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Development-Accelerator-Releasing (DAR) Couplers. Part I: The Effect of DAR Couplers with Different Normal Couplers on the Photographic Characteristics of Color Negative Material

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ABSTRACT

Two development-accelerator-releasing couplers were synthesized with different conventional couplers and the effect of the two compounds on the photographic characteristics of color negative material were examined. © 1997 Elsevier Science Ltd

Keywords: DAR coupler, normal coupler, effect, photographic characteristics, color negative material, synthesis.

INTRODUCTION

The development-accelerator-releasing coupler (DAR) can be represented by the general formula Cp-L-A, in which Cp represents a coupler proper (Cyan, Magenta or Yellow), A represents a development accelerating functional group and L represents a divalent linking group. With the inclusion of the DAR coupler the photographic speed of a color negative material can be increased [1–4]. In this paper, two DAR cyan couplers were synthesized with different couplers, and the effect of the two compounds on the photographic characteristics of color negative material were examined in order to clarify the influence of the coupler proper in the DAR coupler on the photographic characteristics of color negative material.

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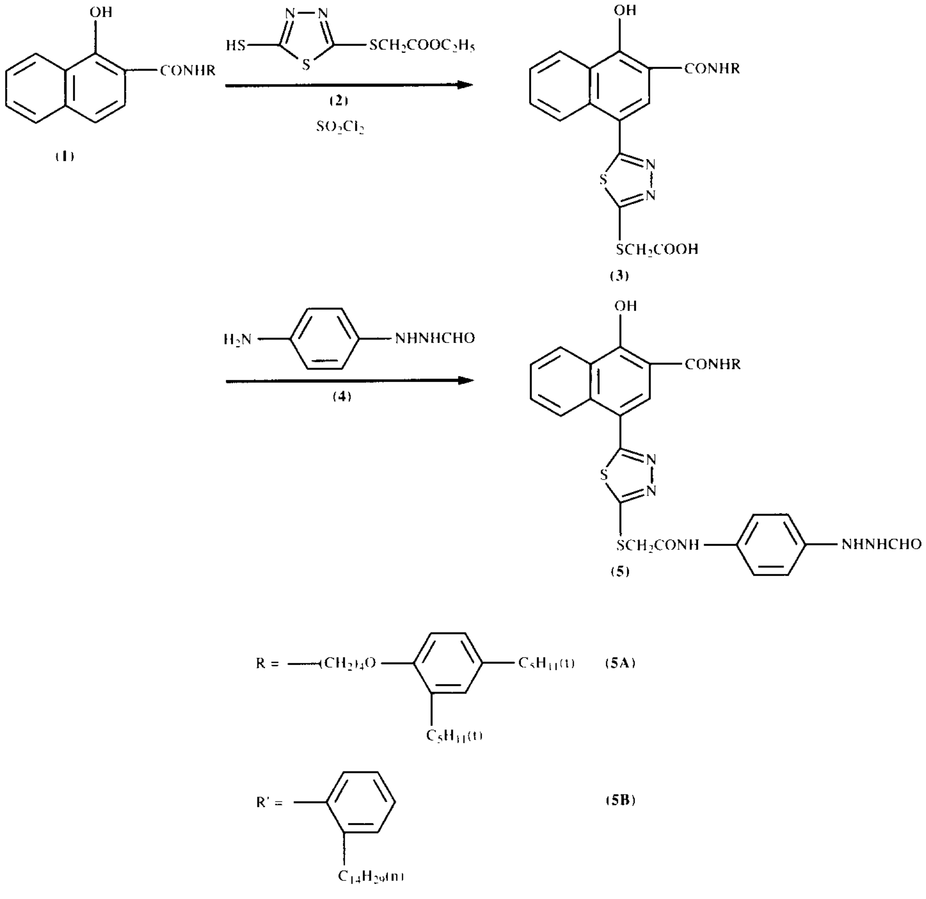
SYNTHESIS OF THE DAR COUPLERS

Results and discussion

The DAR couplers can be synthesized by various routes; a typical synthesis is illustrated below:



Relevant data on yields, melting points, elemental analysis and the spectral data of the intermediates **2**, **3**, **4**, **5** and of the DAR couplers **5A**,**5B** are given in Tables 1–3.

Experimental

General

Melting points are uncorrected. Elemental analyses were obtained using a Carlo Erba 1160R analyzer. Mass spectra were obtained using a Hitachi

M-80 spectrometer, IR spectra on a 7650 spectrometer, and ^{1}H-NMR spectra on a Bruker WP-100SY spectrometer.

1-Hydroxyl-*n*-(2′-*n*-tetradecyloxyphenyl)-2-naphthamide [5],[6]. 2-Ethoxycarbonylmethyl-5-mercapto-1,3,4-thiadiazole [11], 2,5-mercapto-1,3,4-thiadiazole [7,8], and 1-formyl-2-(4-aminophenyl)hydrazide [9,10] were prepared by the literature procedures. 1-Hydroxy-*N*-[4-(2,4-di-*tert*-pentylphenoxy) butyl]-2-naphthamide (**1B**) was obtained commercially.

1-Hydroxy-4-(2-carboxymethylthio-1,3,4-thiadiazole-5-thio)-*N*-{4-(2,4-di-*tert*-pentylphenoxy)-butyl}-2-naphthamide (**3A**) and 1-hydroxy-4-(2-carboxymethylthio-1,3,4-thiadiazole-5-thio)-*N*-(2-*n*-tetradecyloxyphenyl)-2-naphthamide (**3B**): To a solution of 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**2**) (0.1 mol) in CCl_4, a solution of sulfuryl chloride (0.1 mol) in CCl_4 was added dropwise over 1 h with ice cooling; stirring was continued for 1 h and then at room temperature for 0.5 h. A solution of the Cyan coupler (0.1 mol) in CCl_4 was added and the mixture refluxed with vigorous stirring for 4 h. After removal of CCl_4 by distillation, the residue

TABLE 1
Yields, Melting Points and Elemental Analysis

Compound	*Yield (%)*	*M.P. solvent (°C)*	*Molecular formula*	*Analysis (found/calculated, %)*		
				C	*H*	*N*
1A	86	50–52[5,6]				
2	95	68–70	$C_6H_8N_2O_2S_3$	30.47	3.39	11.78
				30.51	3.39	11.86
3A	88	93–95	$C_{35}H_{43}N_3O_5S_3$	61.92	6.19	6.64
				61.65	6.36	6.61
3B	66	92–95				
4	87	124–126[9,10]	$C_7H_9N_3O$	55.73	5.89	27.39
				55.68	6.01	27.79
5A	54	170–172	$C_{42}H_{50}N_6O_5S_3$	62.07	6.47	10.45
				61.91	6.18	10.31
5B	49	165–169	$C_{42}H_{50}N_6O_5S_3$	62.10	6.27	10.08
				61.91	6.18	10.31

TABLE 2
Mass Spectral Data

Compound	*Mass spectra (70 ev) (m/z, %)*
2	236(M^+) 192(M^+–OC_2H_5 + 1) 117(M^+–SCH_2COOEt) 104(M^+–$CSCH_2COOEt$ + 1) 87(CH_2COOEt) 45(OEt) 29(Et)
3A	683(M^+ + 1) 624(M^+–CH_2COOH + 1)
3B	682(M^+) 507(M–C_2N_2S–SCH_2COOH) 475(M^+–S–C_2N_2S–SCH_2COOH)
4	151(M^+) 122(M^+–CHO) 107(M–NHCHO) 92(M^+–NHNHCHO)

was dissolved in ethanol and a solution of KOH (0.1 mol) in water was added, and stirring was continued at 60°C for 0.7 h. After cooling, the solution was poured into a cold solution of conc. HCl (20 ml) and water. The products precipitated readily and were filtered, washed several times with water, and finally recrystallized. Yields, melting point and analytical data are shown in Table 1.

Preparation of DAR couplers (5A, 5B)

1-Hydroxy-4-(2-carboxymethylthio-1,3,4-thiadiazole-5-thio)-*N*-{4(2,4-di-*tert*-pentylphenoxy)-butyl}-2-naphthamide (**3A**) or 1-hydroxy-4-(2-carboxymethylthio-1,3,4-thiadiazole-5-thio)-*N*-(2-*n*-tetradecyloxyphenyl)-2-naphthamide (**3B**) (0.05 mol) and 1-formyl-2-(4-aminophenyl)hydrazide (**5**) (0.05 mol) were dissolved in dimethylformamide (DMF). A solution of dicyclohexylcarbodiimide (0.05 mol) in DMF was added dropwise at 0°C over 0.5 h, and stirring was continued at room temperature for 2 h. The solution was filtered, and the filtrate poured into cold water. When the products precipitated, they were filtered, washed several times with water and recrystallized to give compounds **5A** and **5B**, respectively. Yields, melting points and analytical data are shown in Table 1.

TABLE 3
Spectral Data for Compounds **5**

Product	*IR* *(KBr, ν, cm^{-1})*	*^{1}H-NMR* *(CD_3SOCD_3TMS, δ, ppm)*	*MS* *(FDS[a], m/z)*
5A	3298,3230(s,NH) 2940(s,CH_3.C–H) 2840(s,CH_2.C–H) 1659,1632(s,C=O) 1578(s,C=N) 1536(s,N–H) 1486(s,–Ph–1,2,4) 1450(m,$(CH_2)_4$) 1381(s,C–N) 1226(m,Ph–O) 1040,810,755(m,Ph–1,2,4)	0.4–0.75(t,6H,$2CH_3$) 1.0–1.4(d,12H,$4CH_3$) 1.4–2.0(m,8H,CH_2CH_2,$2CH_3$) 3.9–4.2(md,6H,CH_2O,CH_2N,CH_2S) 6.6–8.5(m,12H,Ph) 8.1(s,1H,CHO) 8.6(s,1H,OH) 9.1–9.5(m,2H,NHCHO,CONH$(CH_2)_4$) 9.7(s,1H,CONHPh) 9.9–10.1(d,1H,PhNHN)	815(M^+)
5B	3323(m,NH) 2924(s,CH_3,C–H) 2850(m,CH_2,C–H) 1623(s,C=O) 1527(s,C=N) 1536(s,NH) 1450(m,$(CH_2)_4$) 1387(m,C–N) 1243(M,Ph–O) 761,745(m,Ph–1,2)	0.6–1.5(m,27H,$C_{13}H_{27}$) 3.9–4.3(m,4H,OCH_2,SCH_2) 6.6–8.6(m,13H,Ph) 8.1(s,1H,CHO) 8.8(s,1H,OH) 9.3–9.5(d,1H,NHNHCHO) 9.7(s,1H,CONHPh) 10.0–10.1(d,1H,PhNHN) 10.5(s,1H,CONHPh)	815(M^+)

[a] FDS, field desorption mass spectrometry.

EFFECT OF THE TWO DAR COUPLERS ON THE PHOTOGRAPHIC CHARACTERISTICS OF COLOR NEGATIVE MATERIAL

Experimental

To examine the effect of the DAR couplers on the photographic characteristics, a single-layer color negative coating structure was employed. For most of the experimentation, one coating contained an experimental 400-speed bromo-iodide T-grain emulsion sensitized to red light, together with a cyan dye-forming image coupler.

Results and discussion

The dye sensitometric data for red-sensitive coatings are given in Tables 4 and 5.

It is apparent from the data in these Tables that the increase in sensitivity was excellent for the coatings incorporating compounds **5A** and **5B**, compared with the coatings without these compounds. For the middle-speed red-sensitive coatings, no increase of fogging was observed, but for the

TABLE 4
Effect of DAR Couplers on the Photographic Characteristics of Middle-speed Red-sensitive Coatings

DAR coupler	*Laydown (mol%)*[a]	*Relative sensitivity*	*Contrast*	*Fog*
5A	0	76	1.03	0.2
	0.03	148	0.87	0.25
	0.17	174	0.87	0.17
	0.33	117	1.08	0.12
5B	0.03	174	1.09	0.1
	0.17	191	0.98	0.11
	0.33	166	0.8	0.16

[a] The mol% relative to the image coupler.

TABLE 5
Effect of DAR Couplers on the Photographic Characteristics of High-speed Red-sensitive Coatings

DAR coupler	*Laydown (mol%)*[a]	*Relative sensitivity*	*Contrast*	*Fog*
5A	0	372	0.9	0.36
	0.2	676	0.93	0.49
	0.4	832	0.73	0.79
5B	0.2	851	0.83	0.63
	0.4	486	0.69	0.8

[a] The mol% relative to the image coupler.

high-speed red-sensitive coatings, an increase of fogging occurred. Comparing these two compounds, no different effects on the photographic characteristics were observed and it was therefore concluded that the DAR type coupler in conjunction with different conventional couplers has no influence on the photographic characteristics.

CONCLUSIONS

Two DAR couplers have been synthesized with different couplers. Both of them increased the photographic speed when they were incorporated within the bromo-iodide T-grain coating cyan dye-forming image couplers, and no difference was observed for coatings containing the two compounds in improving the photographic characteristics of color negative material.

REFERENCES

1. Fuji Photo Film Co. Ltd, *German Patent* 3209110 (1982).
2. Fuji Photo Film Co. Ltd, *European Patent* 147765 (1985).
3. Kobayashi, H. and Mihayashi, K., Paper Summaries, *SPSE 38th Annu. Conf.*, Atlantic City, NJ, May 1985, Society of Photographic Scientists and Engineers, USA, p. 58.
4. Jarvis, J. R. and Twist, P. J., *Journal of Imaging Science*, **33** (1989) 217.
5. Eastman Kodak Co., *US Patent* 3227554 (1966).
6. Eastman Kodak Co., *US Patent* 2474293 (1949).
7. Sharples Chemicals Inc., *US Patent* 2685587 (1954).
8. Fields, E. K., *Journal of Organic Chemistry*, **21** (1956) 497.
9. Nobuyiki Fuji Photo Film Co. Ltd, *Japanese Patent* 54-74729 (1977).
10. Horning, E. C., *Organic Syntheses*. John Wiley, New York, 1955, coll. vol. 3, p. 520.
11. Chen, Y., Ph.D. thesis, East China University of Chemical Technology, Shanghai, 1988.