Dyes and Pigments **21** (1993) 87–96

Azo Pigments and their Intermediates. A Facile Synthesis of Photoreceptor Grade Anilide Couplers from 2-Hydroxy-11H-benzo(a)carbazole-3-carboxylic Acid

Kock-Yee Law,* Ihor W. Tarnawskyj & F. Court Bailey

Xerox Webster Research Center, 800 Phillips Road, 0114-39D,
Webster, NY 14580, USA

(Received 7 September 1992; accepted 9 October 1992)

ABSTRACT

*A facile, two-step synthesis for anilide couplers of 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid, by first converting the acid to its phenyl ester and then condensing the phenyl ester with an aniline derivative to form an anilide, is reported. The synthesis is very general and a variety of anilides have been synthesized in an overall yield of ≥60%. The synthesized anilides are of high purity and can be used to synthesize photoreceptor-grade (*IR-sensitive*) azo pigments without further purification. The procedure described in this work is shown to be more efficient than other processes reported in the literature, such as direct condensation of the acid with an aniline or indirect condensation of the acid with an aniline through an acid chloride or methyl ester intermediate. More importantly, we have demonstrated that neither yield-loss nor deterioration in product purity is observed as the scale of the synthesis increases.*

INTRODUCTION

Azo dyes and pigments are well known for their use as colorants in the dye industry. The photoelectrical properties of azo compounds were recognized as early as 1969 by Rau, who reported the spectral characteristics and the photocurrent of 1-phenylazo-2-naphthol in a thin film device.[1] In 1975 Champ and Shattuck showed that the bisazo pigment Chlorodiane

---

* To whom correspondence should be addressed.

Dyes and Pigments 0143-7208/93/$06.00

Blue [4,4'-bis(1"-azo-2"-hydroxy-3"-naphthanilide)-3,3'-dichlorobiphenyl] could photogenerate electron-hole pairs in bilayer xerographic devices.[2] Due to the simplicity of the azo pigment synthesis, these earlier reports seemed to inspire and initiate a very intense subsequent effort in the xerographic photoreceptor industry. Thousands of azo pigments of different structural variations have been prepared, xerographically screened and claimed in the patent literature.[3] Among the azo pigments that have been examined for xerographic applications, (bis or tris) pigments synthesized from 2-hydroxy-3-naphthanilides were consistently found to exhibit moderate to high photo–conductivity. Unfortunately, these pigments primarily absorb and photorespond in the visible region (400–650 nm). They are not candidates for xerographic printer applications, where illuminators of longer wavelengths, such as a GaAlAs diode laser (780 nm) and a light-emitting diode (660–680 nm) are used.

One of the identified approaches to extend the photoresponse of azo pigments beyond 650 nm in xerographic devices is to extend the conjugation of the entire pigment structure using anilide couplers of 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid.[4] Most of these couplers are not commercially available and in-house synthesis is needed. Here a facile, two-step synthesis for these couplers is reported. The advantages of the present process over other literature procedures are discussed.

EXPERIMENTAL

Materials

2-Hydroxy-11H-benzo(a)carbazole-3-carboxylic acid (97·7%) as sodium salt was purchased from Rohner, Inc. Phenol (99+ %), aniline (99·5+ %), *p*-chloroaniline (98%), *p*-fluoroaniline (99%), *p*-toluiline (99·9%), *o*-toluidine (99+%), *o*-ethylaniline (98%), *o*-anisidine (99+%), *o*-chloroaniline (98+%), *o*-fluoroaniline (99+%), 3-aminobenzotrifluoride (99+%) and N-methyl pyrrolidinone, NMP (99+%), were bought from Aldrich. Xylenes (certified), N,N-dimethylformamide, DMF (+99%), acetone (certified), methanol (certified) and concentrated hydrochloric acid (reagent) were obtained from Fisher. All these materials were used without further purification. Phosphorous oxychloride was purchased from Aldrich and was distilled before use.

General techniques

Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and were uncorrected. IR spectra were measured in

KBr pellets on a Perkin-Elmer model 1750 FTIR. ^{13}C NMR spectra were recorded in DMSO-d_6 (from Merck) on a Bruker AM360 spectrometer. Mass spectra were recorded on a Varian VG 7035 mass spectrometer at the University of Rochester. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of phenyl 2-hydroxy-11H-benzo(a)carbazole-3-carboxylate

2-hydroxy-11H-benzol(a)carbazole-3-carboxylic acid (350 g, 1·26 moles), phenol (480 g, 5·1 moles) and 2 liters of xylenes were charged in a 5 liter three-necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. The resulting mixture was stirred under a nitrogen atmosphere, followed by heating to reflux at an oil-bath temperature of about 160°C. Water was removed azeotropically by a Dean-Stark trap. Phosphorus oxychloride (262·5 g) was then added through a pressure equalizing funnel slowly in ~20 min. After the addition was completed, the mixture resulting was maintained at reflux for another 5–6 h. TLC analysis revealed that all the starting acid was consumed. The product mixture was cooled to room temperature, and 1·5 liters of methanol was introduced therein. The resulting mixture was then chilled in an ice water bath for 1 h, and the solid product was isolated by filtration. After washing with methanol (200 ml, twice) and vacuum drying, a yellow-green solid (369 g) was obtained. The crude product was then dissolved in ~2 liters of hot acetone through a Soxhlet Extractor. After cooling the acetone solution to ice cold temperature, the yellow precipitate was isolated by filtration as a first crop. The filtrate was then concentrated to about 400 ml and about 100 ml of water was introduced. An additional amount of yellow precipitate was obtained (second crop) and was isolated by filtration. Both crop 1 and crop 2 were pure as determined by TLC analysis. The total yield was 324·5 g (73%). Analysis gave the following:

m.p.: 273–275°C
IR(KBr): 3372 (N—H), 3068 (aromatic C—H) and 1689 cm^{-1} (C=O)
MS(*m/z*): 353 (M^+)
Calc'd for $C_{23}H_{15}NO_3$: C 78·17, H 4·28, N 3·96
found: C 77·71, H 4·58, N 3·98.

Synthesis of anilides from 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid (3a–3l)

Phenyl 2-hydroxy-11H-benzo(a)carbazole-3-carboxylate (5 g, 14 mmoles), aniline (2·75 g, 28 mmoles) and 15 ml of N-methyl pyrrolidinone were

TABLE 1
Synthesis and Physical Properties of Anilide Couplers from 2-Hydroxy-11H-benzo(a)carbazole-3-carboxylic Acid (**3a**–**3l**)

Compound	*Equivalents of aniline used*	*Yield (%)*	*m.p. (°C)*		*C*	*H*	*N*
3a	2	83	334–336	Calc'd:	78·39	4·58	7·95
				Found:	78·14	4·54	7·91
3b	2	83	>310	Calc'd:	71·41	3·91	7·24
				Found:	71·14	3·88	7·18
3c	4	89	>310	Calc'd:	74·58	4·08	7·56
				Found:	74·50	4·56	7·96
3d	2	93	>310	Calc'd:	78·67	4·95	7·65
				Found:	77·90	4·92	7·53
3e	4	78	311–312	Calc'd:	78·67	4·95	7·65
				Found:	78·66	5·14	7·71
3f	2	83	269·5–270·5	Calc'd:	78·93	5·30	7·36
				Found:	79·11	5·25	7·29
3g	4	74	278–280	Calc'd:	75·38	4·74	7·32
				Found:	75·07	5·12	7·49
3h	6	82	>310	Calc'd:	71·41	3·91	7·24
				Found:	71·84	4·19	7·31
3i	4	92	308–309	Calc'd:	74·58	4·08	7·56
				Found:	74·39	4·32	7·50
3j	4	90	>310	Calc'd:	68·57	3·60	6·66
				Found:	68·47	3·89	6·74
3k	4	81	307–309	Calc'd:	74·99	4·46	7·29
				Found:	76·06	4·86	7·39
3l	4	87	304–306	Calc'd:	68·24	3·49	6·92
				Found:	68·99	3·80	7·05

charged in a 100 ml three-neck flask equipped with a magnetic stirrer and a nitrogen inlet. The resulting mixture was stirred and was heated to reflux at an oil bath temperature of 250°C under a nitrogen atmosphere. After 3 h, TLC analysis revealed that all the starting phenyl ester was consumed. The mixture was cooled to room temperature and was poured into a 1 liter beaker containing 400 ml of ice cold 5% HCl. The yellow precipitate obtained was isolated by filtration. After washing with water (~200 ml) and ~20 ml of methanol and vacuum drying, 4·7 g of crude product resulted. This product was then recrystallized from a mixture of DMF/methanol/water, yielding 4·4 g (83%) of

TABLE 2
IR and Mass Spectral Data of **3a–3l**

Anilide	*IR data*[a]			*M+*[b]
	N—H	*Aromatic C—H*	*Amide C=O*	*m/z (rel. intensity)*
3a	3303, 3448	~3060	1656	352 (38%)
3b	3352, 3438	3062	1658	386 (22%)
3c	3352, 3432	3062	1660	370 (38%)
3d	3352, 3438	~3060	1658	366 (26%)
3e	3321, 3374	3062	1652	366 (37%)
3f	3360, 3400	3063	1658	380 (35%)
3g	3361, 3440	3060	1652	382 (21%)
3h	3322, ~3360, 3428	3060	1660	386 (15%)
3i	3302, 3412, 3440	~3060	~1650	370 (27%)
3j	3378, 3420	~3060	1660	420 (40%)
3k	3280, 3374	3060	1652	384 (7%)
3l	3362, 3430	3060	1658	404 (8%)

[a] In cm^{-1}.
[b] Molecular ion.

2-hydroxy-11H-benzo(a)carbazole-3-carboxanilide (**3a**). Analysis gave the following:

m.p.: 334–336°C
IR(KBr): 3448, 3303 (N–H), 3060 (aromatic C—H) and 1657 cm^{-1} (C=O)
MS(*m/z*): 352 (M^+)
Calc'd for $C_{23}H_{16}N_2O_2$: C 78·39, H 4·58, N 7·95
found: C 78·14, H 4·54, N 7·91.

Anilides **3b–3l** were synthesized in a similar fashion. The yields, the physical properties and the spectroscopic properties of these compounds are tabulated in Tables 1–3.

RESULTS AND DISCUSSION

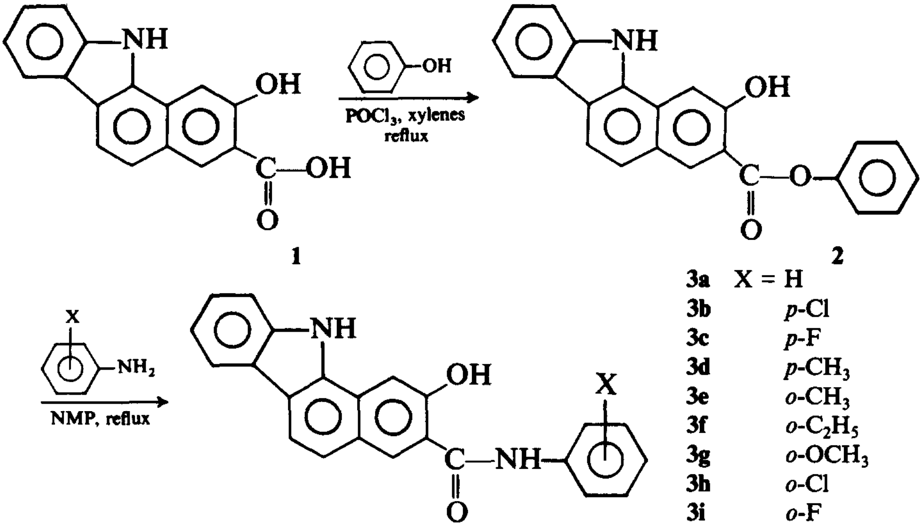
Synthesis of anilide couplers of 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid

Anilide couplers of 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid are synthesized by first converting the acid (**1**) to its phenyl ester (**2**) and then condensing the phenyl ester with an aniline derivative in a high boiling solvent such as N-methyl-2-pyrrolidinone (NMP). The reaction sequence is given in Scheme 1.

TABLE 3

^{13}C NMR Chemical Shift Data (in DMSO-d_6) of **3a–3l**

3a	106·4 (C10), 111·7 (C1), 117·5, 118·5, 119·4, 120·1, 120·2, 121·2 (2 carbons), 123·2, 124·4, 124·8, 125·1, 125·4, 128·9 (2 carbons), 131·0 (C4), 133·7, 138·4, 139·2, 155·2 (C2), and 167·0 (C12)
3b	106·4 (C10), 117·7 (C1), 117·5, 118·6, 119·0, 119·4, 120·1, 120·2, 122·6 (2 carbons), 123·3, 124·9, 125·1, 125·4, 128·1, 128·8 (2 carbons), 131·1 (C4), 133·8, 137·4, 139·2, 155·1 (C2), and 167·1 (C12)
3c	106·3 (C10), 111·6 (C1), 115·3, 115·5, 117·4, 118·3, 118·9, 119·3 120·0, 120·1, 123·0, 123·1, 123·2, 124·7, 125·0, 125·3, 130·7 (C4), 133·7, 134·6, 134·7, 139·1, 155·1 (C2), and 167·0 (C12)
3d	20·7 (CH_3), 106·4 (C10), 111·7 (C1), 117·5, 118·2, 119·0, 119·4, 120·1, 120·2, 121·2, (2 carbons), 123·3, 124·9, 125·2, 125·4, 129·3 (2 carbons), 130·9 (C4), 133·6, 133·8, 135·8, 139·3, 155·5 (C2) and 167·1 (C12)
3e	17·9 (CH_3), 106·4 (C10), 111·6 (C1), 117·5, 118·1, 119·0, 119·3, 120·0, 120·2, 123·2, 124·3, 124·8, 125·0, 125·3, 125·6, 126·4, 130·4, 131·0, 131·7, 133·7, 136·3, 139·2, 154·8 (C2) and 166·0 (C12)
3f	14·4 (CH_3), 24·3 (CH_2), 106·5 (C10), 111·7 (C1), 117·6, 118·2, 119·0, 119·4, 120·2, 120·3, 123·3, 124·9, 125·0, 125·2, 125·7, 125·8, 126·5, 128·9, 131·9 (C4), 133·7, 135·7, 137·0, 139·3, 154·8 (C2) and 166·2 (C12)
3g	56·1 (OCH_3), 106·3 (C10), 111·1, 111·6 (C1), 117·4, 119·0, 119·3, 119·6, 120·0, 120·3, 120·7, 120·8, 123·2, 124·1, 124·6, 125·0, 125·9, 128·0, 133·0 (C4), 133·6, 139·3, 149·0, 153·2 (C2) and 163·7 (C12)
3h	106·4 (C10), 111·6 (C1), 117·6, 118·8, 119·1, 119·3, 120·0, 120·3 123·2, 123·3, 124·0, 124·8, 125·1, 125·4, 125·9, 127·9, 129·4, 133·1 (C4), 133·5, 135·5, 139·3, 153·3 (C2) and 164·4 (C12)
3i	106·4 (C10), 111·6 (C1), 115·2/115·5 (doublet), 117·6, 118·4, 119·1, 119·3, 120·0, 120·3, 123·2, 123·6, 124·7, 124·7$_4$, 124·8, 125·0, 125·3/125·4 (doublet), 125·8, 126·2/126·3 (doublet), 132·5 (C4), 133·6, 139·3, 153·8 (C2), and 165·0 (C12)
3j	106·2 (C10), 111·4 (C1), 116·8, 116·9, 117·3, 118·5, 118·8, 119·1, 119·8, 119·9, 120·3 (doublet), 123·0, 124·2, 124·7, 124·8, 125·2, ~129 (m, CF_3), 129·8, 130·9 (C4), 133·5, 139·0, 139·1, 154·7 (C2) and 167·1 (C12)
3k	18·0 (CH_3), 106·5 (C10), 111·7 (C1), 112·8/113·0 (doublet), 116·8, 117·0, 117·6, 117·9, 119·1, 119·4, 120·1, 120·3, 123·3, 125·0, 125·2, 125·6, 126·7, 131·6 (C4), 132·6, 133·7, 134·5, 139·3, 155·1 (C2), and 166·6 (C12)
3l	106·6 (C10), 117·8 (C1), 114·7/114·9 (doublet), 116·5, 116·8, 117·7, 118·6, 119·3, 119·4, 120·2, 120·5, 123·4, 125·0 (2 carbons), 125·2, 125·4, 126·0, 132·3, 133·1 (C4), 133·8, 139·5, 153·7 (C2) and 164·8 (C12)



1

2

	X =
3a	H
3b	*p*-Cl
3c	*p*-F
3d	*p*-CH_3
3e	*o*-CH_3
3f	*o*-C_2H_5
3g	*o*-OCH_3
3h	*o*-Cl
3i	*o*-F
3j	*m*-CF_3
3k	*o*-CH_3, *p*-F
3l	*o*-Cl, *p*-F

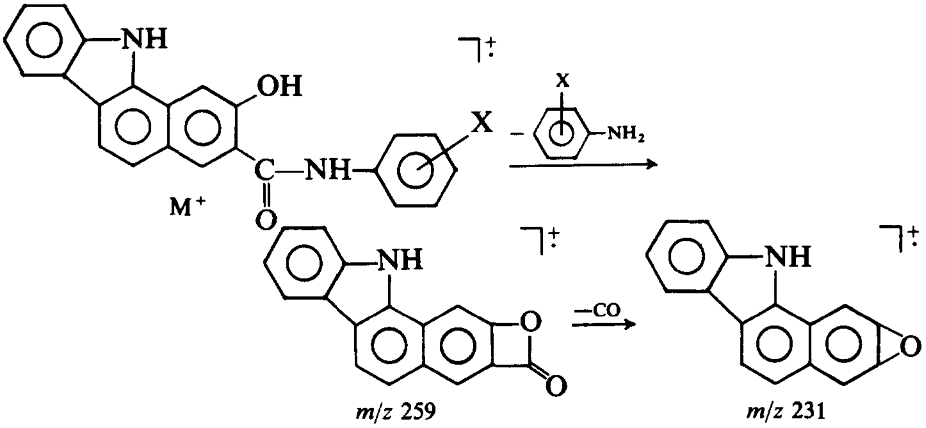
Scheme 1

Since the anilides synthesized in this work are precursors for the synthesis of xerographic photogeneration azo pigments, product purity is our primary concern. In the first step of the synthesis, the carboxylic acid **1** was converted to the phenyl ester **2** using phosphorous oxychloride as a condensing agent in xylenes. To ensure a clean, high-yield reaction, an excess amount (>4 equivalents) of phenol was used. The crude product was usually free from **1** and was chromatographically clean. Pure **2** was obtained by recrystallization from a mixture of acetone and water, yield 73%.

Using **2** and aniline as model reactants, the process latitude of the condensation reaction was examined. Our data showed that NMP is the preferred solvent for the synthesis and that there is a reduction in reaction time as the concentration of aniline increases. The isolated yield of **3a** is >83% when more than 2 equivalents of aniline are used. The reaction is very general. The synthetic data of **3b–3l** are tabulated in Table 1.

Physical properties and structural characterization

Anilides **3a–3l** are high-melting, yellow powders. They exhibit reasonable solubility in polar organic solvents, such as DMF, DMSO, NMP, etc. In the IR spectra, very characteristic bands at 3300–3500, ~3060 and

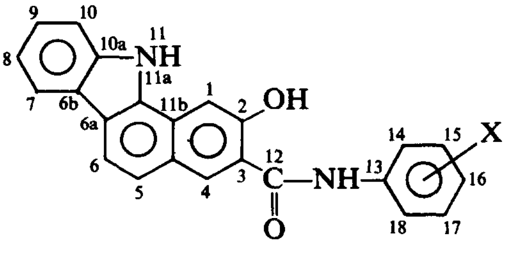


Scheme 2

~1660 cm^{-1}, which are attributable to the N—H, aromatic C—H and amide C=O stretchings, respectively, are observed. The IR spectral data are tabulated in Table 2.

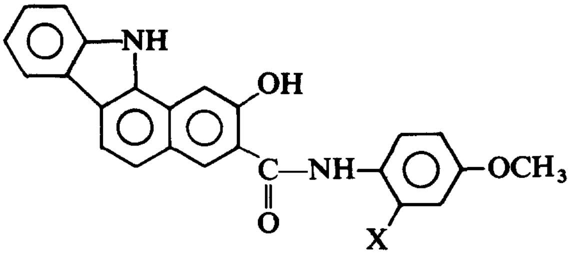
In the mass spectra, molecular ions of **3a–3l** are observed. The major fragmentation process for the molecular ions is to eliminate the aniline moiety. The resulting fragment, which is at *m/z* 259, is the parent peak in all cases. This 259 fragment ion undergoes a decarbonylation reaction to generate an ion at *m/z* 231. The mass spectral reactions of **3a–3l** are summarized in Scheme 2 and the data are given in Table 2.

All synthesized anilides exhibit well behaved ^{13}C NMR spectra in DMSO-d_6 and peaks corresponding to individual carbon resonances are well resolved. The ^{13}C NMR chemical shift data are summarized in Table 3. Although unambiguous assignments of individual peaks are difficult due to the similar shift among sp^2 carbons, characteristic resonances at ~167 and 155 ppm, attributed to the amide carbon (C12) and the aromatic hydroxyl carbon (C2) respectively, are easily identified. By comparison with the chemical shift data of 2-hydroxy-3-naphthanilides,[5] C1, C4 and C10, which are at ~111, ~132 and ~106 ppm respectively, are distinguishable from other ^{13}C signals also.



A comparison with other literature procedures

Procedures for the synthesis of anilide couplers from **1** are known. For example, coupling components **13** and **25** are reported to be synthesized by (direct) condensation of **1** with the corresponding aniline derivative.[6]



Coupling Component 13, X = H
Coupling Component 25, X = CH_3

It is also known that this class of anilides could also be prepared from the acid chloride[7] or the methyl ester of **1**.[8] In this work, we re-visit some of these procedures and compare our procedures with those in the literature. Our findings indicate that direct condensation of **1** with aniline in a solvent (dichlorobenzene) or in neat aniline with or without a condensing reagent ($POCl_3$, $SOCl_2$) gives the anilide product **3a** in low yield (<5%). Esterification of **1** in methanol in the presence of $BF_3.OEt_2$ yields the methyl ester of **1** in 67% yield. Unfortunately, hydrolysis of the methyl ester back to **1** is found to be the dominating reaction when attempts are made to condense the methyl ester with aniline under various conditions. Although we are confident that one can suppress the hydrolysis reaction by excluding moisture or water in the glassware, solvent and reactants during the synthesis, we feel that such a procedure may not be economically attractive from the engineering viewpoint. Thus we have not pursued this direction rigorously.

The acid chloride of **1** can be prepared by reacting **1** with thionyl chloride in dry THF. At a 1 g level, pure **3a** can be synthesized at ~50% by condensing the acid chloride with aniline in THF. Unfortunately, the purity of **3a** deteriorates as the scale of the synthesis increases. For instance, several side products were detected by TLC analysis when the synthesis was at a 5 g scale. Extensive purification, which lowers the yield of pure **3a**, has to be carried out. On the other hand, the two-step synthesis in Scheme 1 produces pure **3a** in ≥60% yield. The synthesis is simple. More importantly, it is scalable. We have scaled the synthesis up to a 30 g level and observe neither yield decrease nor deterioration in product purity.

CONCLUDING REMARKS

A facile, two-step synthesis of anilide couplers from 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid, by first converting the acid to its phenyl ester and then condensing the phenyl ester with an aniline derivative to form the anilide product, is reported. The synthesis is simple and is shown to produce high purity anilide couplers suitable for the synthesis of azo pigments for xerographic photoreceptor applications. The procedure is found to be scalable without any losses in synthetic yield or product purity.

REFERENCES

1. Rau, H., *Ber. Bunsenges*,**73** (1969) 810.
2. Champ, R. B. & Shattuck, M. D., US Patent 3,898,084 (1975).
3. Nguyen, K. C. & Weiss, D. S., *J. Imaging Technol.*, **15** (1989) 158; and references therein.
4. Ohta, K., *Electrophotography*, **25** (1986) 83.
5. Law, K. Y., Kaplan, S., Crandall, R. & Tarnawskyj, I. W., *Chem. Mater.*, (in press).
6. *Color Index, Vol. 4*, 3rd edn. Society of Dyes and Colorists, 1971.
7. Hashimoto, M. & Sasaki, M., US Patents 4,916,039 and 4,925,758 (1990).
8. Japanese Patent Laid-Open No. 59-137,459 (1984) (by Ricoh).