United States Patent [11] **3,622,327**

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Godfried Mennens, Wilrijk, all of Belgium

[21] Appl. No. **8,525**
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[45] Patented **Nov. 23, 1971**
[73] Assignee **Gevaert-Agfa N.V.**
Mortsel, Belgium
[32] Priority **Feb. 4, 1969**
[33] **Great Britain**
[31] **5,979/69**

[54] PROCESS FOR PREPARING COLOR IMAGES

12 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **96/54,** 96/22
[51] **Int. Cl.** **G03c 5/50**
[50] **Field of Search** 96/22, 54, 73, 55, 100; 960/288

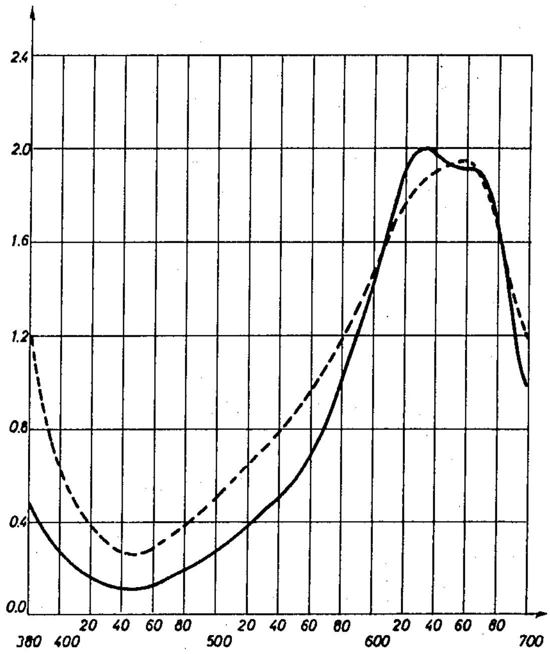
[56] **References Cited**

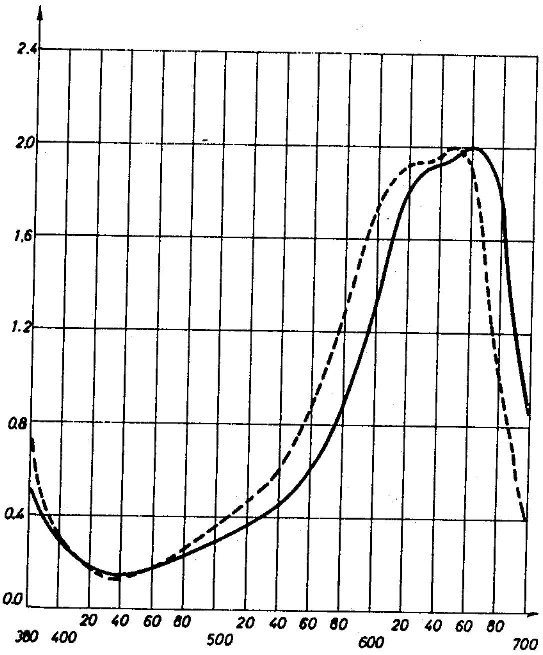
UNITED STATES PATENTS

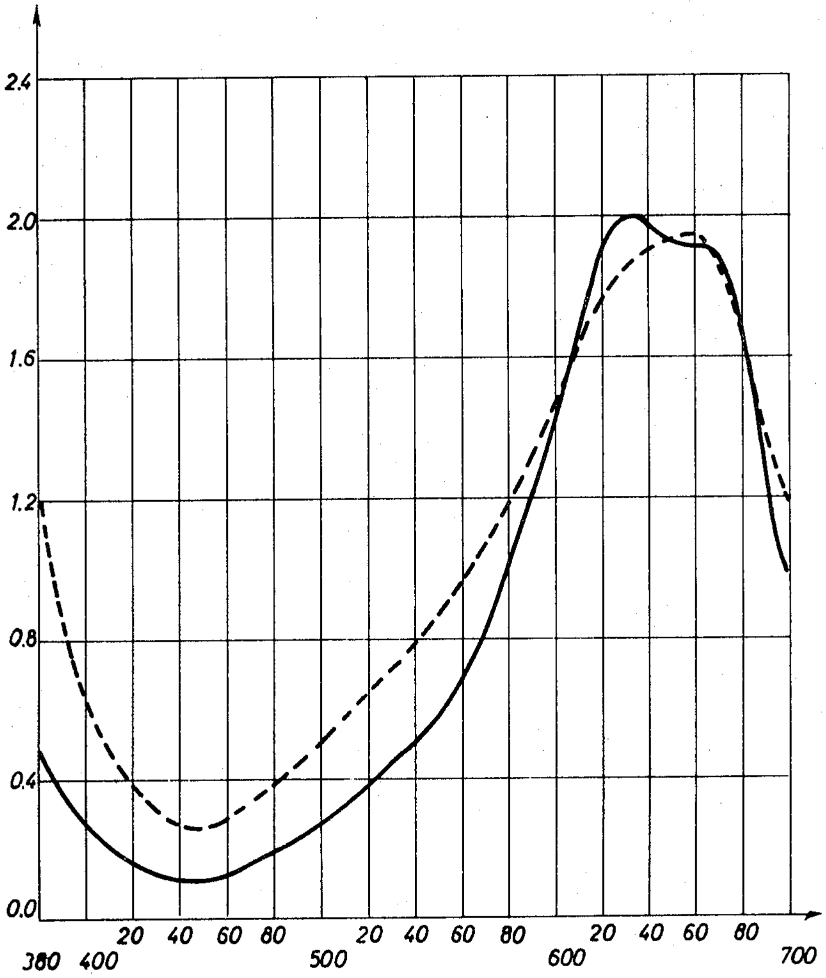
3,293,032 12/1966 Jaeken et al. 96/22

Primary Examiner—Norman G. Torchin
Assistant Examiner—Alfonso T. Suro Pico
Attorney—William J. Daniel

ABSTRACT: Color development in the presence of oxidatively coupling quinolone sulphonylhydrazone couplers to improve the absorption characteristics of the cyan dyes produced and reduce the undesirable blue fog in the cyan dye layer.



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2.0
1.6
1.2
0.8
0.4
0.0
20
40
60
80
20
40
60
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60
80
380
400
500
600
700

FIG. 1

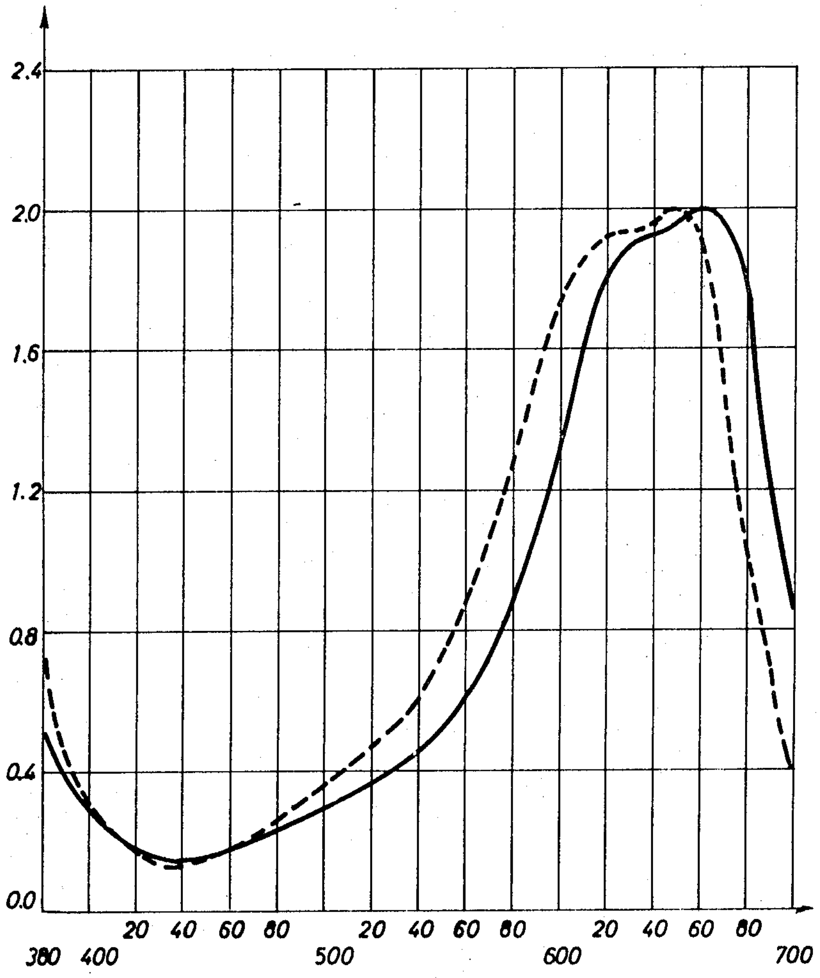

2.4
2.0
1.6
1.2
0.8
0.4
0.0
20 40 60 80
20 40 60 80
20 40 60 80
380 400
500
600
700

FIG. 2

PROCESS FOR PREPARING COLOR IMAGES

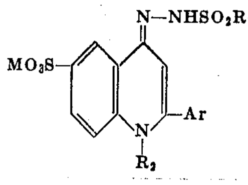
The present invention relates to a process for preparing direct positive color images, to hydrazone compounds of use in said process and to photographic materials containing such hydrazone compounds.

In U.S. Pat. No. 3,293,032 a process for the preparation of direct positive color images is described, which process comprises the steps of (1) imagewise exposing a photographic element comprising (*a*) at least one water-permeable layer which contains light-sensitive silver halide grains, (*b*) a color coupler in effective contact with said silver halide grains, said color coupler being capable of forming on development a dye which by treatment with a strong acidic solution can be converted into colorless products, and (*c*) a compound in effective contact with said color coupler, said compound being capable of forming an acid-resistant dye by oxidative coupling with said color coupler (2) developing the photographic element in a color-forming developer, (3) treating the photographic element in an oxidative bleaching bath, (4) treating the photographic element in a strong acidic solution, and (5) fixing the photographic element no later than after step (4) but not before step (2), to produce colorless reaction products at the places where development occurred and a positive color image of the object to be reproduced as a result of the oxidative coupling at the nondeveloped areas of the photographic element where color coupler is still present after the development.

According to a preferred embodiment of the process of the above United States patent specification a photographic multilayer material is used which comprises a red-sensitive, a green-sensitive and a blue-sensitive silver halide emulsion layer each of said layers containing a color coupler capable of forming on development a quinone-imine or azomethine dye which by treatment with a strong acidic solution can be transformed in colorless product, the red-sensitive emulsion layer also containing a compound which is capable of forming an acid-resistant cyan dye by oxidative coupling with the color coupler present in that emulsion layer the green-sensitive emulsion layer also containing a compound which is capable of forming an acid-resistant magenta dye by oxidative coupling with the color coupler present in that emulsion layer and the blue-sensitive emulsion layer also containing a compound which is capable of forming an acid-resistant yellow dye by oxidative coupling with the color coupler present in that emulsion layer.

It has now been found that the absorption characteristics of the cyan dyes produced as described and claimed in the above United States patent specification can still be improved as regards the undesirable side-absorption in the blue and green region of the spectrum by the use of novel oxidatively coupling quinolone hydrazone compounds. Moreover, the undesirable blue fog produced in the layer containing the cyan dye formed by means of the oxidatively coupling compounds listed in the above United States patent specification can be reduced or eliminated by the use of these novel quinolone hydrazone compounds.

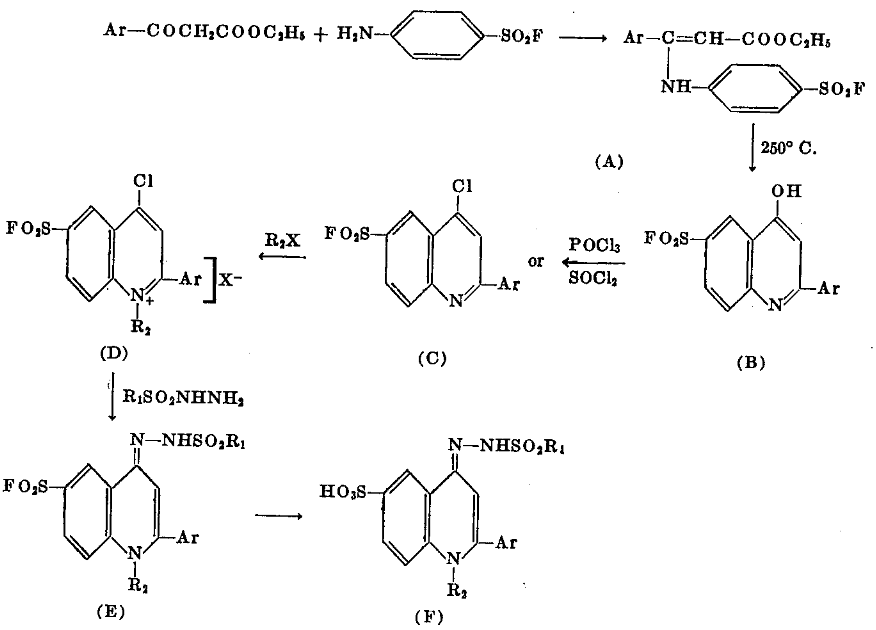
The quinolone hydrazone oxidatively coupling compounds according to the present invention can be represented by the following general formula:



wherein:

- Ar stands for aryl including substituted aryl e.g. phenyl and phenyl substituted by alkyl including substituted alkyl, aryl including substituted aryl, aralkyl including substituted aralkyl, cycloalkyl, carboxyl or sulpho in acid or salt form, halogen, alkoxy including substituted alkoxy, aryloxy including substituted aryloxy, alkylthio including substituted alkylthio, arylthio including substituted arylthio, alkylsulphonyl including substituted alkylsulphonyl, arylsulphonyl including substituted arylsulphonyl, nitro, amino including substituted amino, heterocyclic residues, etc.
- R_1 stands for alkyl including substituted alkyl, aryl including substituted aryl, aralkyl including substituted aralkyl or amino including substituted amino,
- R_2 stands for alkyl including substituted alkyl such as methyl and chloroethyl,
- M stands for hydrogen or an alkali metal atom such as potassium, sodium.

The oxidatively coupling hydrazone compounds corresponding to the above general formula can be prepared as is illustrated by the following reaction scheme:



wherein R_1, R_2 and Ar have the same significance as above and $X^{'7E'}$ stands for an acid radical.

The quinolones (B) prepared by a Conrad-Limpach reaction as illustrated by the above reaction scheme are sparingly soluble compounds having a melting point almost ever lying above 260° C. The qunolones (B) are converted into the chloroquinolones (C) by means of phosphorus oxychloride or thionyl chloride whereupon by quaternization compounds (D), having an unsharp melting point, are formed. The sulphonyl hydrazones (E) are formed by reaction of compounds (D) with the appropriate sulphonylhydrazide whereupon the fluorosulphonyl group in the 6-position is saponified thus forming the oxidatively coupling sulphonylhydrazone compound, the melting point of which generally lies above 260° C.

The following preparation illustrates in detail how the sulfonyl hydrazone compounds according to the present invention are prepared.

Preparation

1. β-(p-fluorosulphonylanilino)-cinnamic acid ethyl ester

175 ml. (1mole of benzoylacetic acid ethyl ester, 175 g. (1mole) of p-amino-benzene sulphofluoride and 50 g. of polyphosphoric acid were heated with stirring at 50° C. until the mixture became homogeneous. The mixture was placed for 5 days in a vacuum drying oven (50° C./2–5 mm. Hg.) over sulphuric acid. The precipitate formed was washed with 250 ml. of methanol and then with water until the product was sufficiently acid free.

Yield: 225 g. (64.5 percent).

Melting point: 134° C.

2. 2-phenyl-4-hydroxy-6-fluorosulphonylquinoline

260 (0.75 mole) of β-(p-fluorosulphonylanilino)-cinnamic acid ethyl ester were rapidly added at 250° C. and with stirring to 2.5 liters of diphenyl ether. Stirring was continued for 10 minutes whereupon the reaction mixture was allowed to cool. The precipitate formed was filtered by suction and washed with ether.

Yield: 205 g. (91 percent).

Melting point: >260° C.

3. 2-phenyl-4-chloro-6fluorosulphonylquinoline

205 (0.68 mole) of 2-phenyl-4-hydroxy-6fluorosulphonylquinoline and 186 ml. (0.72 mole) of phosphorous oxychloride were heated for 2 hours at 80° C. After having been cooled the reaction mixture was poured into ice. The precipitate formed was filtered by suction and washed completely acid free with water and sodium acetate. The product was recrystallized from 1.5 liter of ethylene glycol monomethyl ether taking care that the mixture did not boil since otherwise the active chlorine atom of the quinoline would react with the ethyleneglycol monomethyl ether.

Yield: 195 g. (89.5 percent).

Melting point 128° C.

4. 1-methyl-2-phenyl-4-chloro-6-fluorosulphonyl-quinolinium methyl sulfate.

100 g(0.31 0.31 mole) of 2-phenyl-4-chloro-6-fluorosulphonylquinoline and 88 ml. (0.93 mole) of dimethyl sulphate (distilled and dried on molecular sieves) were heated for 20 hours at 85° C. At the beginning of the reaction the mixture was stirred as long as possible. The solid product formed was washed with ether and then further used as such.

Melting point: 180° C.

5. 1-methyl-2-phenyl-6fluorosulphonyl-quinolone-4n-hexadecylsulphonyl hydrazone

Two-hundred thirty-five gram (0.525 mole) of 1-methyl-2-phenyl-4-chloro-6-fluorosulphonyl-quinolinium methyl sulphate and 168 g. (0.525 mole) of n-hexadecyl sulphonylhydrazide were refluxed for 4 hours in 2 liters of chloroform. The solvent was thoroughly removed by evaporation at a maximum temperature of 60° C. The residue was dissolved in 500 ml. of boiling ethanol and the solution formed, after addition of 200 ml. of pyridine, was poured into 8 liters of water. The precipitate formed was filtered by suction and recrystallized from acetonitrile.

Yield: 257 g. (79 percent).

Melting point: 158° C.

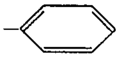
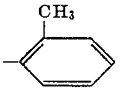
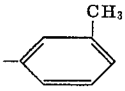
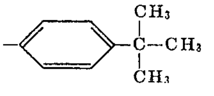
6. 1-methyl-2-phenyl-6-sulphoquinolone- 4n-hexadecylsulphonyl hydrazone

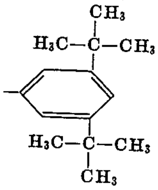
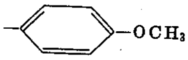
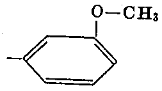
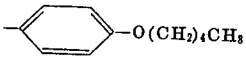
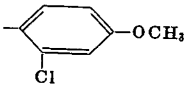
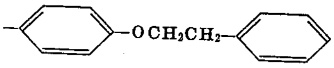
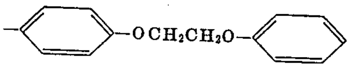
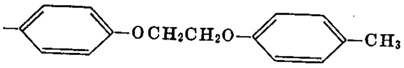
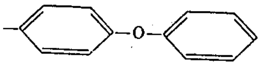
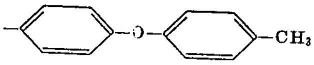
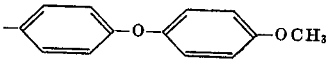
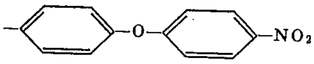
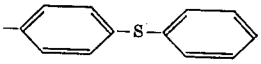
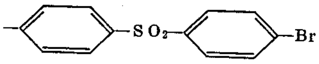
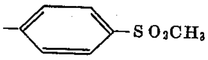
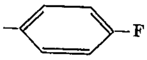
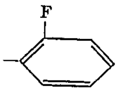
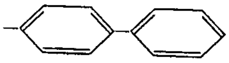
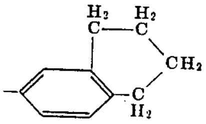
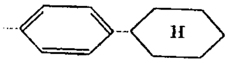
Three-hundred ten gram (0.5 mole) of 1-methyl-2-phenyl-6-fluorosulphonylquinolone -4n-hexadecylsulphonyl hydrazone were dissolved with heating in 4 liters of acetone. While stirring and introducing a nitrogen current a solution of 64 g. (1.6 mole) of sodium hydroxide in 300 ml. of water was added dropwise. The mixture was refluxed for 1 hour and cooled whereupon the precipitate formed was filtered by suction and washed with a mixture of acetone and water (95:5). The product was recrystallized from acetic acid and washed with methanol.

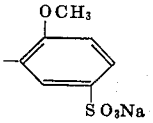
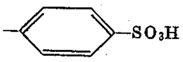
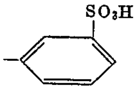
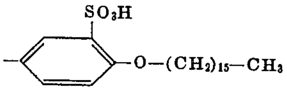
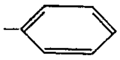
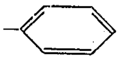
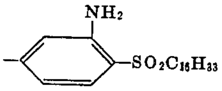
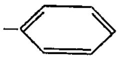
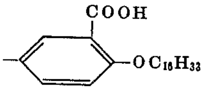
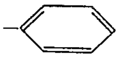
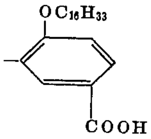
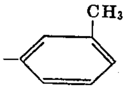
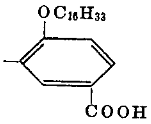
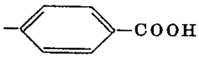
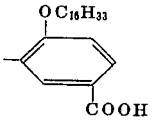
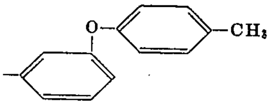
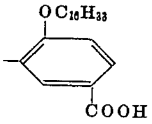
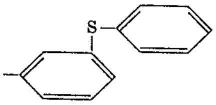
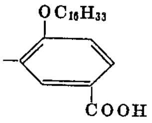
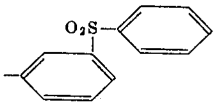
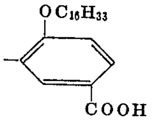
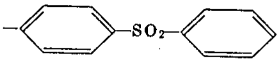
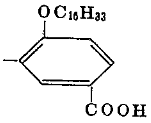
Yield: 275 g. (89 percent).

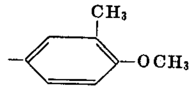
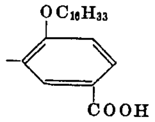
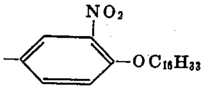
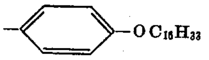
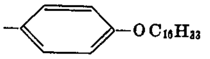
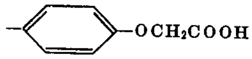
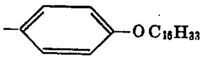
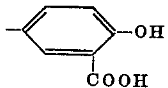
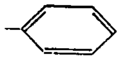
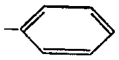
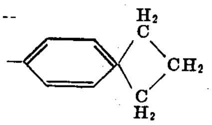
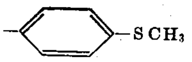
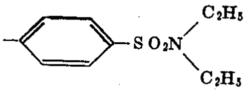
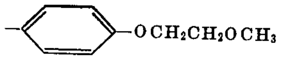
Melting point: >260° C.

In the following table are listed compounds corresponding to the above general formula, which were found to be particularly suitable for use in accordance with the present invention and which were prepared as described in the above preparation.

				Melting point of intermediate product (° C.)		Absorption maximum (nm.) of the cyan dyes formed according to Example 2 hereinafter (With colour coupler)	
Compound	Ar	R_1	R_2	(C)	(E)	1	2
1		$-C_{16}H_{33}$	$-CH_3$	128	158	663	660
2		$-C_{16}H_{33}$	$-CH_3$	152	167	660	662
3		$-C_{16}H_{33}$	$-CH_3$	123	155	653	648
4		$-C_{16}H_{33}$	$-CH_3$	130	140	665	660
5		$-C_{16}H_{33}$	$-CH_3$	163	190	670	663

Compound	Ar	R_1	R_2	Melting point of intermediate product (° C.)		Absorption maximum (nm.) of the cyan dyes formed according to Example 2 hereinafter (With colour coupler)	
				(C)	(E)	1	2
6		$-C_{16}H_{33}$	$-CH_3$	140	190	654	654
7		$-C_{16}H_{33}$	$-CH_3$	163	162	665	665
8		$-C_{16}H_{33}$	$-CH_3$	140	145	665	656
9		$-C_{16}H_{33}$	$-CH_3$	116	170	664	663
10		$-C_{16}H_{33}$	$-CH_3$	159	180	656	663
11		$-C_{16}H_{33}$	$-CH_3$	132	150	662	665
12		$-C_{16}H_{33}$	$-CH_3$	155	180	675	668
13		$-C_{16}H_{33}$	$-CH_3$	201	180	670	665
14		$-C_{16}H_{33}$	$-CH_3$	164	150	660	666
15		$-C_{16}H_{33}$	$-CH_3$	158	165	660	662
16		$-C_{16}H_{33}$	$-CH_3$	150	152	658	665
17		$-C_{16}H_{33}$	$-CH_3$	182	85	656	659
18		$-C_{16}H_{33}$	$-CH_3$	170	135	656	663
19		$-C_{16}H_{33}$	$-CH_3$	250	170	660	658
20		$-C_{16}H_{33}$	$-CH_3$	240	200	658	658
21		$-C_{16}H_{33}$	$-CH_3$	132	135	660	658
22		$-C_{16}H_{33}$	$-CH_3$	111	130	658	660
23		$-C_{16}H_{33}$	$-CH_3$	190	210	666	663
24		$-C_{16}H_{33}$	$-CH_3$	153	170	660	666
25		$-C_{16}H_{33}$	$-CH_3$	126	200	668	660

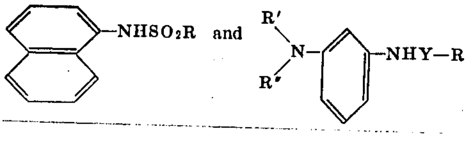
Compound	Ar	R_1	R_2	Melting point of intermediate product (° C.)		Absorption maximum (nm.) of the cyan dyes formed according to Example 2 hereinafter (With colour coupler)	
				(C)	(E)	1	2
26		$-C_{16}H_{33}$	$-CH_3$	216	110	662	650
27		$-C_{16}H_{33}$	$-CH_3$	210	165	665	654
28		$-C_{16}H_{33}$	$-CH_3$	168	190	664	666
29		$-CH_3$	$-CH_3$	97	150	680	664
30		$-(CH_2)_{11}-CH_3$	$-CH_3$	128	152	663	660
31			$-CH_3$	128	180	663	660
32			$-CH_3$	128	138	664	657
33			$-CH_3$	128	167	664	657
34			$-CH_3$	130	200	665	658
35			$-CH_3$	220	230	658	650
36			$-CH_3$	149	160	660	668
37			$-CH_3$	170	185	658	655
38			$-CH_3$	207	220	660	655
39			$-CH_3$	190	210	654	650

Compound	Ar	R_1	R_2	Melting point of intermediate product (° C.)		Absorption maximum (nm.) of the cyan dyes formed according to Example 2 hereinafter (With colour coupler)	
				(C)	(E)	1	2
40			$-CH_3$	172	175	665	665
41		$-CH_3$	$-CH_3$	92	120	662	660
42		$-CH_3$	$-CH_3$	88	120	660	660
43			$-CH_3$	88	160	660	654
44			$-CH_3$	88	185	660	658
45		$-C_{16}H_{33}$	$-C_2H_5$	128	135	657	651
46		$-C_{16}H_{33}$	$-C_2H_4Cl$	128	120	646	642
47		$-C_{16}H_{33}$	$-CH_3$	146	166	668	666
48		$-C_{16}H_{33}$	$-CH_3$	156	150	668	662
49		$-C_{16}H_{33}$	$-CH_3$	155	158	660	660
50		$-C_{16}H_{33}$	$-CH_3$	142	140	669	664

Color couplers preferably used in conjunction with the quinolone hydrazone compounds according to the present invention to form cyan dyes on oxidatively coupling therewith are colorless color couplers capable of forming on color development with aromatic primary amino developing agents e.g. N,N-diethyl-p-phenylene diamine, indophenol or quinone-imine and indo-amine dyes which by treatment with a strong acidic solution can be converted into colorless products.

Among these color couplers there may be mentioned phenol and α-naphthol compounds, which in the common color development with aromatic primary amino developing agents form cyan, indophenol or quinone-imine dyes that are not completely acid resistant, and m-acylamino-N,N-dialkylanilines and α-naphthylsulphamoyl compounds, which form on color development with aromatic primary amino developing agents indoamine dyes that are also not completely acid resistant.

Though, in conjunction with the quinolone hydrazone oxidatively coupling compounds according to the present invention the α-naphthol color couplers, for which there can be referred to the above U.S. Pat. specification and the patent literature referred to therein, to Belgian Pat. Nos. 548,880 and 596,509 and to United Kingdom Pat. No. 1,104,729, are preferably used, the α-naphthylsulphamoyl and m-acyl-amino-N,N-dialkylaniline color couplers corresponding to the following general formulas having also been found to be particularly suitable:



wherein:

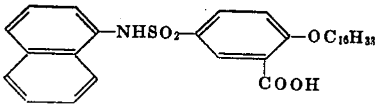
each of R′ and R″ stands for an alkyl group,

Y stands for —CO—or —SO_2—, and

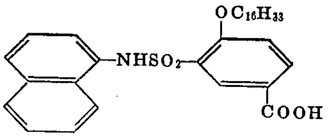
R stands for alkyl, preferably alkyl comprising from five to twenty carbon atoms in straight line or for aryl including substituted aryl, preferably aryl comprising a group rendering the compound fast to diffusion having from five to twenty carbon atoms in straight line.

Examples of color couplers corresponding to the above general formulas are:

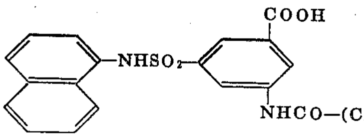
(a)



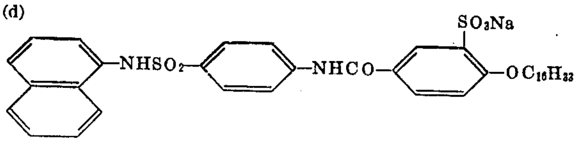
(b)



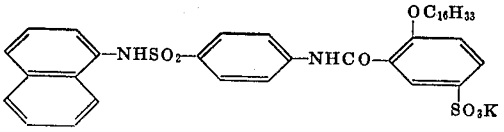
(c)



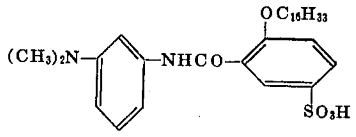
(d)



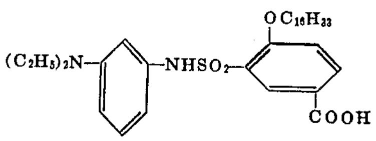
(e)



(f)



(g)



The oxidatively coupling quinolone hydrazone compounds according to the present invention and the color couplers used in conjunction therewith are preferably incorporated in the photographic material in a form fast to diffusion. For that purpose they contain in their structure a long aliphatic carbon chain, preferably a carbon chain having from five to twenty carbon atoms in straight line.

In the preparation of a light-sensitive color element for producing direct positive color images according to the method of the above U.S. Pat. specification, the color coupler and quinoline hydrazone compound are preferably incorporated into a light-sensitive silver halide emulsion layer of the said element. They may however, also be added to the composition of a water-permeable non-light-sensitive layer, which is in direct contact with the light-sensitive silver halide emulsion layer, or they may be incorporated into a non-light-sensitive layer, which is separated from the light-sensitive layer by a water-permeable non-light-sensitive layer.

Thus, a photographic element according to the present invention which is suitable for use in the process of the above U.S. Pat. specification for the production of direct positive color images comprises

a. at least one water-permeable layer containing light-sensitive silver halide grains,

b. a color coupler in effective contact with said silver halide grains, said coupler being capable of forming on color development a dye, which by treatment with a strong acidic solution can be converted into colorless products, and

c. in effective contact with said color coupler a quinolone hydrazone compound which corresponds to the above general formula and which is capable of forming an acid-resistant cyan dye by oxidative coupling with said color coupler.

By "effective contact of the color coupler with the silver halide" is to be understood that the oxidized developing agent formed by the reduction of the exposed silver halide can come into contact with the color coupler in order to react therewith at the exposed areas.

By "effective contact of the color coupler with the oxidatively coupling compound" is to be understood that the oxidatively coupling compound can oxidatively couple with the color coupler in the colloid layer wherein the latter is present on treatment in oxidative medium.

In accordance with the present invention the photographic element for producing direct positive color images comprises more specifically at least one water-permeable colloid layer wherein light-sensitive silver halide grains are present and wherein said water-permeable colloid layer or a colloid layer in water-permeable relationship therewith comprises at least one color coupler which on development couples in the exposed areas with the oxidation product of an aromatic primary amino developing agent to form on these areas a dye which can be destroyed or transformed into colorless products by treatment with a strong acidic solution, and wherein the said water-permeable colloid layer containing the silver halide or a colloid layer in water-permeable relationship therewith contains a quinolone hydrazone compound corresponding to the above general formula, which on treatment of the color developed photographic element in an oxidizing solution oxidatively couples with said color coupler to form in the non-developed areas a secondary cyan dye which cannot be destroyed or transformed into colorless products by the said treatment with a strong acidic solution.

The quinolone hydrazone oxidatively coupling compounds described in the present invention are usually incorporated into a red-sensitive silver halide emulsion forming one of the differently sensitized silver halide emulsion layers of a photographic multilayer color material suitable for producing a direct positive multicolor image according to the method of the above U.S. Pat. specification. A photographic multilayer material according to the present invention therefore comprises a support, a red-sensitized silver halide emulsion layer, a green-sensitized silver halide emulsion layer, and a blue-sensitive silver halide emulsion layer each of said emulsion layers containing a color coupler capable of forming on development a quinone-imine or azomethine dye and an oxidatively coupling compound which, after development, on treatment with an oxidative bleaching bath, reacts with the residual color coupler so as to form an acid-resisting cyan, magenta, and yellow dye respectively wherein the oxidatively coupling compound of the red-sensitive emulsion layer is a hydrazone compound corresponding to the above general formula.

The color couplers and oxidatively coupling compounds can of course be present not only in their respective light-sensitive silver halide emulsion layers but also in adjacent non-light-sensitive colloid layers.

In the above U.S. Pat. No. 3,293,032 which should be read in conjunction with the present invention more details can be found as regards the appropriate color couplers and oxidatively coupling compounds for forming the yellow and magenta direct positive separation images in addition to the cyan direct positive separation image formed in accordance with the present invention by means of the oxidatively coupling compounds corresponding to the above general formula.

According to a preferred embodiment of the present invention for forming with a multilayer material as described above direct positive multicolor images the yellow separation image is formed by oxidative coupling of a pyrazolone color coupler with a benzothiazolone hydrazone coupling compound, the magenta separation image is formed by oxidative coupling of an α-naphthol color coupler with a 4-amino-pyrazolone-3 coupling compound and the cyan separation image is formed by oxidative coupling of an α-naphthol color coupler with a quinolone hydrazone coupling compound according to the present invention. The α-naphthol color coupler used for the formation of the magenta separation image may be the same as that used for the formation of the cyan separation image.

As described in the above U.S. Pat. specification the ratio in moles of light-sensitive silver halide to color coupler is preferably comprised between 6:1 and 15:1 and the ratio of color coupler to oxidatively coupling compound preferably varies from 1:1 to 1:3.

The color couplers and oxidatively coupling compounds can be incorporated into the photographic material according to any technique known by those skilled in the art for incorporation of photographic ingredients, more particularly color couplers and mask-forming compounds, into colloid compositions. For instance, the water-soluble compounds can be incorporated into the coating composition of the layer in question from an aqueous solution or alkaline aqueous solution and the water-insoluble or insufficiently water-soluble compounds from a solution in the appropriate water-miscible or water-immiscible high-boiling or low-boiling organic solvents or mixtures thereof whereupon the solution obtained is dispersed, if necessary in the presence of a wetting or dispersing agent, in a hydrophilic colloid composition forming or forming part of the binding agent of the colloid layer. The hydrophilic colloid composition may of course comprise in addition to the colloid carrier all other sorts of ingredients.

The solutions of the color couplers and oxidatively coupling compounds need not necessarily be dispersed or dissolved directly in the coating composition of the silver halide emulsion layer or other water-permeable layer. Said solution may advantageously be first dispersed or dissolved in an aqueous non-lightosensitive hydrophilic colloid solution whereupon the resultant mixture, if necessary after the removal of the organic solvents employed, is intimately mixed with the said coating composition of the light-sensitive silver halide emulsion layer or other water-permeable layer just before coating.

For more details about particularly suitable techniques that can be employed for incorporating the color couplers and oxidatively coupling compounds into a hydrophilic colloid layer of a photographic material there can be referred to United Kingdom Pat. Nos. 791,219, 1,098,594, 1,099,414, 1,099,415, 1,099,416, 1,099,417, to Belgian Pat. Nos. 705,889, 722,026, to U.S. Pat. application Ser. No. 856,825 and to U.S. Pat. No. 2,304,940.

The hydrophilic colloid used as the vehicle for the silver halide may be, for example, gelatin, colloidal albumin, zein, casein, a cellulose derivative, a synthetic hydrophilic colloid such as polyvinyl-alcohol, poly-N-vinylpyrrolidone etc. If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide.

Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride, or mixed silver halides, such as silver chlorobromide, silver bromoiodide and silver chlorobromoiodide.

Though for the formation of direct positive images according to the present invention, a photographic element comprising differently sensitized silver halide emulsion layers each containing a color coupler and an oxidatively coupling compound, is preferably used, photographic materials can be used containing mixed packet photographic silver halide emulsions. For further details as regards this kind of emulsions there can be referred to the above U.S. Pat. No. 3,293,032 and the patent literature referred to therein.

The light-sensitive silver halide emulsions of use in the preparation of a photographic material according to the present invention may be chemically as well as optically sensitized. They may be chemically sensitized by effecting the ripening in the presence of amounts of sulphur containing compounds such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in French Pat. No. 1,146,955 and in Belgian Pat. No. 568,687, imino-amino methane sulphinic acid compounds as described in United Kingdom Pat. No. 789,823 and small amounts of noble metal compounds such as of gold, platinum, palladium, iridium, ruthenium and rhodium. They may be optically sensitized by means of cyanine and merocyanine dyes.

The said emulsions may also comprise compounds which sensitized the emulsions by development acceleration for example compounds of the polyoxyalkylene type such as alkylene oxide condensation products as described among others in U.S. Pat. Nos. 2,531,832 and 2,533,990, in United Kingdom Pat. No. 920,637, 940,051, 945,340 and 991,608 and in Belgian Pat. No. 648,710 and onium derivatives of amino-N-oxides as described in United Kingdom Pat. No. 1,121,696. Further, the emulsions may be stabilized with heterocyclic nitrogen-containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-2-tetrazoline-5-thione and compounds of the hydroxy-triazolo-pyrimidine type. They can also be stabilized with mercury compounds such as the mercury compounds described in Belgian Pat. Nos. 524,121, 677,337, 707,386 and in U.S. Pat. No. 3,179,520.

The light-sensitive emulsions may also comprise all other kinds of ingredients such as plasticizers, hardening agents, wetting agents, etc.

The emulsions can be coated on a wide variety of photographic emulsion supports. Typical supports include cellulose ester film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, and related films of resinous materials, as well as paper and glass.

In accordance with the present invention photographic direct positive cyan images are produced by the steps of:

1. imagewise exposing a photographic element comprising
   a. at least one water-permeable layer which contains light-sensitive silver halide grains,
   b. a color coupler in effective contact with said silver halide grains, said coupler being capable of forming on development a dye which by treatment with a strong acidic solution can be transformed in colorless products, and
   c. in effective contact with said color coupler a quinolone hydrazone compound corresponding to the above general formula, said compound being capable of forming an acid-resistant cyan dye by oxidative coupling with said color coupler,
2. developing the photographic element in a color-forming developer,
3. treating the photographic element in an oxidative bleaching bath,
4. treating the photographic element in a strong acidic solution, and
5. fixing the photographic element no later than after said step (4), but not before said step (2).

The strong acidic solution which causes the destruction of the non-acid-resistant primary dye formed on color development at the exposed areas is an acidic solution the pH of which is preferably at least 1 i.e. an acidic solution the hydrogen ion concentration of which is preferably at least 1 i.e. an acidic solution the hydrogen ion concentration of which is preferably at least $10^{'7E'1}$ gram equivalent per liter.

According to a preferred embodiment for preparing direct positive multicolor images according to this invention, this process comprises the steps of imagewise exposing a photographic element comprising a red-sensitive, a green-sensitive and a blue-sensitive silver halide emulsion layer each of said layers containing a color coupler capable of forming on development a dye which by treatment with a strong acidic solution can be transformed into colorless products, the blue-sensitive and green-sensitive layers also containing compounds capable of forming acid-resistant yellow and magenta dyes respectively by oxidative coupling with the color couplers present in the said layers and the red-sensitive layer also containing a quinolone hydrazone compound corresponding to the above general formula and capable of forming an acid-resistant cyan dye by oxidative coupling with the color coupler present in the red-sensitive layer, developing the photographic element in a color-forming developer, treating the photographic element in an oxidative bleaching bath, occasionally fixing the photographic element, treating the photographic element in a strong acidic solution containing at least one reducing agent or oxidizing agent, fixing the photographic element if not fixed before the acid treatment, finally rinsing and drying the photographic element whereby a positive color image is formed consisting of superposed cyan, magenta and yellow dye separation images which are built up in the photographic element by the dyes formed on oxidatively coupling by treatment with the oxidative bleaching solution.

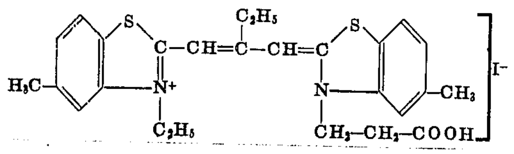
For further details as regards suitable color-developing agents, the oxidative bleaching bath, the acid treatment, etc. there can be referred to the above U.S. Pat. specification which should be read in conjunction with the present invention.

The following examples illustrate the present invention.

Example 1

To a light-sensitive silver bromoiodide emulsion containing 4.5 mole percent of silver iodide are added per 150 millimole of silver halide:

Eighteen millimole of a 1 percent solution in ethanol of a sensitizing agent for red light having the following structural formula:



8.5 millimole of the color coupler N-(2′-methyl-n-hexadecylamino- 5′-sulphophenyl)-1-hydroxy-2-naphthoic acid amide sodium salt from a 10 percent solution in a mixture of diacetone alcohol and water (1:4) occasionally comprising some alkali to promote dissolution, and

after neutralization of the emulsion: 10 millimole of the oxidatively coupling compound 1 of the above list from a 10 percent solution in 0.2 N sodium hydroxide.

After the addition of the common emulsion additives such as wetting agent, hardener and stabilizer the emulsion is coated on a support and dried.

The light-sensitive material is imagewise exposed to an original and then processed at 20° C. in the following baths:

1. developing bath (8 min.) having the following composition:

sodium hexametaphosphate	2 g.
potassium bromide	0.5 g.
hydroxylamine hydrochloride	1 g.
anhydrous sodium carbonate	30 g.
sodium sulfite	2 g.
N-ethyl-N-sulphopropyl-p-phenylenediamine	6 g.
water to make	1 liter
(pH: 10.5–10.6)	

2. Intermediate bath (4 min.) having the following composition:

borax	30 g.
sodium hydroxide necessary to obtain pH 10.1	
water to make	1 liter

3. bleach bath (2 min.) having the following composition:

potassium hexacyanoferrate (III)	25 g.
sodium bromide	25 g.
borax	2 g.
magnesium chloride	40 g.
water to make	1 liter
(pH: 8.5–8.6)	

4. rinsing bath (2 min.)

5. acid treatment bath (8 min.) having the following composition:

potassium dichromate	5 g.
conc. sulfuric acid	75 ml.
potassium fluoride	0.5 g.
water to make	1 litre
	(pH: 7.5)

6. fixing bath (4 min.) having the following composition:

ammonium thiosulphate	70 g.
sodium thiosulphate	96 g.
sodium hydrogen sulfite	4 g.
water to make	1 liter
(pH: 7.5)	

7. rinsing bath (6 min.).

The total processing lasts about 34 min.

A positive cyan image of high density is obtained.

The absorption maximum of the dye lies at 660 nm.

Example 2

In an analogous way as described in example 1 the oxidatively coupling compounds listed in the above table are incorporated in a silver bromoiodide emulsion together with one of the following color couplers:

1. N-(2′-n-hexadecylsulphonyl-5′-sulphophenyl)-1-hydroxy-2-naphthoic acid amide sodium salt;
2. N-(2′-methyl-n-hexadecylamino-5′-sulphophenyl)-1-hydroxy-2-naphthoic acid amide sodium salt.

After exposure and processing as described in example 1, cyan images are produced the absorption maxima of which are listed in the above table.

Example 3

In an analogous way as described in example 1, the oxidatively coupling compound 1 of the above table is incorporated in a silver bromoiodide emulsion together with one of the α-naphthylsulphamoyl or m-acylamino-N,N-diethylaniline color couplers given above.

After exposure and processing as described in example 1, cyan images are produced the absorption maxima of which are as follows:

Color coupler	Absorption maximum (nm.)
a	665
b	654
c	626
d	652
e	656
f	640
g	642

Example 4

A photographic multilayer material is used for preparing direct positive color images. This multilayer material consists of the following superposed layers in the indicated sequence: a support, an antihalation layer, a red-sensitive silver halide emulsion layer, a gelatin interlayer, a green-sensitive silver halide emulsion layer, a yellow filter layer, a blue-sensitive silver halide emulsion layer and a gelatin antistress layer.

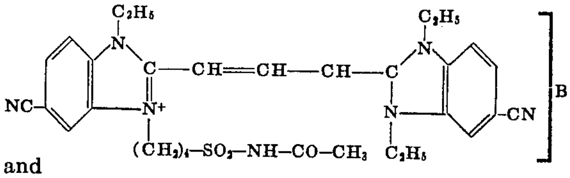
The red-sensitive emulsion layer has the composition given in example 1.

The gelatin interlayer may comprise a magenta to magenta-red colored dyestuff as screening dye.

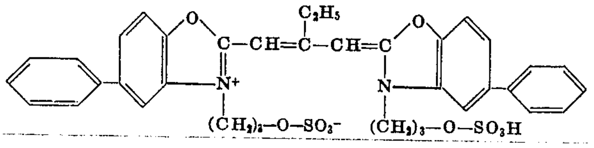
The green-sensitive emulsion layer is prepared as follows:

To a light-sensitive silver bromoiodide emulsion containing 4 mole percent of silver iodide are added per 150 millimole of silver halide:

twenty millimole of a 1 percent alcoholic solution of the following sensitizers:



and



twenty millimole of the color coupler N-(2′-n-hexadecylsulphonyl-5′-sulphophenyl)-1-hydroxy-2-naphthoic acid amide sodium salt from a 10 percent solution in alcohol and water, and

17 millimole of the odixatively coupling compound 1-methyl-2-methyl-3-n-pentadecyl-4-amino-antipyrine monohydrochloride from a 10 percent solution in ethanol.

After the addition of the usual additives such as hardeners, stabilizers and wetting agents the emulsion is coated.

The yellow filter layer may comprise colloidal silver or organic yellow dyes.

The blue-sensitive silver halide emulsion layer is prepared as follows:

To a light-sensitive bromoiodide emulsion containing 3 mole percent of silver iodide are added per 150 millimole of silver halide:

fifteen millimole of the color coupler 1-(3′-sulpho-4′-phenoxyphenyl)- 3-stearoylamino-pyrazolone-5 from a 10 percent solution in alcohol-water (1:1), and

fourteen millimole of the oxidatively coupling compound 1-methyl-6-sulpho- benzothiazolone-2(4′-n-hexadecylsulphonyl-3′-acetylaminophenyl)-sulphonyl hydrazone from a 10 percent solution of alkaline diacetone alcohol.

After adjustment of the pH to 7–8 the usual additives such as hardeners, wetting agents and stabilizers are added whereupon the emulsion is coated.

The multilayer material formed is exposed to a colored original and processed as described in example 1.

A positive color image of the original is obtained having brilliant colors and correct color rendition and having a high stability on storing under various circumstances of heat, light, and humidity.

The yellow, magenta and cyan separation images have absorption maxima: 440 nm., 540 nm. and 660 nm. respectively.

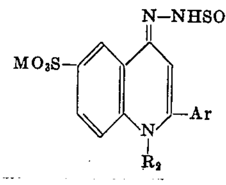
The improved absorption characteristics of the cyan images formed in accordance with the present invention as compared with the cyan images formed by the use of oxidatively coupling compounds described in U.S. Pat. No. 3,293,032 is clearly apparent from the density versus wavelength (nm) curves on FIGS. 1 and 2 of the accompanying drawings.

In FIG. 1 the absorption curves are given of the cyan dyes formed by oxidative coupling of the color coupler 1 of example 2, with oxidative coupling compound 1 according to the present invention (solid line curve) and with the oxidative coupling compound of preparation 7 of the above U.S. Pat. specification (dashline curve).

In FIG. 2 the absorption curves are given of the cyan dyes formed by oxidative coupling of the color coupler 2 of example 2 with oxidative coupling compound 1 according to the present invention (solid line curve) and with the oxidative coupling compound of preparation 7 of the above U.S. Pat. Specification (dashline curve).

We claim:

1. A photographic element comprising a quinolone hydrazone compound corresponding to the formula:



wherein:

Ar stands for an aryl group,

R_1 stands for an alkyl group, an aryl group, an aralkyl group, or an amino group,

R_2 stands for an alkyl group, and

M stands for hydrogen or an alkali metal atom.

2. A photographic element according to claim **1**, wherein said element comprises at least one water-permeable light-sensitive silver halide layer, and a color coupler in effective contact with said silver halide and with the said quinolone hydrazone compound, said color coupler being capable of forming on color development a dye, which by treatment with a strong acidic solution can be converted into colorless products, and of forming an acid-resistant cyan dye by oxidative coupling with the said quinolone hydrazone compound.

3. A photographic element according to claim **2**, wherein the said color coupler and the said quinolone hydrazone compound are present in the said water-permeable light-sensitive silver halide layer or in a colloid layer in water-permeable relationship with said layer.

4. A photographic element according to claim **2**, wherein said element is a multilayer color element comprising three silver halide emulsion layers which are differently spectrally sensitized of which a red-sensitized silver halide emulsion layer or a non-light-sensitive colloid layer in water-permeable relationship therewith comprises a color coupler capable of forming on development a quinone-imine or azomethine dye which can be destroyed or transformed into colorless products by treatment with a strong acidic solution and a said quinolone hydrazone compound which on treatment of the color developed photographic element in an oxidizing solution oxidatively couples with said colorless color coupler to form in the nondeveloped areas a cyan dye which cannot be destroyed or transformed into colorless products by the said treatment with a strong acidic solution.

5. A photographic element according to claim **2**, wherein said color coupler is a color coupler of the α-naphthol type.

6. A photographic element according to claim **2**, wherein said color coupler is a α-naphthylsulphamoyl color coupler.

7. A photographic element according to claim **2**, wherein said color coupler is a m-acylamino-N,N-dialkylaniline color coupler.

8. Process for the production of direct-positive color images which comprises the steps of imagewise exposing a photographic element according to claim **2**, developing the photographic element in a color forming developer, treating the photographic element in an oxidative bleaching bath, treating the photographic element in a strong acidic solution and fixing the photographic element no later than after the said acid treatment step but not before the said color development step, thus forming colorless reaction products at the exposed areas where development occurred, and a positive color image as a result of oxidative coupling at the unexposed areas.

9. Process according to claim **8**, wherein the color-forming developer comprises a primary amino developing agent.

10. Process according to claim **8**, wherein the oxidative beaching bath is an alkaline bleaching bath containing potassium hexacyanoferrate (III).

11. Process according to claim **8**, wherein the strong acidic solution has a hydrogen ion concentration of at least 10^{-7E-1} gram equivalent per liter.

12. Process according to claim **11**, wherein the acidic solution also comprises an oxidizing agent or reducing agent.

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