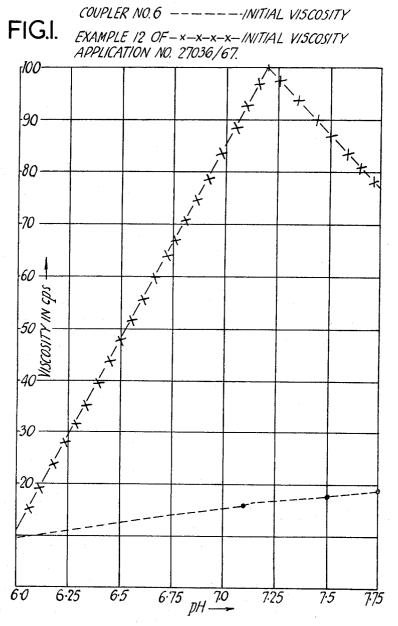
COLOUR COUPLERS

Filed April 14, 1970

2 Sheets-Sheet 1

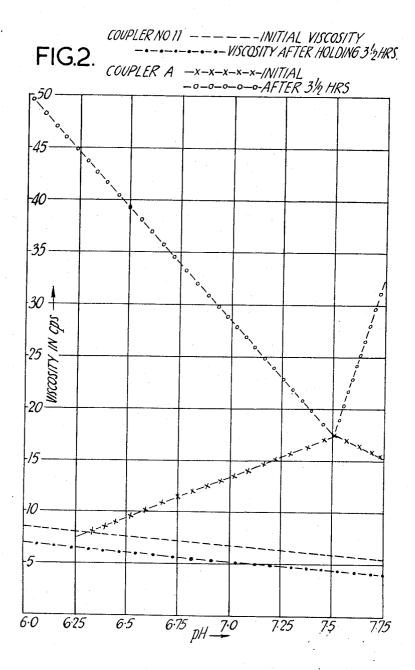


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Filed April 14, 1970

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Patented June 12, 1973

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3,738,840 COLOUR COUPLERS

Brian Anderson, Bury, England, assignor to Ilford Limited, Ilford, England Filed Apr. 14, 1970, Ser. No. 28,422

Filed Apr. 14, 1970, Ser. No. 28,422 Claims priority, application Great Britain, Apr. 18, 1969, 20,003/69

Int. Cl. G03c 1/40

U.S. Cl. 96-100

1 Claim

ABSTRACT OF THE DISCLOSURE

This application describes a colour coupler selected from the class consisting of compounds of the general formula:

and of the general formula:

$$B-Q X-R_1$$

wherin in the above two formulae B represents a colour coupler residue, Q is a group containing an alkali solubilising radical, R_1 is an alkyl group containing at least 12 carbon atoms and X is a direct link or --O,

— SO_2 — or — SO_2NH —, corresponding compounds in which there is a linking group between B and \hat{Q} and corresponding compounds in which there is a linking group between Q and the phenyl group.

This invention relates to colour photography and in particular to photographic colour couplers.

Many modern processes of colour photography are 40 based on the development of a developable silver salt photographic image by means of an aromatic primary amine compound, for example N:N-diethyl p-phenylene diamine, or a derivative thereof in the presence of a so-called colour coupler, this being a compound which will 45 couple with the oxidation products of the developer to yield a dye image, usually an azamethine or quinone-imine dye image, in situ with the developed silver.

In many of the processes the coupler contains alkali solubilising groups and is incorporated as an alkali solution into the emulsion layer or layers in which the corresponding dye image is ultimately to be formed. It is important that the coupler is fully compatible with the medium, usually gelatin, of the photographic emulsion since this allows thin layers to be obtained. A thin layer improves the sharpness of the image therein. It is also important that the colour coupler is substantive, i.e. it remains in the layer in which it is incorporated.

Alkali-soluble substantive colour couplers can be said to have the general structure: B—Q—G where B is the colour coupler residue, by which is meant a group such that the compound B—H (and therefore also the compound B—NH₂) is a compound which will react with the oxidation products of N·N-diethyl-p-phenylene diamine, formed during the development of a silver salt image with that compound to yield a dyestuff, Q is a group which includes an alkali solubilising radical, i.e. a radical which renders the colour coupler soluble in alkali solution so that it may be incorporated into an emulsion and G is a photographically inert organic radical of such molecular size and configuration as to render the coupler non-diffusing in the material during processing, i.e. it renders the

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colour coupler substantive to the gelatin once it has been incorporated therein. There may also be linking groups between the B and the Q group and between the Q and the G group.

It is well known that the interaction of such couplers with gelatin may increase the viscosity of the formulation. In some cases the viscosity increase occurs immediately on mixing, in others it takes place slowly over several hours. and the increase may also depend on the pH of the formulation. Ideally the coupler should give little or no viscosity increase with gelatin solutions at pH 6–8, and the formulation should have a constant viscosity for the time necessary to complete its coating as a layer.

One particular G group which has been widely used to achieve substantivity is the para-n-dodecylphenyl group. It has now been found that surprising advantages may be obtained if instead of the para-n-dodecylphenyl group an ortho-n-dodecylphenyl group or a meta-n-dodecylphenyl group, or the phenyl groups having a long chain alkyl group linked directly or indirectly to the ortho or meta position is used.

According to the present invention, therefore, there is provided a colour coupler selected from the class consisting of compounds of the general Formula I:

and of the general Formula II:

$$B-Q$$
 $X-B_1$
(II)

wherein the above two formulae B represents a colour coupler residue, Q is a group containing an alkali solubilising radical, R₁ is an alkyl group containing at least 12 carbon atoms and X is a direct link or —O—,

—SO₂— or —SO₂NH—, corresponding compounds in which there is a linking group between B and Q and corresponding compounds in which there is a linking between Q and the phenyl group.

The colour couplers containing such ortho or metasubstituted groups in general show a greater solubility and lower increase in viscosity when added to gelatin solutions, and tend to give dye images with better spectral absorption characteristics than the corresponding parasubstituted isomers.

Exemplary of the general structure of the colour couplers of the present invention are colour couplers of the general Formulae II to XIII.

$$\begin{array}{c} \text{X-R}_{\mathbf{i}} \\ \text{B-N} & \text{CO} \\ \text{CO} & \text{CO} \\ \\ \text{B-NHOC-A} & \text{CO} \\ \end{array}$$

$$(III)$$

$$B-NH-A \bigcirc N - \bigcirc (V)$$

$$\begin{array}{c} X-R_1 \\ \\ B-NHOC-A-N(R_2) \\ \\ COOH \end{array} \hspace{1cm} (VI)$$

(VII)

(VIII)

(XI)

(XII)

35

$$\begin{array}{c} CO \\ A-SO_2NH- \end{array} \hspace{1cm} \begin{array}{c} X-R_1 \\ \end{array} \hspace{1cm} \hspace{1cm} (XIII) \end{array}$$

$$B-N \xrightarrow{CO} A \xrightarrow{CO} N- \xrightarrow{X-R_1} (XIV)$$

wherein the above formulae X, R_1 and B have the meanings assigned to them above, R_2 is a hydrogen atom or an acyl group and A is a linking group. The linking groups A which may be present are, for example:

(1) in general Formulae III and IX, phthalimide linkages as described in British patent specification No. 1,039,-452. Couplers of this type are exemplified herein in colour couplers 1-36 and 61-68 as set forth later,

(2) in general Formulae IV and X, phthalimide linkages described in British patent specification No. 944,838. Colour couplers of this type are exemplified herein in colour couplers 37-41 as set forth later,

(3) in general Formulae V and XI, imide and in particular succinimide or phthalimide linkages as described in British patent specification No. 949,944. An example of such a colour coupler is 1-hydroxy-2-N(3-n-dodecylphenyl) 3:4-phthalimide naphthamide,

(4) in general Formulae VI and XII, n-propionylamino linkages as described in British patent specification No. 830,797. An example of such a colour coupler is 1phenyl - 3-β-[N-(m-n-dodecylphenyl)-acetylamino]-βcarboxy-n-propionylamino)-5-pyrazolone,

(5) in general Formulae VII and XIII, phthalimide linkages as described in British patent specification No. 997,550. An example of such a colour coupler is 2-carboxy - N - (1-phenyl-5-pyrazolonyl-3) benzamide-4-N'-(3-dodecylphenyl) sulphonamide,

(6) in general Formulae VIII and XIV, pyromellitic diamide linkages as described in British patent specifica-75 tion No. 1,004,675. Colour couplers of this type are exemplified herein in colour couplers Nos. 42-60 as set forth later.

The colour couplers of this invention contain a solubilising group, for example a carboxyl group, or a group which is converted to a carboxyl group by aqueous alkali. For example colour couplers of general Formulae III, IV, V, VII, IX, X, XI and XIII contain five membered cyclic imide rings, colour couplers of general Formulae VIII and XIV contain two such rings, which imide rings may be converted to the amic acid having a free carboxylic acid group by treatment with aqueous alkali in the presence of a solvent such as a lower alcohol, for example n-propanol, followed by acidification. The couplers of this invention are generally incorporated in a gelatino silver halide emulsion by means of their alkali solubilising groups, i.e. as the salts of the amic acid. The behaviour of the imide rings may be written

When mixed with the emulsion the exact state of the free carboxylic group will be determined by the particular colour forming structure and the pH of the mixture.

Suitable B groups which may be used in the color cou-30 plers of the invention are for example:

(1) Those which contain a —COCH₂CO— group, for example benzoyl-4-amino-2-methoxyacetanilide, 4' - methoxybenzoylacet-4-amino-2-methoxyanilide, the 2-alk-oxybenzoylacet-amino-anilides described in British patent specification No. 595,314, or the aminobenzoylacet-methoxy-anilides of British patent specification No. 800,408, and which give yellow dyestuffs on colour development with substituted p-phenylene diamines.

40 (2) Those which contain a cyanacetyl group or a pyrazolone ring for example $4 - \omega$ - cyanacetylaniline, 1 - methyl - 3 - amino - 5 - pyrazolone, $1-(\beta-hydroxy$ ethyl) - 3- amino - 5 - pyrazolone, 1-phenyl-3-amino-5pyrazolone and substituted 1-aryl-3-amino-5-pyrazolone as described in British patent specification Nos. 547,-064; 680,474; 680,488; the 1 - heterocycle-3-amino-5pyrazolones as described in British patent specification No. 599,919, the 1-(aminoaryl)-3-coumarilyamine - 5pyrazolones of British Patent specification No. 865,720 or the 1-phenyl-3-aminoarylamin - 5 - pyrazolones described in British patent specification No. 968,461 and British patent specification No. 956,261 or the 1-halogen-phenyl-3-amino pyrazolones described in British patent specification No. 1,173,943 or the 1-cyanohalogenphenyl-3-amino pyrazolones of British patent specification No. 1,170,859 and which give magenta dyestuffs on colour development with substituted p-phenylene diamines,

(3) phenols and 1-naphthols, which contain an amine group, for example, 4-chloro-5-methyl-2-aminophenyl or the aminophenols described in British patent specification Nos. 797,131; 754,306; 1-amino-5-naphthol N(β-amino-ethyl)-1-hydroxy - 2 - naphthamide or similar N-substituted naphthamides containing an amino group, as described in British patent specification No. 902,266 which may also be substituted in the 4-position, as described in British patent specification No. 757,368 and which give cyan dyestuffs on colour development with substituted p-phenylene diamines.

The following examples will serve to illustrate the invention.

EXAMPLE 1

Examples of couplers of General Formula III

Colour couplers of general Formula III were produced

wherein B has the value indicated in the following Table 1, A is a phenyl group and X is a direct linkage and R_1

is a straight chain dodecyl group as shown in the following general formula:

	TABLE 1	C ₁₂ H ₂₅	
Cou- pler No.	В	M.P., ° C.	λ_{\max} of derived dye
1	N—N C—NHOC—	256-258	544
2		192-194 _	
3.,	O OH,	170-172	545
4	C1 CH,	184–185	551
2	Cl-N-N Cl O'CH ₃	101-100	
5	Cl-N-N C C-NHOC-	158	562
6	CI CH,	182-184	553
7	O CH,	212-213	543
8	CN-NHOC-NHOC-	202-204	548
9	O CH, CI-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N	204-208	549
10,,,,,	CH ₁ O-COCH ₂ CONH-CONH-CONH-CONH-COCH ₃	ı 175–177	' -
11	OH CONH(CH ₃) ₆ CH ₃ —	175–176	688

¹ This particular coupler was prepared in the "amic" acid form.

The colour couplers of Table 1 are obtained by condensing an anhydride of formula

with a colour coupler amine B.NH2, where B is as defined in the table. The condensations are generally carried out in acetic acid at the boil and where the couplers precipitate they are collected from the hot reaction mixture, 15 otherwise they crystallise on cooling and are filtered off. The colour coupler is then recrystallised from an organic solvent where possible.

In some cases e.g. coupler No. 10 it is advantageous to prepare the coupler not in the "imide" form but in 20 the "amic acid" form. In these instances the condensation is generally carried out in ethyl acetate at the boil, often in the presence of a small amount of acetic acid.

A typical preparation is as follows:

Coupler No. 1

Ċ12H25

A mixture of 2.95 parts of 1-phenyl-3-(3-aminobenzonylamino)-5-pyrazolone, 4.35 parts of 4-(3-dodecylphenylaminocarbonyl) phthalic anhydride and 50 parts of acetic acid is stirred under reflux for 2 hours. The yellow precipitate formed is collected by filtration from 40 the hot reaction mixture, washed first with acetic acid and finally with ethyl acetate. The 5.6 parts of 4-(4dodecylphenylaminocarbonyl)-N - (3-[1-phenyl-5-pyrazolyl-3-Jaminocarbonyl phenyl)phthalimide are obtained as a yellow solid melting at 255-256° C. On analysis 45 the compound was found to contain 72.4% carbon, 6.2% hydrogen and 9.9% nitrogen ($C_{43}N_{45}N_5O_5$ requires 72.5% of carbon, 6.3% hydrogen and 9.8% nitrogen).

The 4-(3-dodecylphenylaminocarbonyl) phthalic anhydride used in the above may itself be prepared as follows:

A solution of 10.4 parts of m-dodecylaniline in 40 parts of monochlorobenzene is added dropwise over 2 hours to a stirred solution of 8.4 parts of trimellitic anhydride acid chloride in 60 parts of monochlorobenzene at 95-100° C. The mitxure is stirred for a further 30 minutes at 95-100° C. and then allowed to cool overnight to crystallise. The pale yellow solid is collected by filtration and washed well with ethyl acetate. The 13.4 parts of 4-(3 - dodecylphenylaminocarbonyl)phthalic anhydride are obtained as a yellow solid melting at 122-124° C.

The trimellitic anhydride acid chloride used here may be prepared by the action of thionyl chloride on trimellitic 10 anhydride.

The wavelength of maximum light absorption quoted in the table relates to the dye obtained by reversal processing of a coated layer containing the colour coupler using 4-amino-N-ethyl-N-β-hydroxyethylaniline sulphate as colour developing agent.

In some cases the colour couplers have been examined in negative or paper systems using the same colour developing agent. In these instances the λ_{max} value quoted is suffixed with the letter N or P.

A typical example of the preparation and processing of a photographic layer is as follows:

A mixture of 2.35 parts of coupler No. 1, 3.3 parts of 2 N potassium hydroxide solution and 5 parts of npropyl alcohol is warmed to dissolve. The solution so 25 obtained is screened and diluted with 30 parts of distilled water, and added to 160 parts of a green sensitised

gelatino silver halide emulsion containing silver halide equivalent to 2.4 parts of silver and 7.5 parts of gelatin, The emulsion is made up to a total of 250 parts by the addition of distilled water and then coated onto film base and the coated layer dried. When the photographic layer is exposed to green light, developed in a black and white developer, reexposed to light and developed in a colour developer containing 4-amino-N-ethyl-N-βhydroxyethyl aniline sulphate, bleached and fixed, a magenta dye image with light absorption maximum at 544 millimicrons is obtained.

EXAMPLE 2

Further colour couplers of general Formula III were produced. In these couplers B has the value indicated in Table 2 which follows, A is a phenyl group, X is —O and R₁ is a dodecyl group as shown in the following formula:

	TABLE 2				
Cou- pler No.	В	M.P.,	λ_{max} , of derived dye		
12	N N CH ₃	166-170	538		
13	N N N N N N N N N N N N N N N N N N N	265-266	542		

TABLE 2—Continued		
Coupler No. B	М.Р., ° С.	λ _{max} , of derived dye
14 Cl	243	548
ССН		
15 C1	245-248	540
16 Cl	156-158	546
Cl OCH,		
Cl————————————————————————————————————	211-212	550
Cl OCH;	266	540
Cl CH ₂ CH ₃		
19 CN	208-209	549
20 CN	232	
21 CN—N—N	212-214	
0 CH ₂ 22 CN-N-N C C-NHOC	164-165	
23 CN CINN	208-208	549
CH ₃	233-234	
CN-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-		
O CH ₃ 25 Cl	187–189	557
CN O CH.		

TABLE 2—continued				
Cou- pler No.	в		м.р., ° С.	λ_{max} , of derived dye

26 ОН	166–168	678
CONH(CH ₂) ₅ CH ₂ —	000 000	aue
27 ОН	262-263	675
CONHCH2. CH2		
28 ОН	212-214	677
CONHCH₄CH₂—		
Čl 29 ŅH	184-18 9	689(P)
CONHCH ₂		
30 OH	206-208	650(P)
CH ₃ —CI	-	
31 OH	193–194	671(P)
CI-CH ₃ -CI		
32 OCH ₃	182	
CH ₃ O————————————————————————————————————	160	442
COCH2CONH—CH3		
34 OCH ₃	151	451
COCH2CONH—CH3		
35 NO ₂ ——N	226-228	546 (N)
O CH ₁		
36 NO:	206-208 .	
о сн.		

The colour couplers of Table 2 are prepared in the same manner as the couplers of Table 1 except that in

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A typical preparation is as follows:

place of the anhydride of Formula XV there is used an anhydride of the formula

EXAMPLE 3

Colour couplers of general Formula IV

Colour couplers of general Formula IV were prepared wherein B has the value indicated in Table 3 which follows. A is a phenyl group, X is -0- and R_1 is a dodecyl group as shown in the following general formula:

This is prepared as follows:

A mixture of 5.9 parts of 1-phenyl-3(3-aminobenzoyl) amino-5-pyrazolone, 9.4 parts of 4-chlorocarbonyl-N(3-n-dodecycloxyphenyl)phthalimide and 75 parts of glacial acetic acid is heated under reflux for 2 hours and allowed to cool. The yellow solid is collected by filtration and washed well with ethyl acetate. The 13.6 parts of 3 - {3 - [1,3-dioxo-2-(3-dodecycloxyphenyl)dihydroisoindol - 5 - ylcarbonylamino]benzamido}-1-phenyl-5-pyrazolone are obtained as a solid melting at 210-212° C. On analysis the compound is found to contain 70.5% carbon, 6.0% hydrogen and 9.4% nitrogen. (C₄₃H₄₅N₅O₆ requires 71.0% carbon, 6.2% hydrogen and 9.6% nitrogen).

The 4-chlorocarbonyl - N - (3 - n - dodecyloxyphenyl) phthalimide may be prepared by the method described

TABLE 3

	TADDEO		
Cou- pler No.	В	М,Р., °С,	λ _{max} , of derived dye
37	N—N C—NHOC—	210-212	540
88	CH ₄ O————————————————————————————————————))	441(P)
39	COCH ₂ CONH	153	443(P)
40 39	COCH,CONH—OCH,	164-168	452(P)
41	CONH(CH ₃) ₆ CH ₃ -	117-120	689(N)

The colour couplers of Table 3 are obtained by condensing an acid chloride of formula

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with a colour coupler amine BNH₂ where B is as defined in the table.

for 4-chlorocarbonyl-N-n-octadecylphthalimide in Example 1 of British patent specification No. 944,838.

A photographic layer containing one of these colour couplers is prepared by the method described in Example 1.

EXAMPLE 4

Colour couplers of general Formula VIII

A colour coupler of general Formula VIII was prepared wherein B had the value indicated in Table 4 which follows, A was a phenyl group, X was a direct link and R₁

$$\begin{array}{c|c} CO & CO \\ \hline \\ CO & CO \\ \hline \\ CO & C_{12}H_{25} \end{array}$$

The above coupler is obtained by condensing an anhydride of formula

with 1-phenyl-3-amino-5-pyrazolone using the conditions given for the couplers of Table 5 which follows in 10 Example 5.

EXAMPLE 5

Further colour couplers of general Formula VIII were prepared wherein B has the value indicated in Table 5 which follows, A is a phenyl group, X is -O- and R_1 is a dodecyl group as shown in the following general formula:

δ1....

C1

294-296

546

17
TABLE 5—Continued

Cou- pler No.	В	М.Р., °С.	$\lambda_{max.}$ of derived dye
	CI—N—N		
	Cl CH2 C-NHOC-		
52		230-232	542
	N—N C—C—		
53		232-234	555 (N)
54		200	438 (P)
	CH ₂ O-COCH ₂ CONH-		
55		210	440 (P)
	COCH4CONH		
56		215	440 (P)
	CH;		
57	осн,	219-223	452 (P)
	COCH₂CONH—CO		
58	С1	212-213	
	Cl—N—N Cl O CH2		
59	. он	252-254	
	CH ₅		
60	. он	252-256	
	CH.		
	Ċ1		

The colour couplers of Table 5 are obtained by condensing an anhydride of formula

$$0 \xrightarrow{CO} CO \xrightarrow{OC_{12}H_{25}} (XIX)$$

with a colour coupler amine, BNH_2 , where B is as defined in the table.

The condensations are carried out in acetic acid at the boil, where the colour couplers precipitate they are collected from the hot reaction mixture otherwise they crystallise on cooling and are filtered off and recrystallised from an organic solvent where possible.

A typical preparation is as follows:

A mixture of 2.8 parts of 1-(3:4:5-trichlorophenyl)3-amino-5-pyrazolone, 4.76 parts of N-(3-dodecyloxyphenyl)pyromellitic mono-imide mono-anhydride and 50
parts of glacial acetic acid is stirred under reflux for 2
hours. The yellow precipitate formed is filtered from the

hot reaction mixture, washed with acetic acid then ethanol and dried. The 3.1 parts of N-(3-dodecyloxyphenyl)- N'-(1-phenyl-5-pyrazolonyl-3-)pyromellitic diimide are obtained as a solid melting at 234–236° C. On analysis the compound is found to contain 60.3% carbon, 4.7% hydrogen, 7.4% nitrogen and 14.8% chlorine. ($C_{37}H_{35}N_4O_6Cl_3$ requires 60.2% carbon, 4.7% hydrogen, 7.6% nitrogen and 14.4% chlorine.)

The N-(3-dodecyloxyphenyl) pyromellitic mono-imide mono-anhydride used in the above preparation may be 10 obtained in the manner described for N-(4-dodecylphenyl) pyromellitic mono-imide mono-anhydride in Example 1 of British patent specification No. 1,004,075.

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A photographic layer containing one of the above colour couplers may be prepared by the method given for the couplers of Example 1, except that an additional equivalent of 2 N potassium hydroxide solution is required to dissolve the coupler, i.e. 5.0 parts in place of 3.3 parts.

EXAMPLE 6

Colour couplers of general Formula IX

Colour couplers of general Formula IX wherein B has the value indicated in Table 6 which follows, A is a phenyl group, X is -0— and R_1 is a dodecyl group as shown in the following general formula:

TABLE

TABLE 6		
Coupler No. B	M.P., ° C.	λ _{max} . of derived dy e
O CH2	152-154	543
62 CN N N C C C C H ₂	130-136 :	
63 C1 C1 N N C C C C C C C C C C C C C C C	150–152	554
CI————————————————————————————————————	205-206	
65 CI CN N N C CH2	181–183	
C1 N N C CH2	177-17	nathana
CI————————————————————————————————————	1 154 – 155	658 (P)
OH CONH(CH2)5CH2	1 112-115	686 (P)

¹ These particular couplers were prepared in the "amic" acid form.

The colour couplers of Table 6 are obtained by condensing an anhydride of formula

with a colour coupler amine BNH₂ where B is as defined in Table 6. The condensations are generally carried out in acetic acid at the boil and where the couplers precipitate they are collected from the reaction mixture, otherwise they crystallise on cooling and are filtered off. The product is then recrystallised from an organic solvent where possible.

In some cases it is advantageous to prepare the couplers in the "amic acid" form. In these instances the condensation is generally carried out in ethyl acetate at the boil, often in the presence of a little acetic acid.

A typical preparation is as follows:

A mixture of 2.95 parts of 1-phenyl-3-(3-aminobenzoyl-amino)-5-pyrazolone, 4.51 parts of 4-(2-dodecyloxyphenylaminocarbonyl) phthalic anhydride and 50 parts of acetic acid is stirred under reflux for 2 hours. After cooling the yellow precipitate is collected by filtration, washed with ethanol and dried at 60° C. The 6.3 parts of 4-(2-dodecyloxyphenylamino carbonyl)-N-(3-[1-phenyl-5-pyrazolonyl-3]aminocarbonylphenyl) phthalimide are obtained as a solid melting at 152–154° C. On analysis the compound is found to contain 70.6% carbon, 6.2% hydrogen and 9.8% nitrogen ($C_{43}H_{45}N_5O_6$ requires 70.6% carbon, 6.2% hydrogen and 9.6% nitrogen).

The 4-(2-dodecyloxyphenylaminocarbonyl) phthalic anhydride used above may itself be prepared by the method given for 4-(3-dodecylphenylamino carbonyl) phthalic anhydride using o-dodecyloxyaniline in place of m-dodecylaniline.

A photographic layer containing a coupler from Table 6 may be prepared by the method described for the couplers of Example 1.

EXAMPLE 7

The improvement in viscosity of an emulsion containing a colour coupler of the invention is shown in FIG. 1 which compare Coupler No. 6 (this invention) with Example 12 of British patent specification No. 1,170,859 which is the p-dodecyl isomer of Coupler No. 6.

FIG. 2 compares Coupler No. 13 with its p-dodecyloxy 60 isomer Coupler A which has the following formula

Again the improvement in viscosity is illustrated.

The formulation used for the viscosity determination is obtained by adding a solution of coupler, prepared by dissolving 1 part of coupler in 2 parts of distilled n-propanol and 2 equivalents of 2 N potassium hydroxide solution at the boil, screening and diluting with water, to green sensitised silver halide emulsion so that the final formula-

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tion contains silver halide equivalent to 8.1 parts per litre of silver, 3.26% of gelatin, 1.72% of polyvinyl alcohol and 0.7% of sodium dioctyl succinate. The pH is adjusted in the preparation of the formulation by the addition of the required amount of dilute hydrochloric acid to the emulsion before the addition of the coupler solution.

The formulation viscosities were measured in an Ostwald viscometer relative to water. In the comparison of FIG. 1, the viscosities were measured initially only since on holding the emulsion containing Example 12 of British patent specification No. 1,170,859 became too viscous to measure. In the comparison of FIG. 2 the viscosities were measured initially and again after holding the formulations at 40° C. for 3½ hours.

I claim as my invention:

1. Colour photographic material which comprises a silver halide emulsion layer comprising a colour coupler selected from the class consisting of a colour coupler of the general formula:

$$B-Q X-R_1$$

and of the general formula:

wherein, in the above two formulae B represents
(i) a pyrazolene grouping of the structure

where A is a phenyl group, optionally carrying substituents selected from chlorine, cyano and nitro groups, and n is zero or 1, or

(ii) a grouping of the structure

having a free valency linkage on one or other of the indicated benzene rings either of which may carry alkyl or alkoxy substituent groups, or

(iii) a phenolic grouping of the structure

optionally containing substituent groups selected from

alkyl groups and halogen atoms, or (IV) a naphthol grouping of the structure

O C 12H25

õ

where W represents a radical of up to six methylene groups or a grouping

and Y is hydrogen or chlorine, Q represents a group selected from:

24

 R_1 is an alkyl group containing at least 12 carbon atoms and

X is a direct linkage, or an oxygen atom.

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U.S. Cl. X.R.

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