11) Publication number:

0 271 323 A2

12

EUROPEAN PATENT APPLICATION

21 Application number: 87310810.4

2 Date of filing: 09.12.87

(5) Int. Cl.4: **G 03 C 7/34** // C07C127/19

30 Priority: 12.12.86 US 940830

43 Date of publication of application: 15.06.88 Bulletin 88/24

Designated Contracting States:
 BE CH DE FR GB LI NL

Applicant: EASTMAN KODAK COMPANY
Patent Department 343 State Street
Rochester New York 14650 (US)

(2) Inventor: Kilminster, Kenneth Norman EASTMAN KODAK COMPANY Patent Department 343 State Street Rochester New York 14650 (US)

Hoke, David EASTMAN KODAK COMPANY Patent Department 343 State Street Rochester New York 14650 (US)

(4) Representative: Nunney, Ronald Frederick Adolphe et al Kodak Limited Patent Department Headstone Drive Harrow Middlesex HA1 4TY (GB)

- 54 Dye forming coupler and photographic element containing same.
- (a) A novel phenolic cyan dye-forming coupler contains a p-cyanophenylureido group in the 2-position and in the 5-position an acylamino group containing bulky substituents sufficient to provide steric interaction within the coupler molecule and the dye molecule derived therefrom. The coupler is useful in a photographic emulsion.

EP 0 271 323 A2

Description

DYE FORMING COUPLER AND PHOTOGRAPHIC ELEMENT CONTAINING SAME

The present invention relates to a novel phenolic cyan dye-forming coupler and to a photographic element containing such coupler.

Couplers which are used to obtain cyan dyes for color photography are typically phenols and naphthols. These couplers yield azomethine dyes upon coupling with oxidized aromatic primary amino color developing agents.

U. S. Patent 4,333,999 describes cyan phenolic couplers which comprise a p-cyanophenylureido group in the 2-position of the phenolic ring. This class of couplers has found wide commercial acceptance in photographic applications. Included among the important advantages of these couplers is their ability to provide dyes of excellent purity and hues which are shifted bathochromically to the long wavelength red absorption region.

However, even with these couplers, which have found extensive utility, further improvements in coupler reactivity and enhanced dye absorption continue to be sought. For example, it has been difficult to obtain, with the same coupler, both high coupling effectiveness and a dye of the desired hue purity with long wavelength red absorption. Coupling effectiveness is measured for each coupler of this invention by comparing the gamma or contrast of its dye image sensitometric test curve with that of a control coupler under identical conditions.

Inasmuch as the coupler structures of the '999 patent do not provide a combination of essential moieties which improve coupling effectiveness while maintaining the desired bathochromic shift and hue purity in subsequently obtained dyes, there is a continuing search for couplers which can provide these desirable properties.

The present invention seeks to meet these objectives by providing a cyan phenolic coupler compound, and a photographic element containing such compound, wherein the 5-position acylamino ballast moiety of the compound includes the use of substituent groups defined as R¹, R² and X, in the Formula described below to provide steric bulk in the ballast portion of the coupler compound as well as in the resulting dye molecule.

More particularly, the invention provides a coupler compound, and a photographic element comprising such compound, characterized in that the compound has the following structural formula:

30

35

40

45

60

5

10

20

25

wherein

R¹ is an unsubstituted or substituted alkyl group having from 1 to about 24 carbon atoms, an unsubstituted or substituted aralkyl group having from 7 to about 24 carbon atoms or an unsubstituted or substituted cycloalkyl group having from 3 to about 8 carbon atoms in the ring;

R² is hydrogen or a straight or branched chain, unsubstituted or substituted alkyl group having from 1 to about 16 carbon atoms;

L is oxygen or sulfur;

X is hydrogen, an unsubstituted or substituted primary, secondary or tertiary alkyl group having from 1 to about 24 carbon atoms, an unsubstituted or substituted aryl group having from 6 to about 24 carbon atoms, an unsubstituted or substituted cycloalkyl group having from 3 to about 8 carbon atoms in the ring, an unsubstituted or substituted heterocyclic group having from 4 to about 7 atoms in the ring, wherein hetero ring atoms are nitrogen, oxygen or sulfur, or X is halogen, cyano, nitro, -COR³, -COOR³, -CONR³R⁴, -OR³, -SR³, -OSO₂R³, -SO₂R³, -NR⁴SO₂R³, -SO₂NR³R⁴ or -NR⁴COR³, with the proviso that when X is hydrogen R¹ is an aralkyl or branched alkyl group and R² is an alkyl group having at least 2 carbon atoms;

Y is sulfonamidophenyl of the formula -NHSO₂-phenyl or sulfamoylphenyl of the formula -SO₂NH-phenyl, wherein the phenyl ring is unsubstituted or substituted;

R³ is an unsubstituted or substituted alkyl group having from 1 to about 12 carbon atoms or an unsubstituted or substituted aryl group having from 6 to about 24 carbon atoms;

R4 is as defined for R3 or is hydrogen; and

Z is hydrogen or a coupling-off group.

When R¹ is an aralkyl group, the alkylene portion thereof preferably comprises 1 or 2 carbon atoms. Preferred R¹ groups are unsubstituted or substituted alkyl groups of 1 to about 10 carbon atoms or cycloalkyl of 4 to about 7 carbon atoms Cycloalkyl or branched chain alkyl groups are preferred over straight chain alkyl, since they provide greater steric interaction with adjacent groups thus enhancing the desired properties of the

described coupler compounds. Experimental data has shown that when both R¹ and R² are hydrogen the desired improvement in photographic properties is not realized.

Substituents which may be present on the R¹ and R² groups include hydroxy, halogen, CF₃, CN, NO₂ and amino, including substituted amino, of the formula NRaRb, where Ra and Rb, which may be the same or different, are hydrogen, alkyl of 1 to about 6 carbon atoms or phenyl, which may be substituted, or Ra and Rb may be combined with the nitrogen atom to which they are attached to form a heterocyclic ring of 5 to 6 atoms.

5

10

15

20

25

45

60

The X group, when alkyl, cycloalkyl, aryl or a heterocyclic ring, and the Y group may also be substituted. Such substituents may be alkyl or alkoxy groups having from 1 to about 6 carbon atoms, or hydroxy, halogen, CF₃, CN, NO₂ or amino, including substituted amino as defined above in the R¹ and R² substituent definitions. Preferred X groups are secondary alkyl moieties containing 3 or 4 carbon atoms, chloro, cyano and nitro.

Coupling off groups defined by Z are well known to those skilled in the art. Such groups can determine the equivalency of the coupler i.e., whether it is a two-equivalent coupler or a four-equivalent coupler. Such groups can also modify the reactivity of the coupler or can advantageously affect the layer in which the coupler is coated, or other layers in the element by performing, after release from the coupler, such functions as development inhibition, bleach inhibition, bleach acceleration, color correction and the like.

Typical coupling-off groups are -OR 3 , -NHSO $_2$ R 3 , -OP(OR 3) $_2$ and -O-Q-R 3 wherein Q is -CO-, -COO-, -SO $_2$ - or -CONR 4 .

Preferred coupling-off groups include those having the formula: -OR5, -OCOR5, -OCO₂R5, -NHSO₂R5, -OP(OR5)₃, -OCO₂R5, -OCO₂R5, -OCH₂CONHAlkB or -OAlkNHSO₂R5 where R5 is alkyl having from 1 to about 16 carbon atoms or aryl having from 6 to about 18 carbon atoms; Alk is alkylene having from 1 to about 3 carbon atoms and B is -OH, -OR5 or -OCOR5. These coupling off groups are described in the art, for example, in one or more of the following patents: U. S. Nos. 2,455,169; 3,227,551; 3,432,521; 3,476,563; 3,617,291; 3,880,661; 4,052,212; and 4,134,766; and in U. K. Patents and published applications Nos. 1,466,728; 1,531,927; 1,533,039; 2,006,755A and 2,017,704A, the disclosures of which are incorporated herein by reference.

The ballast portion of the above-described coupler structure which is defined by the moiety:

is of such size and configuration as to confer on the coupler molecule sufficient bulk to render the coupler substantially non-diffusible from the layer in which it is coated in a photographic element. Such ballasting is achieved when one or more of the R¹, R², X or Y groups, as defined above, includes substituted or unsubstituted alkyl or aralkyl groups containing at least 7 and up to about 24 carbon atoms. Representative substituents can be as described above for the R¹, R², X and Y groups.

The desirable objectives of this invention are attained by particular combinations of substituent groups on the ballast moiety of the coupler compounds of this invention. For example, bulky substituent groups are present in at least two of the positions represented by R¹, R² and X, which substituents are spatially arranged so that steric interaction between them, or with adjacent portions of the coupler or the dye molecule formed therefrom, result in cyan dyes having desirably narrow bandwidths while absorbing red light at relatively longer wavelengths.

Moreover, proper choice of R¹, R², X, Y and Z groups results in couplers of higher coupling effectiveness than provided by control Coupler A, disclosed in the '999 patent.

Preferred coupler compounds of this invention include those presented by the structural formula:

wherein:

Z is hydrogen or

L is oxygen or sulfur;

15

30

35

40

45

50

55

60

65

R6 is an alkyl or alkoxy group having from 1 to about 10 carbon atoms;

R1 is an unsubstituted or a substituted alkyl group having from 1 to about 10 carbon atoms;

R² is hydrogen or an alkyl group having from 1 to about 10 carbon atoms;

- X is a secondary alkyl group having from 3 to about 18 carbon atoms, alkylcarbonyl, alkoxycarbonyl, alkanesulfonyl or alkanesulfonamido where the alkyl, alkane or alkoxy moieties have from 3 to about 18 carbon atoms, or X is chloro, cyano or nitro, or X is hydrogen when i) R¹ is aralkyl having from 7 to about 10 carbon atoms or branched chain alkyl having from 3 to about 8 carbon atoms and ii) R² is alkyl having from 2 to about 8 carbon atoms; and
- Y is as defined above wherein the sulfonamidophenyl or the sulfamoylphenyl ring is unsubstituted or is substituted with a hydrophilic group, particularly with a hydroxy or a carboxy group.

Especially preferred coupler compounds are those where Y is substituted in the 5-position of the phenyl

Specific coupler compounds of this invention are shown below in Table I with reference to the following structural formula:

TABLE I

Coupler Compound	<u>R</u> 1	<u>R²</u>	<u>x</u>		<u>Y</u>	<u>Z*</u>	5
1	-с ₁₀ н ₂₁	—н	-cn	5-NHSO ₂ -	-ОН	A	10
2	**	11	-соосн	3	11	**	
3	**	11 .	-NHSO ₂	сн ₃	11	**	15
4	**	**	-с1		11	**	
5	11	11	-C1	5-NHSO ₂ -	· • *	11	20 25
6	**	"	-C1	5-NHSO ₂ -	OH	11	30
7	**	" _	-С ₄ Н ₉ t	4-NHSO ₂ -	-ОН	99	35
		* A rep	presents	-0-	ОСН	3	40

Couplers of this invention can be prepared by reacting p-cyanophenylisocyanate with an appropriate aminophenol, such as 2-amino-5-nitrophenol or 2-amino-4-chloro-5-nitrophenol to form the 2-(p-cyanophenyl)ureido compound. The nitro group can then be reduced to an amine and the ballast group attached thereto by conventional procedures. Two equivalent couplers can be prepared by known techniques, for example, by substitution of the 4-chloro group on the starting phenol.

The following synthesis illustrates preparation of a 4-aryloxy substituted coupler compound of this invention:

Synthesis of coupler compounds of this invention is accomplished by combining a separately prepared phenolic coupler moiety with a separately prepared ballast moiety. Details of such preparations are noted below relative to a specific coupler compound identified in Table I.

Preparation of Coupler Compound No. 1 was carried out according to the following scheme:

55

60

A. Preparation of ballast moiety

$$S-16 + (COC1)_{2} \longrightarrow \begin{matrix} C_{10}H_{21}CHCOC1 \\ O \\ O \\ SO_{2} \end{matrix} \qquad \begin{matrix} 5 \\ II \\ O \\ O \\ CH_{2} \end{matrix} \qquad \begin{matrix} 5 \\ II \\ O \\ O \end{matrix} \qquad \begin{matrix} 5 \\ II \\ O \\ O \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \qquad \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 6 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ O \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \\ II \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \begin{matrix} 1 \\ II \end{matrix} \end{matrix} \end{matrix}$$

Preparation of ballasted intermediate Compound S-17

To a stirred solution of 61 g (372 mmol) 2-cyano-5-nitrophenol in 500 ml dimethylacetamide was added 22 g (558 mmol) sodium hydride (60% oil dispersion) to form the sodium salt (S-12). After evolution of hydrogen was complete, 171 g (558 mmol) methyl 2-bromododecanoate (S-11) was added and stirring continued overnight. Addition of dilute hydrochloric acid followed by extraction with ethyl acetate and purification through silica gel yielded a gummy material, which in heptane provided 113 g tan crystalline S-13. A solution of this nitroester in 500 ml tetrahydrofuran was shaken overnight with 10 g 10% palladium on carbon catalyst, 5 drops hydrochloric acid, and 2 ml acetic acid under 40 lb hydrogen pressure. Removal of the catalyst by filtration and crystallization from cyclohexane yielded 99.6 g tan solid S-14.

Next, 88.1 g (312 mmol) 4-benzyloxybenzenesulfonyl chloride was added to a stirred solution of 90 g (260 mmol) S-14 in 500 ml pyridine. After several hours the mixture was poured into ice water/hydrochloric acid, extracted with ethyl acetate followed by silica gel chromatography to produce 138 g S-15 as a yellow oil. This methyl ester was dissolved in 400 ml methanol and 600 ml tetrahydrofuran and was hydrolyzed by treatment with 50 g sodium hydroxide in 200 ml water at 15° for 30 minutes. Extraction and purification yielded 130 g of S-16 acid as a yellow oil. A solution of 105 g (182 mmol) of S-16 in 800 ml methylene chloride was treated with 60 g oxalyl chloride and 1.0 ml dimethylformamide, stirred 1.5 hours, and concentrated to obtain the S-17 acid chloride as a yellow oil.

B. Preparation of phenolic coupler moiety

$$NO_{2} \xrightarrow{\text{II}} -NHCONH - \cdot \cdot -CN$$

$$NH_{2} \xrightarrow{\text{II}} -NHCONH - \cdot \cdot -CN$$

$$O \xrightarrow{\text{II}} -NHCONH - -CN$$

$$O \xrightarrow{\text{II}} -NHCONH$$

C. Coupler formation

5

15

40

45

50

55

60

Coupler Compound No. 1

Preparation of phenolic coupler moiety and Coupler Compound No. 1

A suspension of 92.6g (182 mmol) of the nitrobenzyl ether S-4 (prepared as described above in Synthesis 1) in 1 liter of tetrahydrofuran was shaken for 6 hours with 15 g 5% palladium on carbon catalyst, 5 drops hydrochloric acid, and 5 ml acetic acid under 40 lb hydrogen pressure to provide the aminophenol S-5. Then, under nitrogen, 66 g (550 mmol) dimethylaniline and 182 mmol S-17 acid chloride were added and stirring continued 15 minutes. Removal of catalyst by filtration followed by treatment with dilute hydrochloric acid, then extraction with ethyl acetate and purification through silica gel yielded 68 g white crystalline S-18 with the expected elemental analysis, infrared and mass spectra.

Coupler S-18 was dissolved in 800 ml tetrahydrofuran and shaken 7 hours with 6 g 10% palladium on carbon catalyst under 40 lb hydrogen pressure. Removal of catalyst, followed by concentration and crystallization from acetonitrile yielded 50 g of colorless Coupler No. 1, m.p. 175-177°

Other couplers described above were prepared by similar procedures, including the following for which melting points are available: Coupler No. 2 (183-185°), Coupler No. 3 (105-107°), Coupler No. 5 (191-192°), and Coupler No. 6 (138-140°).

The cyan dye-forming couplers of this invention can be used in the ways and for the purposes that cyan dye-forming couplers are used in the photographic art.

Typically, the couplers are incorporated in silver halide emulsions and the emulsions coated on a support to form a photographic element. Alternatively, the couplers can be incorporated in photographic elements adjacent the silver halide emulsion layer where, during development, the coupler will be in reactive association with development products such as oxidized color developing agent.

As used herein, the term "in reactive association" signifies that the coupler is in a silver halide emulsion layer or in an adjacent layer where, during processing, it is capable of reacting with silver halide development

The photographic elements can be single color elements or multicolor elements. In a multicolor element, the cyan dye-forming coupler is ususally associated with a red-sensitive emulsion, although it could be associated

with an unsensitized emulsion or an emulsion sensitized to a different region of the spectrum. Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various order as known in the art.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, at least one of the cyan dye-forming couplers being a coupler of this invention, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layer, interlayers, overcoat layers, subbing layers, and the like.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1978, Item 17643, published by Kenneth Mason Publications Ltd., Emsworth Hampshire, PO10 7DD, England, the disclosures of which are incorporated herein by reference. This publication will be identified hereafter by the term "Research Disclosure."

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited herein. Suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Section IX and the publications cited herein.

In addition to the couplers of this invention, the elements of the invention can include additional couplers as described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These couplers can be incorporated in the elements and emulsions as described in Research Disclosure Section VII, paragraph C and the publications cited therein.

The photographic elements of this invention, or individual layers thereof, can contain brighteners (Research Disclosure Section V), antifoggants and stabilizers (Research Disclosure Section VI), antistain agents and image dye stabilizers (Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (Research Disclosure Section VIII), hardeners (Research Disclosure Section XI), plasticizers and lubricants (Research Disclosure Section XIII), antistatic agents (Research Disclosure Section XIII), matting agents (Research Disclosure Section XVI) and development modifiers (Research Disclosure Section XXI).

The photographic elements can be coated on a variety of supports as described in Research Disclosure Section XVII and the references described therein.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed to form a visible dye image as described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and to oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

Preferred color developing agents are p-phenylene diamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N- β -(methanesulfonoamido)-ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N- β -hydroxyethylaniline sulfate, 4-amino-3- β -(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxy-ethyl)-m-toluidine di-p-toluene sulfonic acid.

With negative working silver halide this processing step leads to a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniform fogging of the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

In the following examples, a measure of each coupler's coupling effectiveness is illustrated by G, the ratio of its photographic dye image gamma (the slope of the sensitometric curve) to that of Control Coupler A, which is normalized to 1.0. Coupler A is identical to coupler number 7, in Table I, of U.S. Patent 4,333,999, the structural formula for which is noted below.

Normalization of the data compensates for coating and processing variations by relating the performance of each coupler as described herein to that of a control coupler coated and processed in the same manner. In these comparisons 2-equivalent couplers were coated at half the silver level of 4-equivalent couplers.

Processing and testing procedures were kept constant. Hue measurements on a normalized spectral absorption curve included λ max (the peak absorption wavelength) and HBW (the half-bandwidth). The HBW value serves to indicate the degree of unwanted absorption tailing into the green region. Particularly useful couplers provided dye images with G > 1.00, λ max > 680 nm and HBW <145 nm.

The following examples further illustrate the invention.

65

60

10

15

20

25

35

40

45

50

Photographic Example

Photographic elements were prepared by coating a cellulose acetate-butyrate film support with a photosensitive layer containing a silver bromoiodide emulsion at 0.91 g Ag/m², gelatin at 3.78 g/m², and a cyan phenolic coupler, as identified below, dispersed in one-half its weight of di-n-butyl phthalate and coated at 1.62 x 10^{-3} moles/m². The photosensitive layer was overcoated with a layer containing gelatin at 1.08 g/m² and the hardener compound bis-vinylsulfonylmethyl ether at 1.75 weight percent based on total gelatin.

Samples of each element were imagewise exposed through a graduated-density test object and processed at 40°C employing the following color developing solution, then stopped, bleached with a ferric EDTA solution, fixed, and washed to produce stepped cyan dye images.

K ₂ SO ₃	2.0 g	10
K ₂ CO ₃ (anhydrous)	30.0 g	
KBr	1.25 g	4.5
KI	0.6 g	15
4-Amino-3-methyl-N-ethyl	0.6 g	
N-β-hydroxyethylaniline	3.55 g	m
sulfate		20
Water to 1.0 liter,	pH 10.0	

The structural formulae of couplers used for comparison with the invention are as follows:

Coupler A:

$$t-C_{5}H_{11}-C_{5}H_{11}-C_{6}H_{11}-C_$$

Coupler B:

Results are recorded below in Table II.

60

50

55

5

25

		M (nm)	140	134	137	140	138	128	129	
		G Amax (nm) HBW (nm)	069	675	694	069	069	683	692	
	-CN	G Nma	1.00	1.47	}OH 1.48	1.30	1.20	1.37	1.55	соон
	OH O OH O	X Y	$4-t-c_{5}H_{11}$	5C ₁₅ H ₃₁	5-NHSO ₂	=	3H ₃ "	=	5-NHSO ₂	ຮ
Table II	R10 H	×	$t-c_5H_{11}$	Ħ	-CN	-соосн ³	-NHSO ₂ CH ₃	-C1	=	
		R ²	Ħ	=	=	=	=	=	=	-
	×	$\frac{\mathbb{R}^1}{\mathbb{R}^1}$	$-c_4H_9$	$-c_2H_5$	-C ₁₀ H ₂₁	=	=	Ξ	Ξ.	
		Coupler No.	А	В	₽	2	ю	4	5	

	G Amax (nm) HBW (nm)	1.39 693 134	1.16 695 142		10 15
	Y 5 HO		HOOH		20
	¥	5-NHSO ₂	4-NHSO ₂		<i>25</i> <i>30</i>
- Cont'd	I	-c1	-C4H9-t		35
II	×	T	T	·	40
Table	R ²	*	=		45
	$\frac{R}{R}$	=	=		50
	Coupler No.	9	7		55
					60

Comparison Couplers A and B of Table II represent structures in which the Y values do not conform to the requirements of the present invention. As shown in Table II, couplers of this invention provide improved

coupler effectiveness (G) with improved hue purity (HBW) while preserving the desirably high λ max absorption values.

Claims

5

10

15

20

25

30

35

40

45

50

55

60

65

1. A photographic element comprising a support and a photosensitive silver halide emulsion having associated therewith a cyan dye-forming coupler compound characterized in that said compound has the structural formula:

wherein:

R¹ is an unsubstituted or substituted alkyl group having from 1 to about 24 carbon atoms, an unsubstituted or substituted aralkyl group having from 7 to about 24 carbon atoms or an unsubstituted or substituted cycloalkyl group having from 3 to about 8 carbon atoms in the ring;

R² is hydrogen or a straight or branched chain, unsubstituted or substituted alkyl group having from 1 to about 16 carbon atoms;

L is oxygen or sulfur;

X is hydrogen, an unsubstituted or substituted primary, secondary or tertiary alkyl group having from 1 to about 24 carbon atoms, an unsubstituted or substituted aryl group having from 6 to about 24 carbon atoms, an unsubstituted or substituted cycloalkyl group having from 3 to about 8 carbon atoms in the ring, and unsubstituted or substituted heterocyclic group having from 4 to about 7 atoms in the ring, wherein hetero ring atoms are nitrogen, oxygen or sulfur, or X is halogen, cyano, nitro, -COR³, -COR³, -CONR³R⁴, -OR³, -SR³, -OSO₂R³, -SO₂R³, -SO₃R³, -NR⁴SO₂R³, -SO₂NR³R⁴ or -NR⁴COR³ with the proviso that when X is hydrogen R¹ is an aralkyl or a branched alkyl group and R² is an alkyl group having at least 2 carbon atoms;

Y is sulfonamidophenyl of the formula -NHSO₂-phenyl or sulfamoylphenyl of the formula -SO₂NH-phenyl, wherein phenyl is unsubstituted or substituted;

 R^3 is an unsubstituted or substituted alkyl group having from 1 to about 12 carbon atoms or an unsubstituted or substituted aryl group having from 6 to about 24 carbon atoms;

R4 is as defined for R3 or is hydrogen; and

Z is hydrogen or a coupling-off group.

- 2. The photographic element of claim 1 characterized in that R¹ is an aralkyl group the alkyl portion of which has 1 or 2 carbon atoms.
- 3. The photographic element of claim 1 characterised in that R¹ is an alkyl group having from 1 to about 10 carbon atoms.
- 4. The photographic element of claim 1 characterized in that R¹ is a cycloalkyl group having from 4 to about 7 carbon atoms.
- 5. The photographic element of any one of the preceding claims characterized in that R² is an alkyl group having from 1 to about 10 carbon atoms.
 - 6. The photographic element of any one of claims 1 to 4 characterized in that R² is hydrogen.
- 7. The photographic element of any one of the preceding claims characterized in that X is a secondary alkyl group having from 3 to about 18 carbon atoms.
- 8. The photographic element of any one of claims 1 to 6 characterized in that X is chloro, cyano or nitro.
- 9. The photographic element of any one of claims 1 to 6 characterized in that X is hydrogen.
- 10. The photographic element of any one of the preceding claims characterized in that Y is substituted in the 5-position of the phenyl ring.
- 11. The photographic element of claim 10 characterized in that Y a sulfonamoylphenyl group.
- 12. The photographic element of claim 10 characterized in that Y is a sulfonamidophenyl group.
- 13. The photographic element of claim 11 or 12 characterized in that the phenyl group is substituted with a hydroxy or a carboxy group.
- 14. The photographic element of any one of the preceding claims characterized in that Z is hydrogen.
- 15. The photographic element of any one of claims 1 to 13 characterized in that Z is -OR³, -NHSO₂R³, OP(OR³)₂ or -O-Q-R³ where Q is -CO-, -COO-, -SO₂- or -CONR⁴.
- 16. The photographic element of claim 15 characterized in that Z is a 4-alkoxysubstituted phenoxy group.

- 17. The photographic element of any one of the preceding claims characterized in that L is oxygen.
- 18. The photographic element of claim 1 characterized in that the cyan dye-forming coupler compound has the structural formula:

19. A cyan dye-forming coupler compound as defined in any one of the preceding claims.