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Synthesis and photographic properties of novel development-accelerator-releasing couplers

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Abstract

Several novel development-accelerator-releasing couplers (DAR couplers) were synthesized. The structure of DAR couplers was confirmed by MS, IR and ^{1}H NMR spectroscopy. At the same time, the effect of DAR couplers derived from different hydrazines on the photographic properties of color negative material were studied. It was found that the DAR couplers examined may be used together with cyan coupler or yellow coupler in a color negative material to increase the photosensitivity; DAR couplers 4c and 8c that contained 1-trifluoroacetyl-2-(4-aminophenyl)hydrazine increased photosensitivity the most.

Keywords: DAR coupler; Synthesis; Photographic properties

1. Introduction

Hydrazine derivatives can be used to increase the photosensitivity and contrast of a silver halide light-sensitive material during development [1–3]. A hydrazine derivative may be introduced, as a functional group, at the active position of a color coupler, and the resulting compound is termed a development-accelerator-releasing (DAR) color coupler [4–6]. The inclusion of a DAR color coupler in a color negative imaging layer has been suggested as a means of increasing photosensitivity and photo efficiency in the color development process. A detailed photomicrographic study has revealed that the action of a DAR color coupler involves a localized fogging of unexposed grains in close proximity to a strongly developing grain, and hence increases the number of developed silver halide grains per unit area [7]. The DAR coupler can be represented by the general formal Cp–L–A in which "Cp" represents a coupler residue (cyan, magenta or yellow), "A" represents a development accelerating functional group and "L" represents a divalent linking group. In the present paper, a class of novel DAR couplers—three cyan DAR couplers and three yellow DAR couplers were synthesized and their photographic properties on color negative material were studied. It was found that all DAR couplers could increase photosensitivity, but the 4c and 8c DAR couplers that contained 1-trifluoroacetyl-2-(4-aminophenyl)-hydrazine compounds (4c and 8c) as development accelerators were the best and increased photosensitivity the most.

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2. Experimental

2.1. Synthesis of DAR couplers

2.1.1. General

Mass spectra have been obtained with a HITACHI M-80 spectrometer, IR spectra with a NICOLET FT-IR 20sx spectrometer and ^{1}H NMR spectra with a BRUKER ADVANCE 500 spectrometer, model WP-500SY; TMS was the initial standard used. All melting points reported are uncorrected.

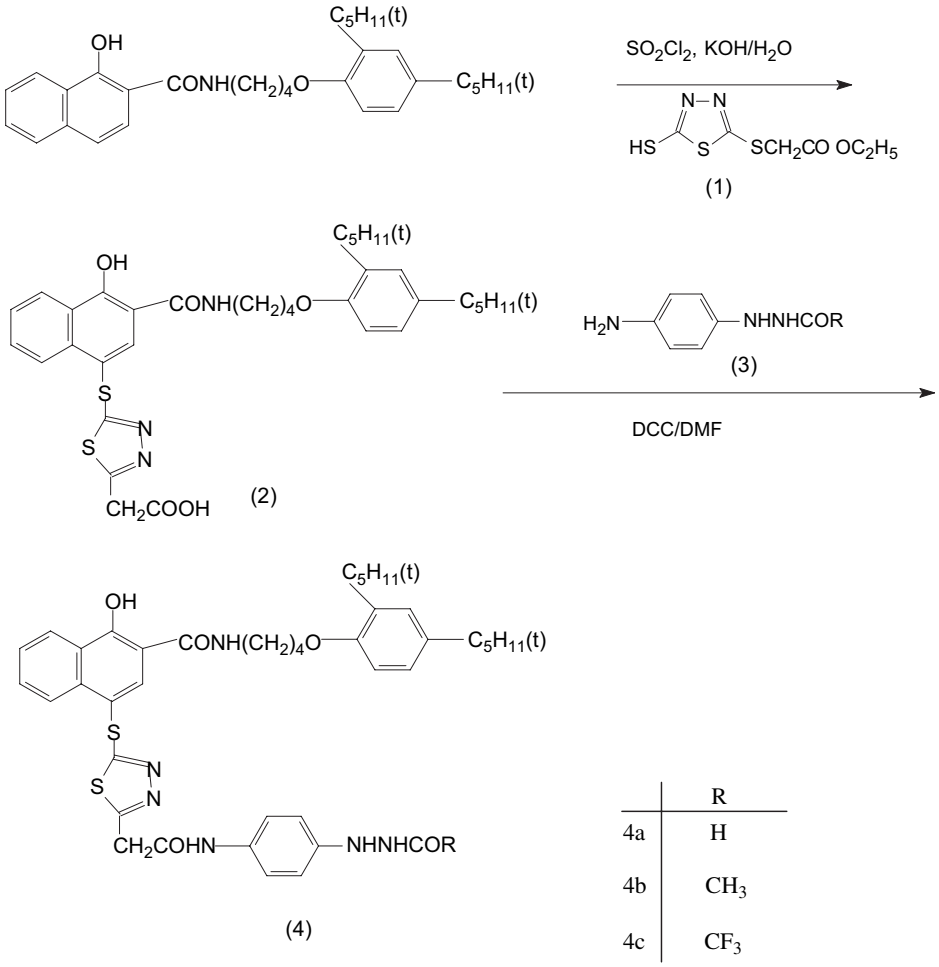
2,5-Dimercapto-1,3,4-thiadiazole [8], 2-ethoxycarbonylmethlithio-5-mercapto-1,3,4-thiadiazole [9], 2-(carboxylene)thio-5-mercapto-1,3,4-thiadiazole [9], 5%Pd–C catalyst [10], 1-formyl-2-(4-aminophenyl)hydrazine (3a) [5,11], 1-acetyl-2-(4-aminophenyl)hydrazine (3b) [5,12] were prepared according to the literature procedures.

The DAR couplers can be synthesized by various routes and typical syntheses are illustrated in Schemes 1 and 2.

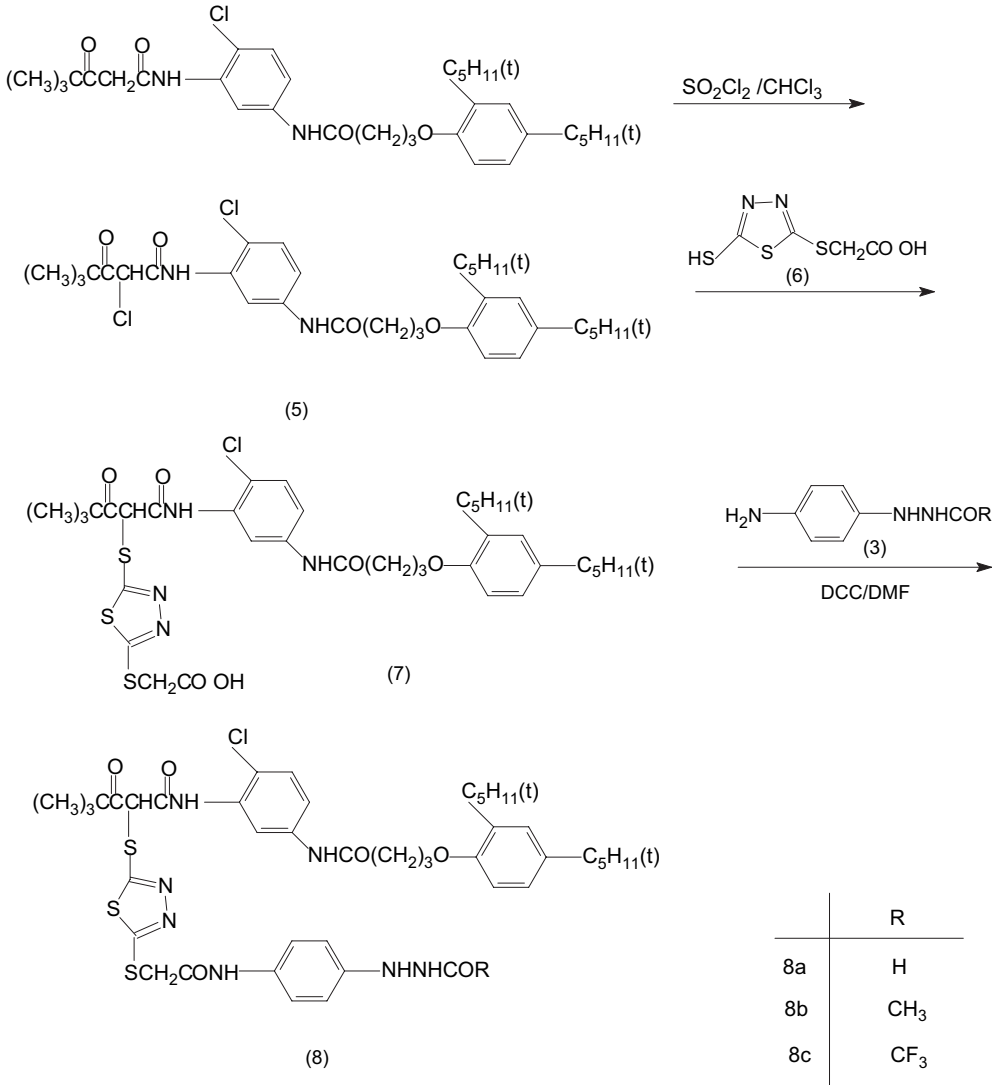
2.1.2. Synthesis of 1-trifluoroacetyl-2-(4-aminophenyl)hydrazine (3c)

p-Nitrophenylhydrazine (0.3 mol) was dissolved in acetonitrile (160 ml). A solution of trifluoroacetic anhydride (0.6 mol) in acetonitrile (20 ml) was added dropwise over 20 min at room temperature, the mixture refluxed with stirring for 2 h, cooled to 5 °C, the solution was filtered and solids were washed with acetonitrile and recrystallized to give 1-trifluoroacetyl-2-(4-nitrophenyl)-hydrazine as yellow solids. Yield: 98.6%.

To 10 g 1-trifluoroacetyl-2-(4-nitrophenyl)-hydrazine was added 1 g of 5%Pd–C catalyst and 250 ml of ethanol and the mixture was subjected to catalytic hydrogenation in an autoclave. After removing the catalyst by filtration, the filtrate was cooled and the precipitated crystals were collected by filtration to obtain 3c as white solids. Yield, melting point and MS data are shown in Table 1.



Scheme 1. The route of cyan DAR couplers were synthesized.



Scheme 2. The route of yellow DAR couplers were synthesized.

2.1.3. Preparation of cyan DAR coupler (4a)

Compound 2 (0.05 mol) and 1-formyl-2-(4-aminophenyl)hydrazine (3a) (0.05 mol) were dissolved in DMF (100 ml). A solution of *N*,*N*-dicyclohexylcarbdimide (DCC) (0.05 mol) in DMF (20 ml) was added dropwise at 0 °C over 30 min and stirring was continued at room temperature for 2 h. The solution was filtered, and the filtrate poured into cold water, when the products

Table 1
Yields, melting points and mass spectra data of compounds 1–7

Compound	Yield (%)	Melting point (°C) of recrystallization solvent	MS (*m*/*z*)
1	95	68–70 CCl_4	236(M^+) 192($M^+ - OC_2H_5 + 1$) 117($M^+ - SCH_2COOEt$) 104($M^+ - CSCH_2COOEt$) 87(CH_2COOEt)
2	88	92–94 EtOH	683($M^+ + 1$) 624($M^+ - CH_2COOH + 1$)
3a	87	123–125 EtOH	151(M^+) 122($M^+ - CHO$) 107($M^+ - NHCHO$) 92($M^+ - NHNHCHO$)
3b	84	140–142 EtOH	165(M^+) 122($M^+ - COCH_3$) 107($M^+ - NHCOCH_3$) 92($M^+ - NHNHCOCH_3$)
3c	98.6	110–112 EtOH	219(M^+) 122($M^+ - COCF_3$) 108($M^+ - NHCOCF_3 + 1$) 92($M^+ - NHNHCOCF_3$)
5	86.8	96–98 Petroleum ether	604($M^+ - 1$)
6	97.5	164–166 H_2O	208(M^+) 150($M^+ - CH_2COOH + 1$) 58(SC=N)
7	89	99–101 EtOH	

Table 2
IR and mass spectra data for compounds 4 and 8

Product	IR(KBr) ν (cm^{-1})			^1H NMR (DMSO-d_6)
	NH	C=O	C=N	
4a	3280	1686 1614	1588	0.45–0.6(6H,2CH_3,t), 1.0–1.3(12H,4CH_3,d), 1.5–1.9(8H,CH_2, 2CH_3,m), 3.9–4.1(6H,CH_2O,CH_2N,CH_2S,m), 6.6–8.5(12H,Ph,m), 8.6(1H,CHO,m),9.2–9.4(1H,CONH$(CH_2)_4$,m), 9.7(1H,CONHPh,s), 9.9–10.1(1H,PhNHN,s)
4b	3282	1658 1615	1588	0.45–0.6(6H,2CH_3,t), 1.0–1.3(15H,5CH_3,d), 1.5–2.0(8H,CH_2,2CH_3,m), 3.9–4.1(6H,CH_2O,CH_2N,CH_2S,m), 6.6–8.5(12H,Ph,m), 9.6(1H,CONH$(CH_2)_4$,m), 9.9(1H,CONHPh,s), 10.1(1H,PhNHN,d).
4c	3299	1734 1667 1615	1588	0.45–0.6(6H,2CH_3,t), 1.0–1.4(12H,4CH_3,d), 1.5–2.0(8H,CH_2,2CH_3,m), 3.9–4.2(6H,CH_2O,CH_2N,CH_2S,m), 6.6–8.5(12H,Ph,m), 9.2–9.4(1H,CONH$(CH_2)_4$,m), 10.1(1H,CONHPh,s), 11.4(1H,PhNHN,s)
8a	3326	1687	1601	0.5–0.6(6H,2CH_3,t), 1.0–1.4(21H,7CH_3,s), 1.5–1.6(2H,CCH_2CH_3,d), 1.75–1.8(2H,CCH_2CH_3,d), 2.0–2.1(2H,$CH_2CH_2CH_2$,m), 2.49(2H,$COCH_2$,t), 3.9–4.0(2H,CH_2O,t), 4.2(2H,CH_2S,t), 6.2(1H,COCHCO,m), 6.6–7.9(10H,Ph,m), 8.1(1H,CHO,m), 9.3(1H,NHCO$(CH_2)_3$,m), 9.7(1H,CONHPh,s), 10.0–10.2(1H,PhNHN,s).
8b	3263	1671	1609	0.5–0.6(6H,2CH_3,t),1.1–1.3(24H,8CH_3,s) ,1.5–1.6(2H,CCH_2CH_3,d), 1.8(2H,CCH_2CH_3,d), 2.0–2.1(2H,$CH_2CH_2CH_2$,m), 2.49(2H,$COCH_2$,t), 4.0(2H,CH_2O,t), 4.2(2H,CH_2S,t), 6.2(1H,COCHCO,m), 6.6–7.7(10H,Ph,m), 9.6(1H,NHCO$(CH_2)_3$,m), 10.0–10.2(1H,CONHPh,s), 10.4(1H,PhNHNH,s)
8c	3263	1735 1672	1601	0.5–0.6(6H,2CH_3,t), 1.0–1.4(21H,7CH_3,s), 1.5–2.0(4H,2CCH_2CH_3,d), 2.0–2.1(2H,$CH_2CH_2CH_2$,m), 2.49(2H,$COCH_2$,t), 3.9(2H,CH_2O,t), 4.1–4.2(2H,CH_2S,t), 6.2(1H,COCHCO,m), 6.6–7.7(10H,Ph,m), 10.1–10.7(1H,CONHPh,s) ,11.3(1H,PhNHN,s)

precipitated, then was filtered, washed several times with water and recrystallized from EtOH to give cyan coupler 4a as white solids.

Compounds 4b and 4c were synthesized as 4a. Yield, melting point, MS, IR and ^1H NMR data are shown in Tables 2 and 3.

2.1.4. Synthesis of 2-pivaloyl-2-[4-chloro]-2-chliro-5-r-(2,4-diter-phenylphenoxy)-butyl-formamido]-acetanilide (5)

2-Pivaloyl-2-chliro-5-r-(2,4-diter-phenylphenoxy)-butyl-formamido]acetanilide (0.05 mol) was dissolved in $CHCl_3$ (50 ml). A solution of SO_2Cl_2 in $CHCl_3$ (20 ml) was added dropwise over 30 min at 0 °C for 3 h. After removal of $CHCl_3$, the residue was dissolved in petroleum ether (50 ml) with heating, then was cooled and the product precipitated readily and filtered, washed several times with petroleum ether to give compound (5) as a white solid. Yield, melting point and MS data are shown in Table 1.

2.1.5. Synthesis of 2-pivaloyl-2-[5-thio-2-carboxymethylene)thio-1,3,4-thiadiazol]-2-[4-chloro]-2-chliro-5-r-(2,4-diter-phenylphenoxy)-butyl-formamido]-acetanilide (7)

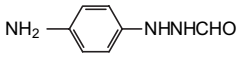
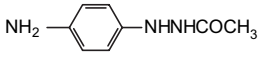
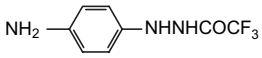
Compound (5) (0.001 mol) and 2-(carboxymethylene)-thio-5-mercapto-1,3,4-thiodiazol (0.001 mol) were dissolved in acetone (20 ml), triethylamine (0.002 mol) was added dropwise at room temperature with continuous stirring for 3 h, before cooling to below 15 °C. The solution was filtered and the filtrate poured into water (200 ml), the product precipitated readily and was filtered, washed several times with water and recrystallized to give compound (7) as a white solid. Yield, melting point and MS data are shown in Table 1.

Table 3
Yields, melting points and mass spectra data of compounds 4 and 8

Product	Yield (%)	Melting point (°C), recrystallization solvent	Molecular formula	MS (ESI,m/z[a])
4a	62.1	170–172 EtOH	$C_{42}H_{50}N_6O_4S_3$	838(M^+ + 23)
4b	60.8	123–135 EtOH	$C_{43}H_{52}N_6O_5S_3$	868(M^+ + 39)
4c	60.2	106–108 EtOH	$C_{43}H_{49}N_6O_5S_3F_3$	905(M^+ + 23)
8a	58.8	119–121 EtOH	$C_{44}H_{56}N_7O_6S_3Cl$	930(M^+ −1 + 23)
8b	55.4	158–160 DMF–EtOH	$C_{45}H_{58}N_7O_6S_3Cl$	945(M^+ −1 + 23)
8c	56.7	140–142 DMF–EtOH	$C_{45}H_{55}N_7O_6F_3S_3Cl$	1000(M^+ − 1 + 23)

[a] 23 and 39 are the atom weight of Na and K, respectively.

Table 4
The effect of DAR couplers 4a, 4b and 4c on the photographic properties of red-sensitive coating

DAR coupler	Development accelerating group	Lay-down (ml) 1% methanol solution	Photographic properties			
			S_Γ	D_{min}	γ	RMS
–	–	0	100	0.28	1.55	17.8
4a		1	125	0.28	1.35	17.8
		3	130	0.33	1.30	16.6
		5	140	0.37	1.25	17.1
		7	150	0.46	1.00	17.3
4b		1	110	0.28	1.37	17.6
		3	124	0.30	1.21	16.1
		5	124	0.40	1.19	16.6
		7	133	0.41	1.10	16.8
4c		1	135	0.31	1.46	16.8
		3	150	0.35	1.15	16.5
		5	150	0.45	1.02	16.8
		7	150	0.55	1.04	16.7

2.1.6. Preparation of DAR coupler 8a

Compound (7) (0.05 mol) and 1-formyl-2-(4-aminophenyl)hydrazine (0.05 mol) were dissolved in DMF (100 ml). A solution of DCC (20 ml) in DMF (20 ml) was added dropwise at 0 °C over 30 min, and stirring was continued at room temperature for 2 h. The solution was filtered, and the filtrate was precipitated by pouring into cold water, filtered, washed several times with water and recrystallized from EtOH to give yellow coupler 8a as a white solid.

Compounds 8b and 8c were synthesized by the same method as 8a. Yields, melting point, MS, IR and ^{1}H NMR data are shown in Tables 2 and 3.

2.2. Photographic properties of DAR couplers

To examine the effect of DAR couplers on the photographic properties, a single-layer color negative coating structure was employed.

First, the amount of the DAR couplers on the color negative material was studied and this clarified that the effect of DAR couplers on photographic properties was best with a 3 ml (cyan DAR couplers) or 0.3 ml (yellow DAR couplers) with 1% DAR coupler in methanol solution.

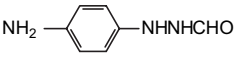
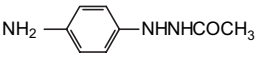
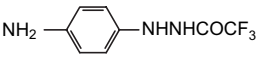
To obtain dye sensitometric response curves, the coatings were exposed stepwise to white light, followed by C-41-processing.

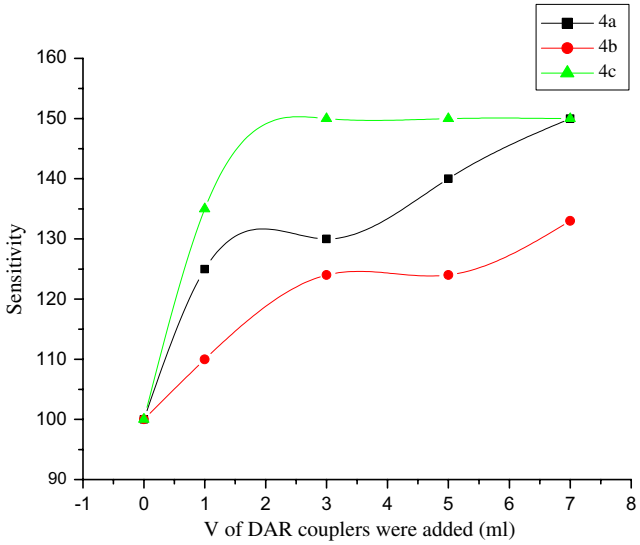
3. Results and discussion

The dye sensitometric data for red- and blue-sensitive coatings, measured by increased photosensitivity for the coating, are given in Tables 4 and 5, and Schemes 3–6.

It is apparent from Tables 4 and 5, and Schemes 3–6 that the increase of photosensitivity was considerable for the coating incorporating the DAR couplers, compared

Table 5
The effect of DAR couplers 8a, 8b and 8c on the photographic properties of blue-sensitive coating

DAR coupler	Development accelerating group	Lay-down (ml), 1% methanol solution	Photographic properties			
			S_Γ	D_{min}	γ	RMS
–	–	0	100	0.22	0.60	17.8
8a		0.1	103	0.28	0.60	18.2
		0.2	117	0.33	0.40	17.8
		0.3	120	0.44	0.27	17.6
		0.4	121	0.47	0.33	17.9
8b		0.1	112	0.22	0.63	17.8
		0.2	119	0.25	0.65	17.3
		0.3	120	0.30	0.60	18.0
		0.4	121	0.35	0.66	17.6
8c		0.1	120	0.25	0.60	17.6
		0.2	131	0.26	0.47	18.0
		0.3	148	0.28	0.42	17.6
		0.4	140	0.29	0.54	17.3

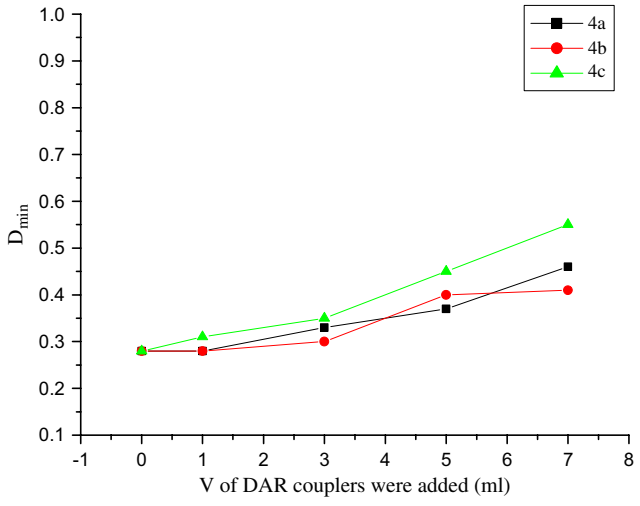


Scheme 3. The effect of DAR couplers 4a, 4b and 4c on photosensitivity.

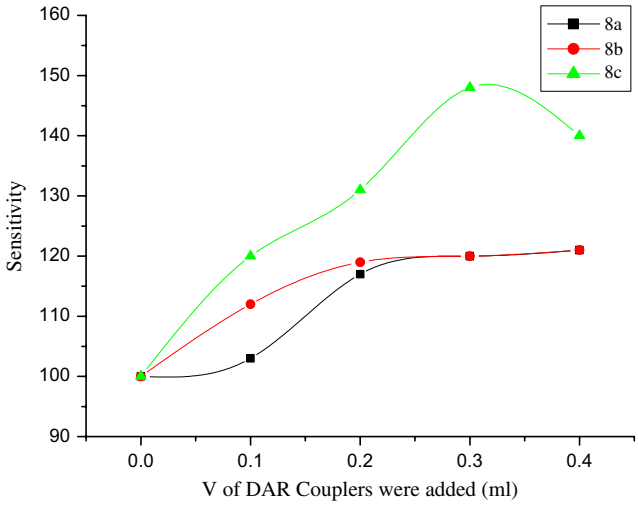
with the coating without the DAR couplers. All DAR couplers had a considerable effect for the coating with different photosensitivity, although a little increase of fogging (D_{min}) was observed. By comparing the lay-down, it was found that with the three cyan DAR couplers 4a, 4b and 4c, an addition of 3 ml was the best in increasing photosensitivity. The same was found for the three yellow DAR couplers 8a, 8b and 8c, again an addition of 0.3 ml was the best in increasing photosensitivity. DAR couplers 4c and 8c increased photosensitivity significantly by 50% and 48%, respectively. They could be of practical importance.

The sensitizing mechanism of DAR coupler was as follows:

(1) In development the DAR coupler reacts with QDI (Qxidized developer—quinondiimine) and produces

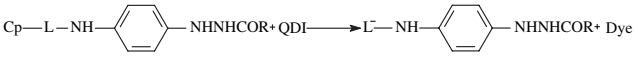


Scheme 4. The effect of DAR couplers 4a, 4b and 4c on D_{min}.

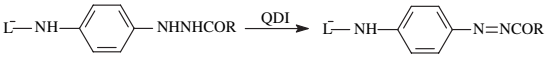


Scheme 5. The effect of DAR couplers 8a, 8b and 8c on photosensitivity.

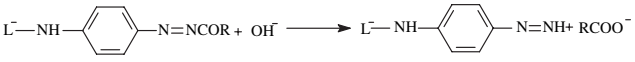
the dye, at the same time releases a development accelerator.



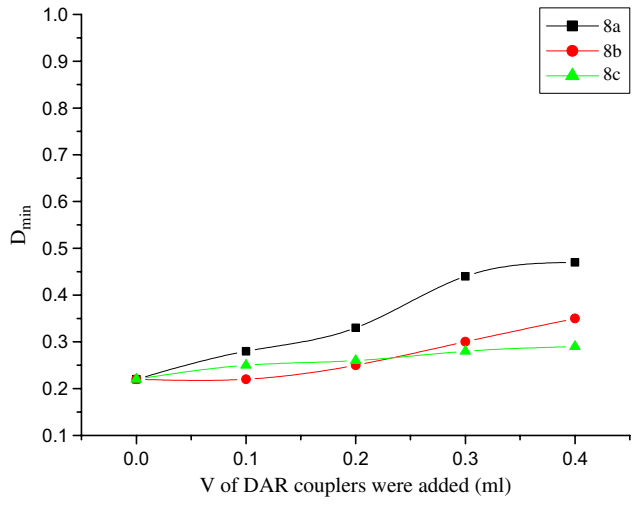
(2) The development accelerator is oxidized to 2-acyl-4-substituent phenylenediamide.



(3) 2-acyl-4-substituent phenyldiamide is hydrolyzed to 4-substituent phenyldiamide.



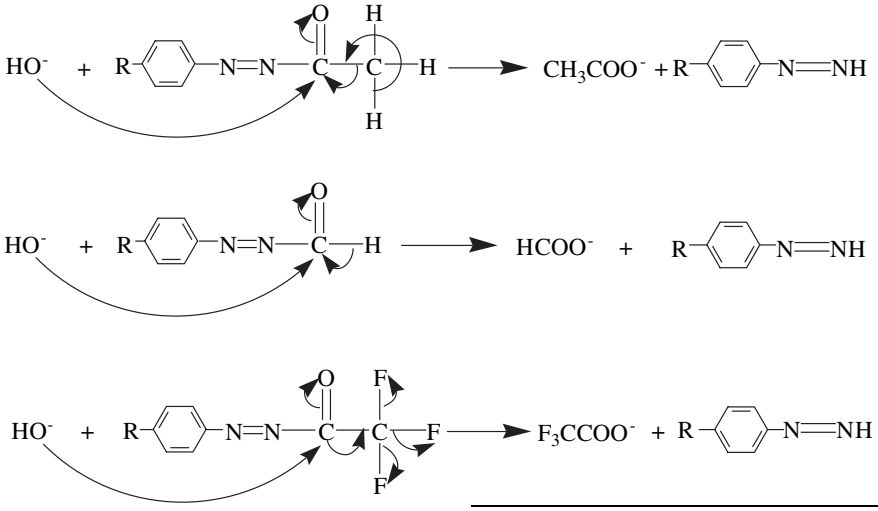
(4) The 4-substituent phenyldiamide is a very strong electron-donating group, it can make AgX (exposure



Scheme 6. The effect of DAR couplers 8a, 8b and 8c on D_{min}.

or nonexposure) reduce to Ag, and so DAR coupler could increase photosensitivity.

In the sensitizing mechanism, (3) was the most important. DAR couplers 4a, 8a; 4b, 8b; 4c, 8c contained different acylphenylhydrazine, so the mechanism in (3) was different.



Comparing the DAR couplers which contained different acylphenylhydrazine, the following conclusion was drawn: in the development of DAR couplers 4c and 8c, the disengaging group was CF_3COO^-. It was a strong electron-withdrawing group and it could make the density of electron cloud of carbon atom on carbonyl lower, and make attack by OH^- easier in the hydrolysis of 2-acyl-4-substituent phenylenediamide. The dissociating power of CF_3COO^- was stronger than CH_3COO^- and $HCOO^-$ in the development process and 4-substituent phenylenediamide was very important in development because it could make AgX (exposure or nonexposure) reduce to Ag. Therefore, the DAR coupler increases photosensitivty. DAR couplers 4c and 8c increased photosensitivity significantly.

4. Conclusions

Six novel DAR couplers with different residues and different accelerating functional groups were synthesized. The structure of the DAR couplers were confirmed by MS, IR and ^1H NMR spectroscopy.

Increased photosensitivity was observed when the DAR couplers employed in the study were incorporated within an experimental bromo-iodide T-grain emulsion. A comparison of these DAR couplers showed that couplers (4c) and (8c), which contained 1-trifluoroacetyl-2-(4-aminophenyl)hydrazine as the development accelerating group were, the best in increasing photosensitivity. They increased photosensitivity 50% in the case of compound (4c) and 48% in the case of compound (8c). They could be considered for future commercial practical application.

References

[1] Stauffer RE, Smith EF, Trivelli APH. J Franklin Inst 1944;238:291.
[2] Shinohara KI, Bayer E. J Photogr Sci 1987;35:181.
[3] Kitchin JP, Hall KP, Mott AW, Marchesano C, Bownan R. J Photogr Sci 1987;35:162.
[4] Kobayashi H, Takahashi T, Hirano S, Hirosa T, Adachi K. German patent 3209110; 1982.
[5] Kobayashi H, Mihayash K. European patent 147765; 1985.
[6] Zhu ZH, Chen SL, Chen Y. Dyes Pigments 1991;17:163.
[7] Jarvis JR, Twist PJ. J Imaging Sci 1989;33:217.
[8] Fields EK. J Org Chem 1956;21:497.
[9] Kiyoshi Murase, Toshiyasu Mase, Hiromu Hara. US patent 4855310; 1982.
[10] Horing EC. Organic syntheses, vol. 3. New York: John Wiley; 1955 coll. p. 520.
[11] Buzykin BI, Sysoeva LP, Kitaev YP. Zh Org Khim 1976;12(8):1670–80.
[12] Mifune Hiroyuki, Hirano Shigeo, Akimura Yoshitaka. US patent 4323643; 1982.