence in the *ortho*-position of the diazo component of the $CONH_2$ group results in higher m.p.

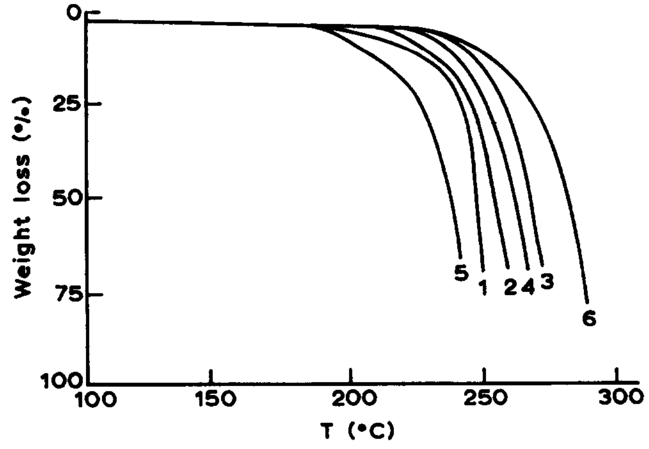


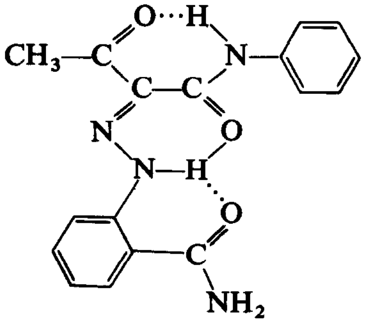
Fig. 3. TGA of pigments I.1–I.6.

TABLE 2
M.p. and Temperature of Color Change of Group II Pigments

No.	*X*	*Y*	*MW*	*M.p. (°C)*	*Temperature of change in color (°C)*
II.1	$CONH_2$	Cl	403·8	288·5–290	230
II.2	$CONH_2$	H	369	277–278	210
II.3	$CONH_2$	CH_3	383	276–277	190
II.4	$CONH_2$	OCH_3	399	307–309	250
II.a	CN	Cl	386	249·5–252	220
II.b	CN	H	351	249–251	170
II.c	CN	CH_3	365	239–240	190
II.d	CN	OCH_3	381	253–254	230

and temperature of change color compared to analogous dyes containing the CN group.

It has been noted that the —$CONH_2$ can readily produce an intermolecular hydrogen bonded configuration having a 'quasi-polycyclic system', hence increasing the molecular plane structure and raising the thermal stability:[5]



3.2.2 *Benzimidazolone and phthalimide pigments*

Azo pigments containing the cyclic —NHCONH— group usually have excellent fastness to light, heat and solvents. Using the intermediates A2, A3 and B2, group **III**, **IV**, **V** series pigments, respectively, were synthesized. M.p. decomposition temperature and percentage of thermal decomposition are summarized in Table 3. The percentage change was evaluated from the TGA curves; the decomposition temperature shows the temperature of loss of weight of *c.* 50% of pigment.

It is apparent that, whilst the molecular weight of **IV.4** and **IV.2** increase to some extent after methylation, the pigments have 50–70°C lower m.p. than

TABLE 3
Thermal Stability of Some Pigments

No.	*Color*	*MW*	*M.p.* (°*C*)	*Temperature of decomposition* (°*C*)	*Percentage (%) change at:*					
					260°C	*300°C*	*340°C*	*380°C*	*420°C*	*500°C*
IV.3	Carmine	571	350	368	3·2	4·0	5·5	23·7	27·9	32·5
IV.4	Carmine	599	300	296	1·8	3·0	12·9	21·9	29·8	42·8
V.1	Violet	570	242	250	18·0	31·0	38·3	44·5	50·1	65·9
V.2	Violet	584	220	240	19·0	34·0	37·1	45·7	50·0	60·0
IV.5	Orange	332	286	262	13·0	22·0	33·0	39·0	44·0	55·8
V.6	Orange	361	180	200	7·1	31·3	41·1	47·0	49·7	56·0
IV.1	Brown	492	353	353	2·8	3·2	5·3	19·5	24·8	42·0
IV.2	Brown	591	284	208	8·5	16·0	20·0	23·0	26·5	47·8
V.3	Brown	505	180	235	14·0	34·0	41·6	44·7	48·8	82·8
V.4	Yellow-brown	519	154	170	17·2	35·4	39·7	42·8	46·2	61·6

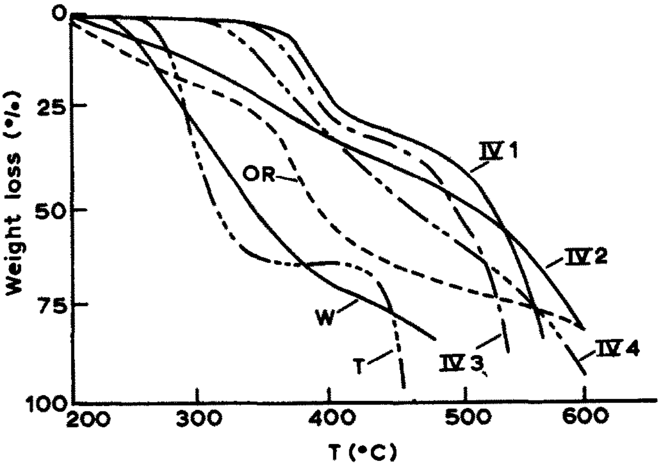
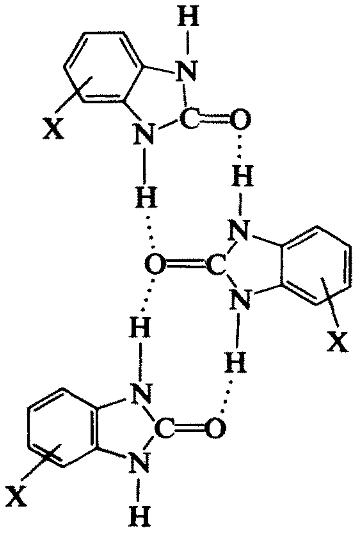


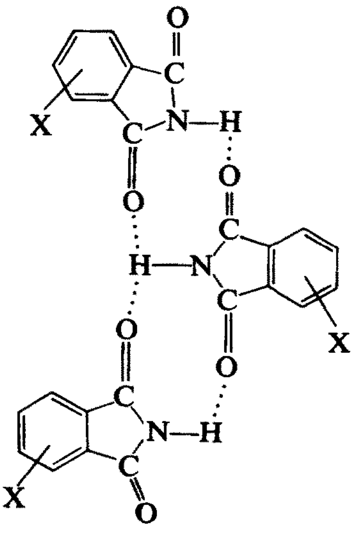
Fig. 4. TGA of **IV.1–IV.4** and pigments T, W and OR. (T, C.I. Pigment Red 1; W, C.I. Pigment Red 21; OR, C.I. Solvent Red 1.)

those of analogous non-methylated derivatives. A similar effect is apparent in the orange pigment **IV.6**, which has m.p. 118°C, compared to a value of 286°C for the unmethylated analogue **IV.5**.

The TGA curves of some pigments (Fig. 4) and the range of thermal stability of **IV.1** and **IV.3** appear broader than those of pigments **IV.2** and **IV.4**, respectively; moreover, C.I. Pigment Red 3, C.I. Pigment Red 21 and C.I. Solvent Red 1 have a lower thermal stability than the pigments investigated in the present study.

The beneficial effect of the —NHCONH— group on thermal stability is thus confirmed. Intermolecular hydrogen bonding in these compounds can be represented as follows:





On methylation of the —NHCONH— group, the ability to form such hydrogen bonds is lost and the m.p., thermal stability and decomposition temperature are consequently decreased. A similar decrease in thermal stability occurs on methylation of the —CONHCO— group.

4 CONCLUSION

Methylation of the —CONHCO— and —NHCONH— groups in the pigments studied decrease the m.p., temperature of color change and decomposition temperature. The presence of —$CONH_2$, —CN and —NO_2 groups in the *ortho*-position of the diazocomponent improves the thermal stability, the —$CONH_2$ group being the more effective; the presence of —OCH_3 or —Cl groups in the coupling component also increases the thermal stability. When diazotizing in nitrosylsulfuric acid at 70°C, 2-amino-5-nitrobenzonitrile is hydrolyzed, giving the diazonium salt of 2-carbamoyl-4-nitroaniline.

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