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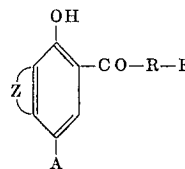
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[33] **Germany**

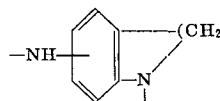
[31] **P 19 22 628.9**

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ABSTRACT: Improved color reproduction can be achieved using a color photographic material which contains as cyan-forming coupler a compound of the following formula:



wherein
F stands for a residue making the coupler diffusion resistant,
A stands for H, halogen or sulfo,
Z completes a condensed benzene or tetrahydrobenzene ring and
R stands for the bifunctional group:



These couplers can advantageously be combined with red azo masking couplers.

[54] **SILVER HALIDE EMULSIONS CONTAINING
CYAN-FORMING COUPLERS**
4 Claims, No Drawings

[52] U.S. Cl. **96/100,**
96/9, 96/56.2

[51] Int. Cl. **G03c 1/40**

[50] Field of Search 96/9, 56.2,
100

[56] **References Cited**
UNITED STATES PATENTS

2,296,306	9/1942	Peterson.....	96/100
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SILVER HALIDE EMULSIONS CONTAINING CYAN-FORMING COUPLERS

The invention relates to an improved color photographic material.

In particular, the invention relates to a color photographic material which contains new cyan-forming couplers and which is improved in its color reproduction, and in particular a material of this type in which the new cyan-forming couplers are used in combination with an azo red masking coupler.

It is known that the color side densities of image dyes produced on chromogenic development of multilayered photographic materials can be compensated by masking processes. In color photographic materials, this can be achieved by using so-called built-in masks. Masks of this type are produced in the course of the photographic process by using color-forming couplers which have the necessary color for masking the unwanted color side densities of the image dyes. Color-forming couplers which are suitable for this purpose generally have the chemical structure of conventional color-forming couplers but at the coupling position for the reaction with the oxidized color developer there is a group, generally an azo dye group, which imparts the color to the color-forming coupler and which is split off in the reaction with the oxidized color-forming developer. The image dye, together with its unwanted side densities, is thus produced by the color-forming development in the exposed and developed areas and at the same time the masking coupler, which has the appropriate color for masking the unwanted side densities of the image dye, is destroyed. In a well-masked cyan-forming coupler, the yellow and magenta side densities measured behind color filters after processing are constant and independent of the exposure.

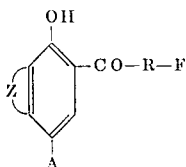
Although the problem of masking may be regarded as solved from a theoretical point of view, numerous difficulties arise in practice since the most highly sensitive color-forming couplers are required for highly sensitive color material, whereas the colored masking couplers which have a suitable color for masking the unwanted side densities of the image dye are generally somewhat less sensitive. A necessary condition for good masking, however, is that the coupler and the masking coupler should have the same photographic sensitivity. It is generally found that if a combination of coupler and masking coupler fulfills this condition, they are not well suited for each other kinetically, i.e. in spite of having the same photographic sensitivity the masking coupler and the colorless coupler react at different velocities with the oxidation products of the color developer. Of the two, the coupler is generally the more highly reactive. It, therefore, removes all the oxidation products of the developer in the region of threshold sensitivity, with the result that the masking coupler cannot exert its masking effect. This shows itself in the fact that in the region of lower densities falsification of color occurs because of the uncorrected side densities, whereas in the region of higher densities a so-called overmasking is often observed.

Another necessary condition for achieving improved color corrected images is, therefore, good kinetic compatibility between the coupler and the masking coupler.

The known cyan-forming couplers generally do not fulfill the above mentioned requirements, especially when special developer substances are used, e.g. 2-amino-5-(N-ethyl-N-β-methanesulphonamidoethylamino)-toluene.

It is the object of the invention to develop new highly sensitive cyan-forming couplers which satisfy practical requirements in their photographic and absorption properties, and which in addition can be used advantageously in conjunction with azo red masking couplers of the type described, for example, in German application P 15 97 510.7.

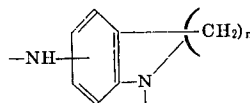
It has now been found that cyan-forming couplers of formula I below are eminently suitable for the production of color corrected photographic materials:



in which

A represents a hydrogen atom, a halogen atom, such as chlorine or bromine, or a sulpho group,

R represents the bifunctional group:



which is linked to the CO group of the above formula I via one of the two nitrogen atoms,

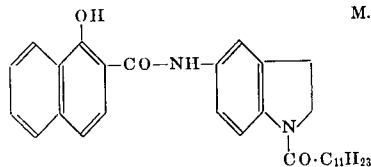
n represents 2 or 3,

F represents a radical which renders the compound resistant to diffusion, which radical is linked to the second nitrogen atom of the group R either directly or indirectly via a CO, CO-NH or CO-O group, e.g. it may represent

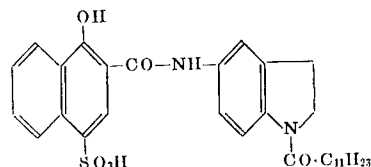
1. a straight chained or branched alkyl radical containing up to 20 C. atoms, preferably from 10 to 18 C. atoms,
2. an acyl radical derived from aliphatic carboxylic acids containing up to 22 C. atoms, preferably from 12 to 18 C. atoms, or derived from aromatic or araliphatic carboxylic acids such as benzoic acid or phenyl acetic acid, the aromatic part of which is linked either directly or indirectly via intermediate groups to a radical which renders the compound resistant to diffusion, for example to one of the radicals mentioned under (1),
3. an alkylcarbonyl radical in which the alkyl radical contains up to 20 C. atoms and preferably from 10 to 18 C. atoms, or
4. a carbalkoxy radical in which the alkyl radical contains from two to 20 C. atoms and may carry further substituents, and Z represents the ring members required for completing a condensed benzene or tetrahydrobenzene ring.

The following are examples of suitable cyan-forming couplers:

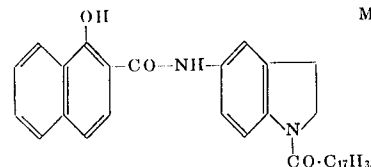
I, 1 M.P. 191-193° C.



I, 2

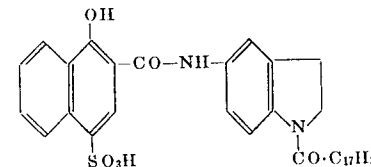


I, 3

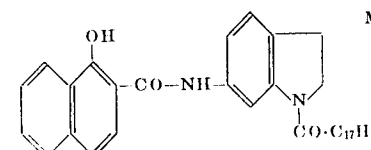


M.P. 180-182° C.

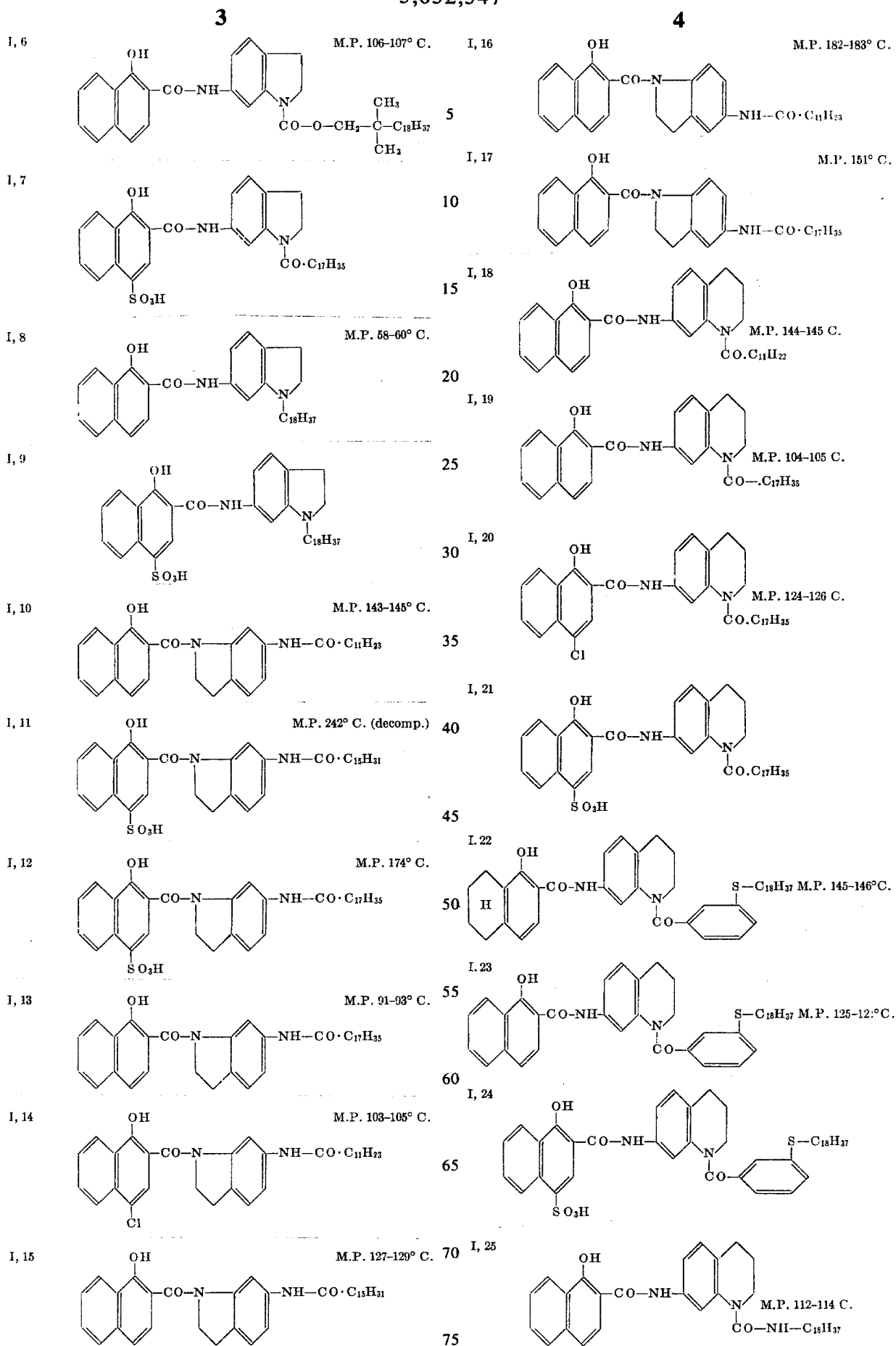
I, 4



I, 5

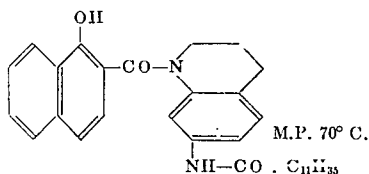


M.P. 112-114° C.

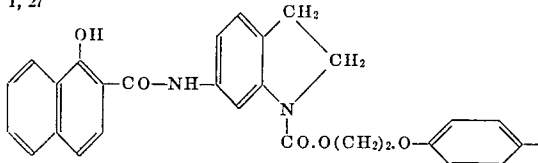


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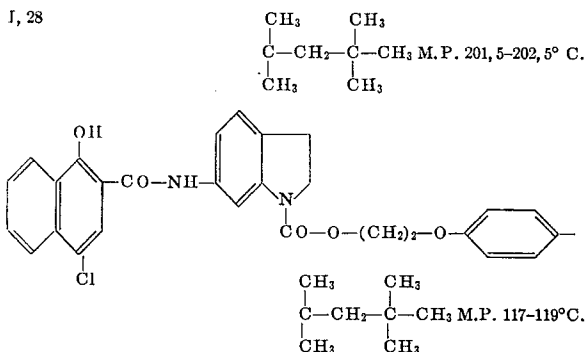
I, 26



I, 27



I, 28



The compounds according to the invention are prepared by known processes. Their method of preparation is explained below with the aid of the example of couplers I, 19 and I, 20.

Preparation of Couplers I, 19 and I, 20

7-nitro-1,2,3,4-tetrahydroquinoline

- 266 g. of tetrahydroquinoline were introduced dropwise into
2 l. of concentrated H₂SO₄ from -5 to 0° C. with stirring.
A mixture of
85.6 ml. of 98% HNO₃ in
460 ml. of concentrated H₂SO₄ was then added dropwise at this temperature. The reaction mixture was then stirred for 30 minutes, poured on to ice and thoroughly stirred and then rendered alkaline with concentrated NaOH. The crude product was removed by suction filtration and washed with water until neutral. When the nitro compound had been dried in air it was dissolved in a little ether, dried over sodium sulphate and precipitated with petroleum ether. It was isolated by suction filtration and washed with petroleum ether. Purification with ether and petroleum ether was carried out once more.

The red-orange nitro compound was isolated, a yield of 306 g. being obtained. Melting point: 61°-62° C.

1-stearoyl-7-nitro-1,2,3,4-tetrahydroquinoline

- 203 ml. of triethylamine were added to a solution of
141 g. of 7-nitro-1,2,3,4-tetrahydroquinoline in
500 ml. of tetrahydrofuran.
282 g. of stearoyl chloride were added dropwise with stirring from +10° to +20° C. The reaction mixture was stirred for a further 30 minutes and then boiled under reflux for 15 minutes. It was then stirred into ice water, made acid to Congo red with 5N HCl, removed by suction filtration and washed neutral with water. To dry it more thoroughly, it was then washed with
2 l. of methanol. The crude product was recrystallized from
2 l. of alcohol with the addition of active charcoal, removed by suction filtration and washed with alcohol and methanol.

262 g. of yellowish crystals of melting point 83°-84° C. were obtained.

1-stearoyl-7-amino-1,2,3,4-tetrahydroquinoline

- 233 g. of 1-stearoyl-7-nitro-1,2,3,4-tetrahydroquinoline were dissolved in
2 l. of hot tetrahydrofuran and catalytically hydrogenated with Raney nickel at 50° C. and 50 excess atmospheres. The product was removed from Raney nickel by suction filtration and the residual solvent was distilled off under vacuum. 210 g. of an oily product were obtained.

Coupler I, 19

- 10 210 g. of oily 1-stearoyl-7-amino-1,2,3,4-tetrahydroquinoline and
141 g. of phenylhydroxy-2-naphthoate were melted together under vacuum at a bath temperature of 170° C. The phenol formed in the process distilled off under these conditions. After 1 hour, the hot melt was stirred into
15 1,300 ml. of alcohol. The product gradually precipitated. It was removed by suction filtration at 20° C. and washed with alcohol until the washings were colorless. The crude product was recrystallized from
20 1,300 ml. of alcohol with the addition of active charcoal, removed by suction filtration at 20° C. and vigorously washed with alcohol. The yield of colorless component was 242 g., melting point 104°-105° C.

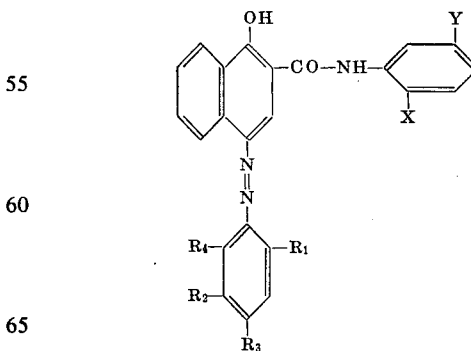
Coupler I, 20

- 215 g. of Coupler I, 19 were dissolved in
1,750 ml. of glacial acetic acid at 60° C. The solution was cooled to 40° C., and
31 ml. of sulphuryl chloride were then added dropwise. An exothermic reaction took place, the temperature rising to +47° C. The reaction mixture was then stirred for 45 minutes, the crude product crystallizing out. It was removed by suction filtration and washed with
500 ml. of glacial acetic acid. The crude product was recrystallized from 675 ml. of glacial acetic acid and washed with glacial acetic acid and alcohol.

A yield of 157 g. of colorless coupler I, 20 of melting point 124°-126° C. was obtained.

- 40 The cyan-forming couplers according to the invention, especially those in which the group R is linked to the CO group of formula I via the NH group, are eminently suitable for the production of color photographic materials. They are highly sensitive and on chromogenic development they yield cyan dyes of great brilliance, very advantageous absorption and only slight yellow and magenta side densities.

- 45 The cyan-forming couplers according to the invention may be used especially advantageously in combination with azo red masking couplers, e.g. those described in German Pat. appli-
50 cation P 15 97 510.7 and having the following general formula:



in which

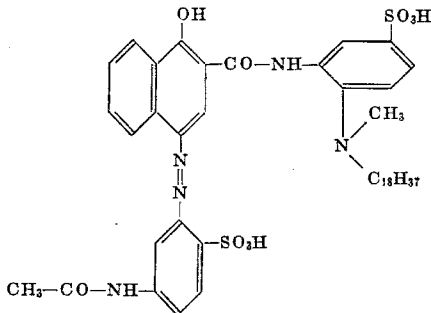
- 55 R₁ = a carboxyl or sulfo group;
60 R₂ = a hydrogen atom or an acylamino group;
65 R₃ = a hydrogen or halogen atom, but if R₂ represents an acylamino group then R₃ represents a hydrogen atom;
70 R₄ = a hydrogen or halogen atom, but if R₂ represents a hydrogen atom, then R₄ represents a halogen atom;
75 X = an amino group, preferably a dialkylamino group,

wherein the alkyl radicals contain up to 20 carbon atoms, an alkoxy group containing up to 20 carbon atoms or a phenylthio group;

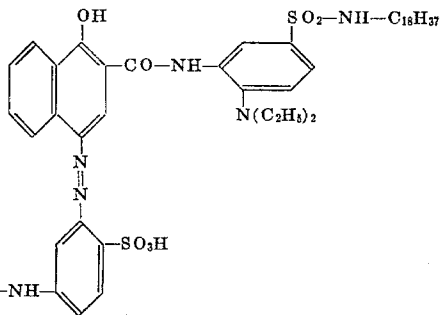
Y = a hydrogen atom or carboxyl, sulpho or a mono- or dialkyl-sulphamyl group.

The cyan-forming couplers according to the invention may, for example, be used together with one of the following compounds:

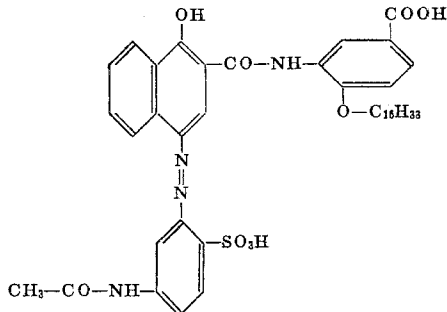
II, 1



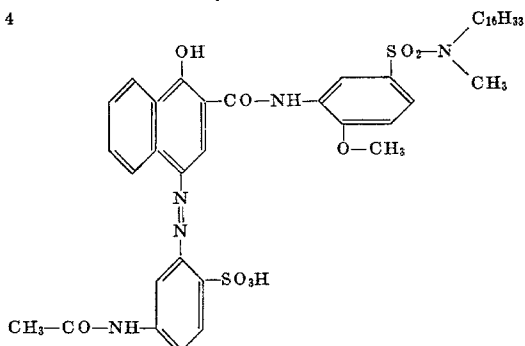
II, 2



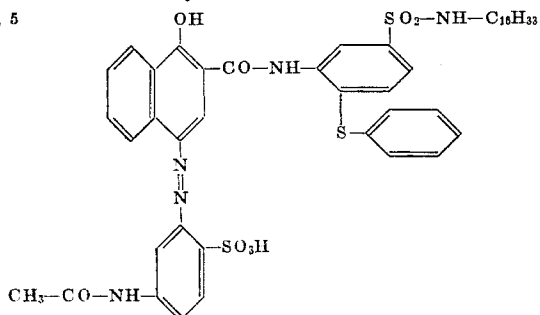
II, 3



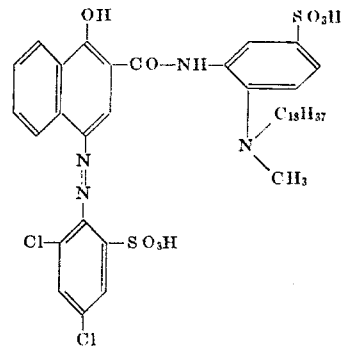
II, 4



II, 5



II, 6

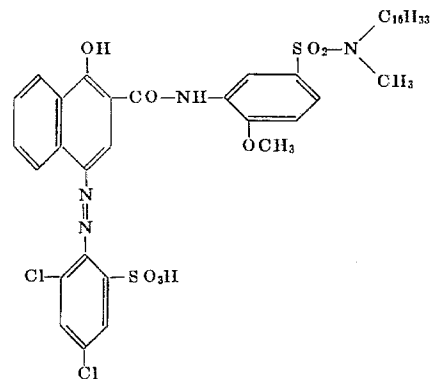


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II, 7

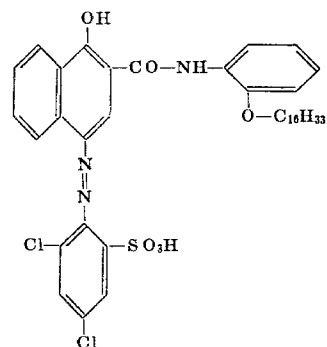


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II, 8

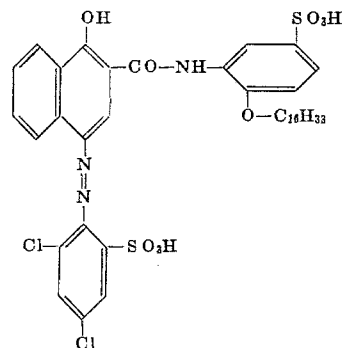


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II, 9

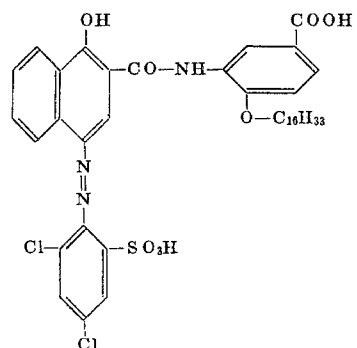


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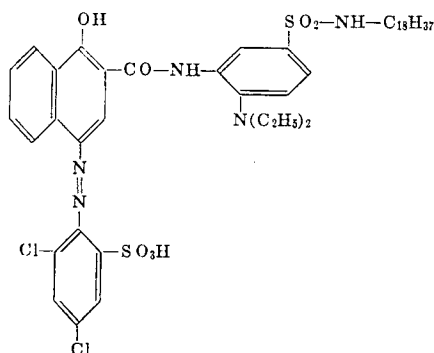
II, 10



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The cyan-forming couplers according to the invention, as well as the azo red masks which are to be used together with them according to the invention, may be incorporated with the silver halide emulsion by one of the known methods. In the case of hydrophobic compounds, for example, incorporation is achieved by dissolving the compounds in suitable organic solvents, e.g. in esters of aliphatic carboxylic acids, especially in ethyl acetate, and emulsifying this solution with the silver halide emulsion which is ready for casting. This method may advantageously be modified by simultaneous use of oily solvents for couplers. This process also known from U.S. Pat. specifications 2,304,940 and 2,322,027. If the couplers or masking couplers are alkali-soluble compounds, they are added to the light-sensitive silver halide emulsions in aqueous alkaline solution. The couplers and masking couplers may, of course, be added one after the other to the silver halide emulsion, but they may also be added simultaneously from a common solution. The method of addition to the emulsion is not critical, and the most suitable process can easily be determined by a few simple tests.

Suitable for use as light-sensitive emulsions are emulsions of silver halides such as silver chloride, silver bromide or mixtures thereof, optionally with a small silver iodide content of up to 10 mols percent in one of the conventional hydrophilic binders such as protein, especially gelatine, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose derivatives such as carboxylalkyl cellulose, especially carboxy methyl cellulose, or derivatives of alginic acid.

The emulsions may also contain the usual additives e.g. spectral or chemical sensitizers, stabilizers, hardeners and plasticizers.

Any color-forming developers which contain a primary amino group may be used for development. Those of the p-phenylene diamine type are preferred, e.g. N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, monomethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, N-butyl-n- ω -sulphobutyl-p-phenylenediamine and 2-amino-5-(N-ethyl-N- β -methanesulphonamido-ethyl-amino)toluene.

The following examples illustrate the invention:

EXAMPLE 1

20 g. of coupler I, 20 are dissolved in 60 ml. of ethyl acetate and incorporated by emulsification with 320 ml. of 10 percent gelatine in a known manner. The emulsion product contains 11 ml. of 10 percent aqueous saponin solution.

250 ml. of this emulsion product are added with stirring to 1 kg. of a photographic silver bromide emulsion which contains 95 g. of gelatine and 0.4 mol of silver. In addition, 140 ml. of a 5 percent aqueous alkaline solution of azo masking coupler II, 6 are added.

To this emulsion which contains coupler and masking coupler there are added 25 ml. of a 1 percent methanolic solution of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 30 ml. of 10 percent aqueous saponin solution and 15 ml. of 0.5 percent aqueous chrome acetate solution, and the emulsion is cast on a layer support of cellulose triacetate in a thickness of about 4.5 μ . The pH of the layer is approximately 6.5 to 7.

When dry, the material is exposed through a stepless grey wedge and developed in a developer of the following composition for 15 minutes:

	5	g.	of	2-amino-5-(N-ethyl-N- β -
				toluene-
5				
				methanesulphonamidoethylamino)
				sesquisulphate monohydrate
				5 ml. of benzyl alcohol
				2.5 g. of sodium hexametaphosphate
				1.85 g. of anhydrous sodium sulphite
10				1.4 g. of sodium bromide
				0.5 g. of potassium iodide
				12.5 g. of sodium hydroxide
				34.22 g. of Na ₂ B ₄ O ₇ ·5H ₂ O
				Water up to 1 l.
15				Subsequent processing includes the following baths:

Short stop bath

				17 ml. of glacial acetic acid
				2.94 g. of anhydrous sodium acetate
20				Water up to 1 l.

Hardening bath

				0.32 g. of sodium hydroxide
				0.5 g. of sodium hexametaphosphate
				9.04 g. of soda
25				20 ml. of 37% formalin
				Water up to 1 l.

Bleaching bath

				6 g. of sodium hexametaphosphate
				42.0 g. of potassium ferricyanide
30				12.0 g. of potassium bromide
				6.0 g. of disodium phosphate
				16.0 g. of monopotassium phosphate
				Water up to 1 l.

Fixing bath

35				150 g. of ammonium thiosulphate
				10 g. of sodium sulphite
				Water up to 1 l.

Final bath

				0.3 g. of sodium tetrapropylene benzene sulphonate
40				Water up to 1,000 ml.

The processing times after development are as follows:

				Short stop bath 4 minutes
				Hardening bath 4 minutes
				Washing 5 minutes
45				Bleaching bath 6 minutes
				Washing 5 minutes
				Fixing bath 8 minutes
				Washing 10 minutes
				Final bath 30 seconds.

50 A cyan dye is formed in the exposed areas, whereas in the unexposed areas the orange red masking dye is preserved. Sensitometric determination shows that the material is very well masked in the blue and green ranges of measurement.

EXAMPLE 2

A photographic emulsion containing a coupler and a masking coupler is prepared as described in example 1 and poured on a support but in this case only 200 ml. of the coupler-emulsion product described in example 1 is used per kg. of emulsion.

When dry, the material is exposed through a stepless grey wedge and developed for 8 minutes in a developer of the following composition:

65				2.75 g. of N,N-diethyl-p-phenylenediamine sulphate
				1.2 g. of hydroxylamine hydrochloride
				2 g. of anhydrous Na ₂ SO ₃
				2 g. of sodium metaphosphate
				75 g. of potassium carbonate
70				2 g. of potassium bromide
				Water up to 1 l.

Subsequent photographic processing comprises the following baths:

				Bleaching bath
75				3 g. of ethylene diaminetetracetic acid

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50 g. of potassium ferricyanide
15 g. of potassium bromide
1 g. of disodium phosphate
10 g. of monopotassium phosphate
Water up to 1 l.

Fixing bath

200 g. of sodium thiosulphate
Water up to 1 l.

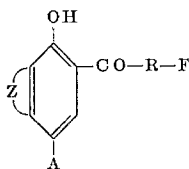
The treatment times after development are as follows:

15 minutes washing
5 minutes bleaching bath
5 minutes washing
5 minutes fixing bath
10 minutes washing.

A cyan color wedge with excellently masked yellow and red side densities is obtained.

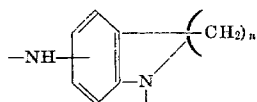
Patent claims:

1. Light-sensitive photographic material comprising at least one silver halide emulsion layer, which contains a cyan-forming coupler of the following formula I:



in which

A represents hydrogen, a halogen atom or a sulpho group,
R represents the bifunctional group:



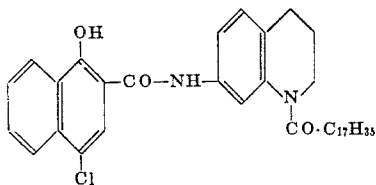
which is linked to the CO group of the above formula I through one of the two nitrogen atoms,

n represents 2 or 3,

F represents a radical which renders the compound resistant to diffusion, which radical is linked to the second nitrogen atom of group R either directly or indirectly through a CO, CO-NH or CO-O group,

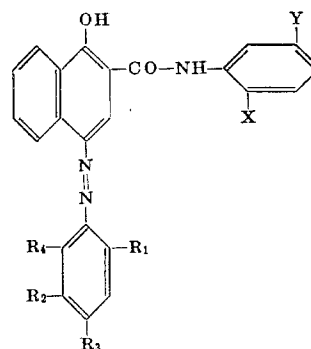
Z represents the ring members required for completing a condensed benzene or tetrahydrobenzene ring.

2. Light-sensitive photographic material according to claim 1, which contains a cyan-forming coupler of the following formula:



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3. Light-sensitive photographic material according to claim 1, which contains in addition, an azo red masking coupler of the following general formula II:



in which

R₁ = a carboxyl or sulpho group;

R₂ = hydrogen or an acylamino group;

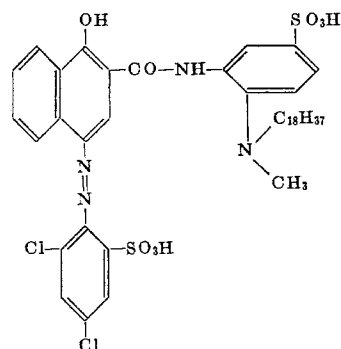
R₃ = hydrogen or a halogen atom but if R₂ represents an acylamino group then R₃ represents hydrogen;

R₄ = hydrogen or a halogen atom but if R₂ represents hydrogen then R₄ represents a halogen atom;

X = an alkoxy group, an amino group with up to 20 carbon atoms, or a phenylthio group;

Y = hydrogen or a carboxyl, sulpho or a mono or dialkyl sulfamyl group.

4. Light-sensitive photographic material according to claim 3, which contain as the additional azo red masking coupler a compound of the following formula:



* * * * *