June 4, 1968 MAKOTO YOSHIDA ETAL **3,386,830**

COLOR PHOTOGRAPHIC SILVER HALIDE EMULSION CONTAINING
A MAGENTA COLORED CYAN COUPLER

Filed Nov. 17, 1964 3 Sheets-Sheet 1

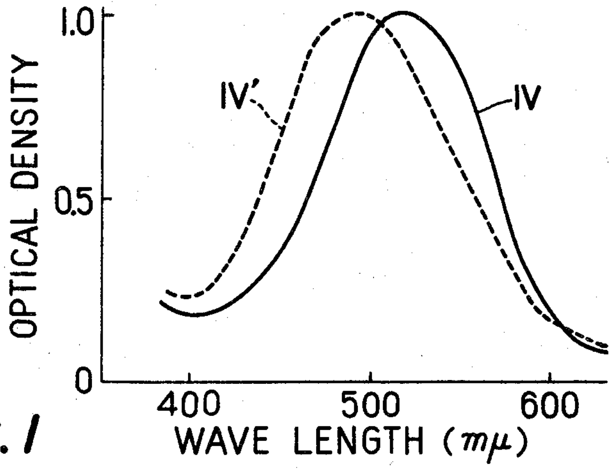

FIG. 1

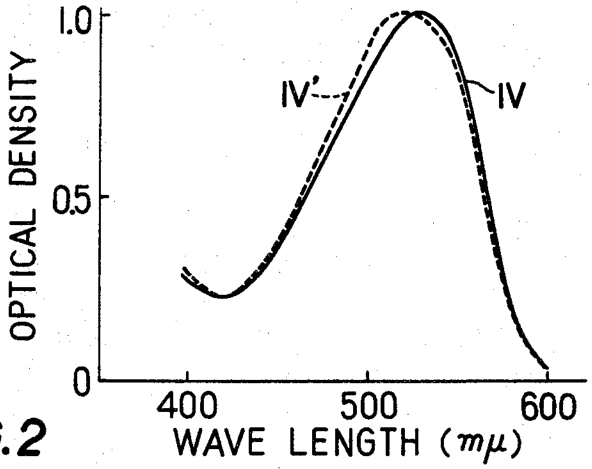

FIG. 2

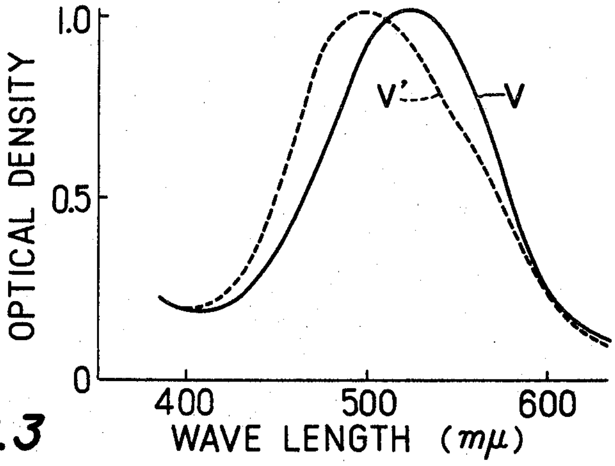

FIG. 3

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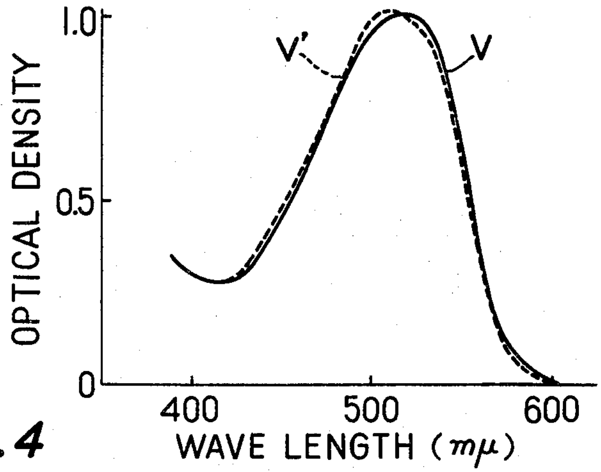

FIG. 4

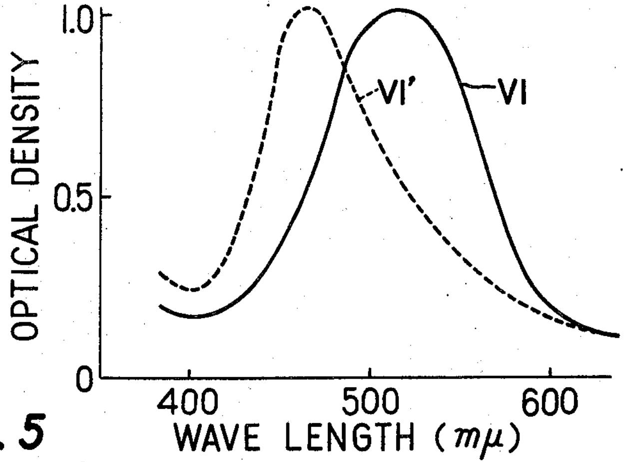

FIG. 5

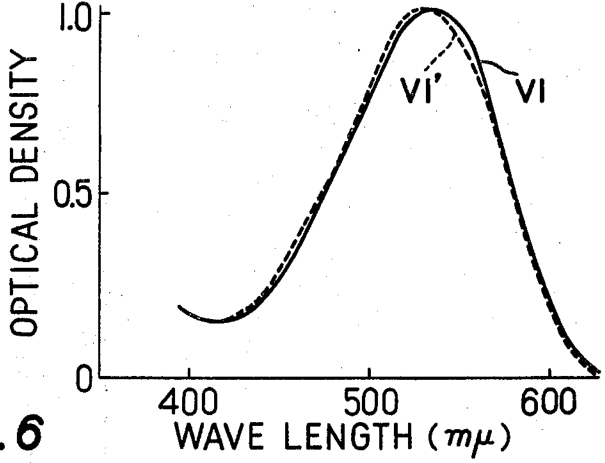

FIG. 6

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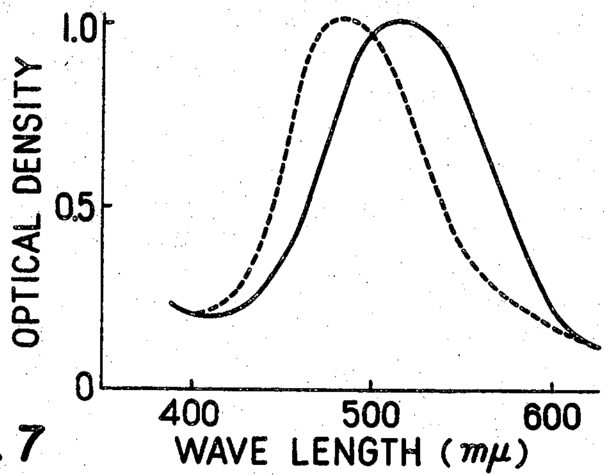

FIG. 7

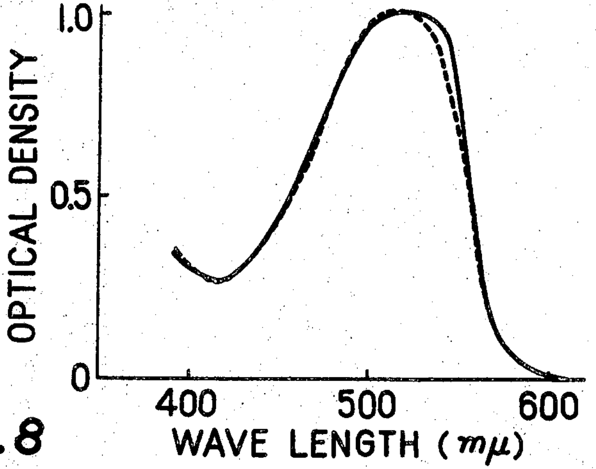

FIG. 8

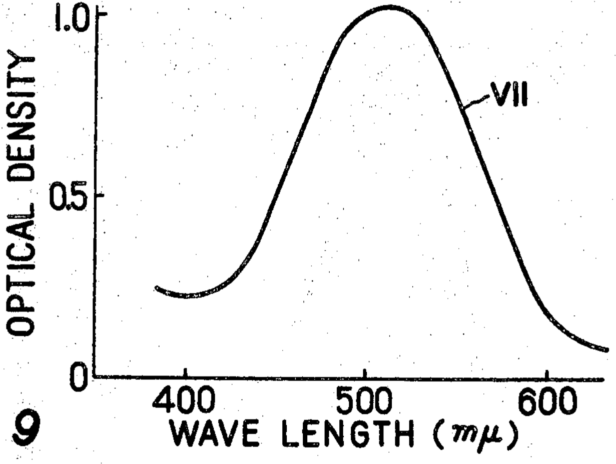

FIG. 9

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United States Patent Office

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COLOR PHOTOGRAPHIC SILVER HALIDE EMULSION CONTAINING A MAGENTA COLORED CYAN COUPLER

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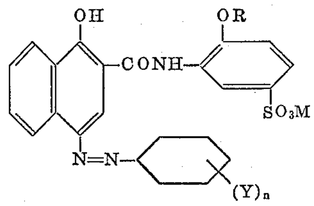
11 Claims. (Cl. 96—100)

ABSTRACT OF THE DISCLOSURE

A color photographic silver halide emulsion containing a magenta-colored cyan coupler having a remarkable auto-masking action, represented by the following formula:



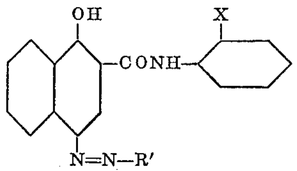
wherein R is an alkyl group having more than 10 carbon atoms; M is a hydrogen atom, an alkali metal, an ammonium group of $—H·NH_p(R'')_q$, wherein $p+q=3$, p and q are 0–3, and R″ is a lower alkyl group; Y is —COOM, $—SO_3M$, or a carboalkyoxy group wherein M has the above significance; and n is 1 or 2.

The present invention relates to color photographic materials containing colored cyan coupler, which is provided with automatic masking mechanism, in order to remove drawbacks of color reproduction of color sensitive materials.

Most of cyan couplers to be used for color photography are 1-naphthol-2-carboxylic acid derivatives or aminophenol derivatives. When these couplers are added in a photographic emulsion layer, the coupler added must not diffuse to any adjacent photographic layers. In order to prevent diffusion from one photographic emulsion layer to another, a long chain alkyl group and the like is introduced thereinto as a group for giving the couplers diffusion resisting property. Moreover, at least one carboxyl group or sulfo group is introduced for making the couplers soluble in aqueous alkali solution. Carboxyl group, however, is not sufficient for this purpose, and therefore sulfo group is used in general cases. In many cases, sulfo group is present at 4-position of naphthol nucleus, or in aryl group or aliphatic hydrocarbon group introduced in naphthol nucleous at 2-position or an aliphatic hydrocarbon group combined with the said aryl group.

Cyan coupler substituted with arylazo group at 4-position is well known as a coupler having automatic masking mechanism for correcting drawbacks of color reproduction of color sensitive materials. (Refer to U.S. Patents Nos. 2,449,966 and 2,455,169.) It is known that when 1-hydroxy-4-arylazo-2-naphthoanilide type coupler substituted with halogen, alkoxy group, or mono nuclear aryloxy group at ortho position against amide group of anilide nucleus, which is represented by the following general formula:

(I)



wherein X is halogen, alkoxy group, or mono nuclear aryloxy group; R′ is mono nuclear aryl group, is dissolved in a solvent such as tricresyl phosphate and dispersed in an emulsion, absorption of green light is great and it is a coupler showing desirable color near magenta. (Refer to U.S. Patent No. 2,706,684.)

However, when the coupler represented by the abovementioned formula is dissolved or mixed in aqueous alkali solution, added into an emulsion and coated on the film base, the maximum value of absorption of the coupler is present on the side of a short-wave length, as shown in dotted lines in FIGS. 1, 3, 5 and 7, absorption of blue light is great, that of green light is small, so quite unsatisfactory color is shown. That is to say, when this kind of coupler is dispersed in an emulsion by use of an organic solvent, it shows excellent properties, but when it is added in the emulsion by use of alkali, the properties thereof become emazingly inferior.

The accompanying drawing shows a spectral absorption curve of a coupler in a photographic film prepared from sensitive materials containing a coupler to be used in the present invention and a well known coupler for comparison, and that of the coupler in a pyridine solution.

An object of the present invention is to provide sensitive materials containing 1-hydroxy-4-arylazo-2-naphthoanilide type coupler which have excellent properties, even when they are used by a process comprising adding into an emulsion by use of alkali.

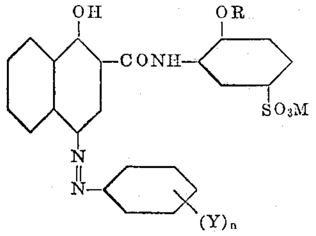
One reason why properties become inferior when this type of coupler is used by a process comprising adding into the emulsion by use of alkali may be that the coupler is hardly soluble in aqueous alkali solution and can not be dispersed well in the emulsion. Accordingly, in order to make the coupler easily soluble in aqueous alkali solution and make it well dispersed in the emulsion, it is necessary to introduce carboxyl group, sulfo group and the like as solubilizing groups in coupler molecules. That is to say, carboxyl groups, sulfo groups, or combination thereof should be introduced in arylazo group at 4-position or anilide group at 2-position or both groups of naphthol nucleus. However, couplers having carboxyl group or sulfo group introduced into only arylazo group at 4-position of naphthol nucleus are hardly soluble in aqueous alkali solution as shown by Table 2. It is clear from the accompanying drawing that when it is added in an emulsion together with alkali, the absorption maximum of the coupler is present on the side of short wave length, the absorption of blue light is great, the absorption of green light is small, and quite unsatisfactory color is shown.

Accordingly, in order to improve solubility of the coupler in aqueous alkali solution, to make dispersion of the coupler in the emulsion better, to produce excellent coupler showing quite suitable color near magenta, it is necessary to introduce carboxyl group or sulfo group into not only arylazo group at 4-position but also anilide group at 2 position of naphthol nucleus. In particular, it is desirable that sulfo group giving better solubility than carboxyl group is introduced into anilide group at 2-position. Moreover, as described later, carboxyl group is not sufficient for making the color absorption better, and it is required that special effect on improvement of the color absorption of sulfo group shall be well displayed. From this reason, sulfo group is better as the group introduced into anilide group at 2-position. Moreover, when this type of coupler is added into an emulsion and used, the diffusion of the coupler should be prevented. It is also necessary for preventing the diffusion of cyan dye resulting from the coupler by the color development. Therefore, the diffusion-resisting group such as long chain alkyl group should be introduced into anilide group at 2-position of naphthol nucleus. That is to say, it is required that three substituents such as halogen or alkoxy group at the ortho position against amido group, sulfo group and a diffusion-resisting group are introduced into anilide group at 2-position of naphthol nucleus. Therefore, the synthesis of the parent coupler is extremely difficult and expensive.

Accordingly, in case of the coupler in the present invention, alkoxy group having more than 10 carbon atoms is introduced into anilide group at ortho-position against amido group, while sulfo group is introduced into anilide group. Moreover, alkoxy group at ortho position against amide group is given properties of a diffusion-resisting group without losing special properties which affect color tone of the coupler. Therefore, merely two substituents are introduced into anilide group. The synthesis of the parent coupler is extremely easy, which is a characteristic from the point of synthesis. It may be said that the coupler to be used in the present invention is a novel compound having a characteristic from the point of molecular structure, too.

That is to say, the present invention relates to color sensitive materials, characterized containing the coupler represented by the following general formula:

(II)



wherein R is alkyl group having more than 10 carbon atoms; M is a member selected from the group consisting of a hydrogen atom, alkali metal, ammonium group, and $-H\cdot NH_p(R'')_q$, wherein $p+q=3$; p, q is 0–3; R'' is lower alkyl group; Y is a member selected from the group consisting of —COOM, $-SO_3M$, and carboalkoxy group; n is 1 or 2.

The coupler to be used in the present invention has not only alkali-solubilizing group in arylazo group at 4-position of naphthol nucleus, but also sulfo group in anilide group at 2-position, as shown by the abovementioned general formula. Therefore, said coupler is well soluble in alkali aqueous solution (refer to Table 2), and when it is dissolved in alkali solution and added in an emulsion, the coupler is satisfactorily dispersed. To our surpise, absorption of green light is great and suitable color almost similar to magenta is displayed. When the coupler in the present invention and a coupler corresponding to the general Formula I which is different from the general Formula II merely in such point that $-SO_3M$ group is not present in anilide group are dissolved in pyridine, respectively, and their absorptions are measured. It is clear that they are almost same with each other in respect to the position of the absorption maximum and shape of the absorption curve (refer to FIGS. 2, 4, 6 and 8). However, when said two couplers are added in the emulsion by use of alkali, coated on a film base, dried, bleached and fixed, and spectral absorption of the resulting film are measured (refer to Example 1 and Example 2), remarkable differences are observed between said two couplers (refer to FIGS. 1, 3, 5 and 7). That is to say, they are almost same with each other in pyridine solutions. However, when they are added into emulsions by use of alkali, the coupler in the present invention which is represented by the general Formula II has the absorption maximum at about 520 mμ and displays quite desirable color, while the comparing coupler corresponding to the general formula I which has not $-SO_3M$ in anilide group has the absorption maximum on the side of short wave length and displays remarkably inferior color. The difference of their absorption maximum reaches from 25 to 50 mμ. As being clear from these facts, it is an important and essential condition that the coupler in the present invention has sulfo group in anilide group at 2-position of the naphthol nucleus.

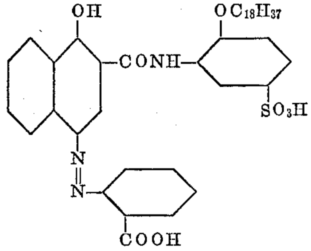
Moreover, when the coupler in the present invention is added into a red-sensitive emulsion, coated on a film base, dried and exposed, developed with a color developer containing a developing agent such as N·N-disubstituted paraphenylenediamine, bleached and fixed, a negative cyan image developed and a positive red image of the residual colored coupler are obtained at the same time. The spectral absorption of the resulting positive image is quite desirable, as mentioned above, and the transparency of the film is quite excellent. On the other hand, the color of the red image which is prepared by treating the comparing coupler by the same treatment is inferior, and the conglomerate of remaining coupler is observed in the film. Therefore, the transparency of the film is inferior. As being clear from this fact, too, it is a very important condition for making dispersion of the coupler in the emulsion better, increasing the transparency of the resulting film and improving the color of the red image that the coupler in the present invention has sulfo group in anilide group.

To our surprise, even in the case where carboxyl group introduced in arylazo group at 4-position of naphthol nucleus, as an alkali solubilizing group, is subjected to esterification and converted into carboalkoxy group having lower alkali-soluble property, when the coupler has sulfo group in anilide group like the coupler in the present invention, it is easily soluble in aqueous alkali solution and dispersed well in the emulsion. The absorption maximum of the resulting film reaches about 520 mμ, quite desirable color is shown, and the transparency of the film is good (refer to FIG. 9). The fact shows that sulfo group present in anilide group can have alkali-soluble property to sufficient degree and disperses well in the emulsion, even though alkali solubilizing group is not included in arylazo group at 4-position of the naphthol nucleus. Moreover, the fact shows that the said sulfo group has special effect on making the color absorption better. The characteristic that the coupler in the present invention has sulfo group in anilide group is very important.

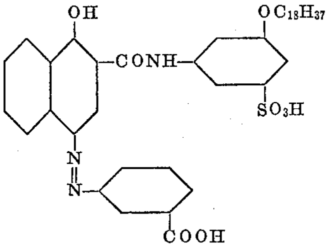
Furthermore, the coupler in the present invention is compared with the comparing coupler having no sulfo group in anilide group with regard to relative speed of the cyan developed negative film prepared by the abovementioned treatment, as shown in the Tables 3 and 5. It clearly depends on such structural characteristic as the coupler in the present invention has sulfo group in anilide group, that the coupler in the present invention has a high speed.

Couplers to be used in the present invention are represented by the following formulae; i.e.

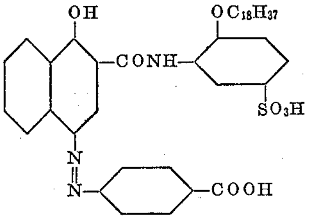
(III)



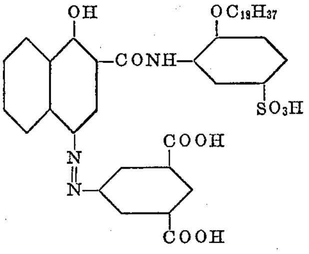
(IV)



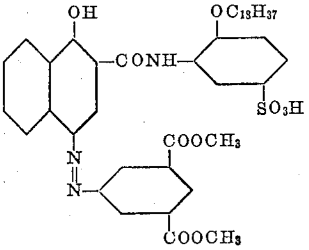
(V)



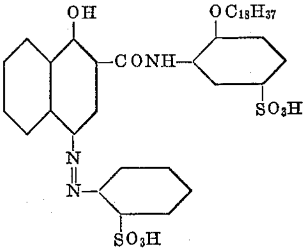
(VI)



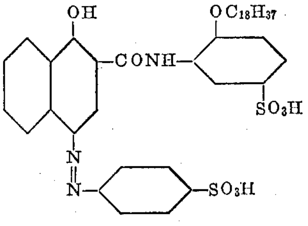
(VII)



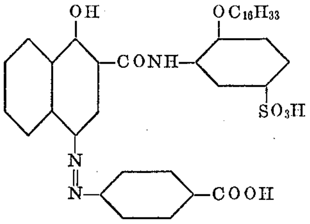
(VIII)



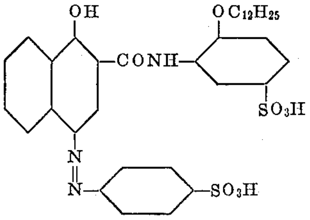
(IX)



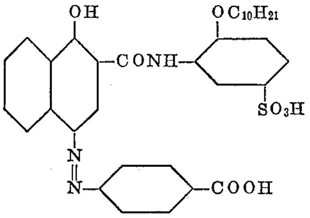
(X)



(XI)



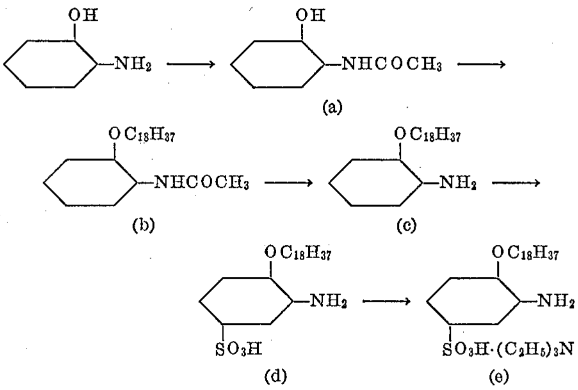
(XII)



The compounds of the present invention in form of free acid or salt have almost the same effect with each other.

The couplers in the present invention were prepared as follows:

(1) (1-a).—Triethylamine salt of 3-amino-4-octadecyloxybenzene sulfonic acid (structural Formula *e*)

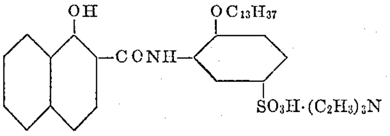


By acetylating 2-aminophenol with acetic anhydride, 2-acetaminophenol (strucural Formula *a*) was obtained. The yield was 90% and the melting point was 204–5° C. 2-acetaminophenol and octadecyl bromide were dissolved in anhydrous alcohol and added with sodium alcoholate. After refluxing, the formed sodium bromide was filtered off, and poured into an aqueous hydrochloric acid solution, whereby 2-octadecyloxyacetanilide (structural Formula *b*) was separated. The resulting 2-octadecyloxyacetanilide was collected, added in a mixture solution containing alcohol and an aqueous potassium hydroxide solution, boiled, and refluxed. Thereafter, it was added in a concentrated aqueous hydrochloric acid solution, whereby hydrolysed products were precipitated in the form of hydrochloride. The precipitates were filtered and treated with an aqueous sodium hydroxide solution, and extracted with ether, to yield 2-octadecycloxyaniline (structural Formula *c*). The yield was 48% and the melting point was 57–58° C.

2-octadecyloxyaniline was sulfonated by use of 30% fuming sulfuric acid according to a usual method, 3-amino-4-octadecyloxybenzene sulfonic acid (structural Formula *d*) was obtained. The yield was 54% and the melting point was 285–287° C.

220 g. of 3-amino-4-octadecyloxybenzene sulfonic acid was suspended in 500 ml. of isopropanol, added with 60 g. of triethylamine, and boiled and refluxed on a steam bath for 30 minutes. After cooling, precipitates were separated and filtered. The collected precipitates were washed with 1000 ml. of acetone and dried to produce triethylamine salt of 3-amino-4-octadecyloxybenzene sulfonic acid (structural Formula *e*). The yield was 225 g. (83%) and the melting point was 111–113° C.

(1–b).—Triethylamine salt of 1-hydroxy-2-(2-octadecyl oxy-5-sulfo)naphthoanilide (structural Formula *f*)



(f)

65 g. of triethylamine solt of 3-amino-4-octadecyloxybenzene sulfonic acid (The preparation method by using triethylamine salt is explained in the specification of Japanese Patent No. 295,087) and 32 g. of 1-hydroxy-2-naphthoic phenylester were heated at 150° C. The formed phenol was distilled off under a reduced pressure and, thereafter, cooled up to room temperature. Then, 150 ml. of acetone was added therein and heated. After the resulting solution was cooled, the separated precipitates were collected, washed with 50 ml. of acetone, and recrystallized from 200 ml. of methanol. 52 g. of triethylamine salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthoanilide was obtained. The yield was 61%. The melting point was 129–131° C. The content of the nitrogen was 3.81% of observed value against 3.93% of calculated value.

(1–c).—1-hydroxy-4-(3-carboxyphenylazo)-2 - (2 - octadecyloxy-5-sulfo)naphthoanilide (structural Formula IV)

6 g. of sodium hydroxide was added in 200 ml. of water, and 16.5 g. of 3-amino benzoic acid was dissolved therein. Then, 9 g. of sodium nitrate was added to the resulting solution. Then, the solution was added with about 50 g. of broken ice, cooled at 0° C., and added with 50 ml. of 36% hydrochloric acid under violent stirring.

On the other hand, 72 g. of triethyl amine salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthanilide was dissolved in 2000 ml. of water together with 50 g. of sodium hydroxide, and cooled with ice to about 7° C. Under stirring, a solution of diazonium salt prepared previously was dropped. After stirring, the mixture for about 1 hour, 150 ml. of 36% hydrochloric acid was added therein. Moreover, 1000 ml. of methanol was added and heated at about 50° C. Red precipitates separated were collected, washed with about 1000 ml. of water, and heated and refluxed for about 30 minutes in 1000 ml. of methanol. Precipitates were collected and dissolved in 250 ml. of dimethylformamide under heating. 300 ml. of methanol was added therein and cooled with water, to separate precipitates. The precipitates were collected, washed with 500 ml. of methanol, and dried, whereby 40 g. of 1-hydroxy - 4-(3 - carboxyphenylazo) - 2 - (2-octadecyloxy-5-sulfo)naphthoanilide was obtained. The yield was 53% and the melting point was 275–276° C.

(2) (2–a).—Sodium salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthoanilide

61 g. of triethylamine salt prepared by the (1–b) was dissolved in 250 ml. of hot methanol, and added with a solution containing 10 g. of anhydrous sodium acetate and 100 ml. of methanol. The resulting solution was cooled with ice and the separated precipitates were collected. The precipitates were washed with 30 ml. of methanol, and dried, to obtain sodium salt of 1-hydroxy-2-(2-ocetadecyloxy-5-sulfo)naphthoanilide. The yield was 32 g. (56%) and the melting point was more than 290° C.

(2–b).—1 - hydroxy-4-(3,5-dicarbomethyloxyphenylazo)-2 - (2 - octadecyloxy-5-sulfo)naphthoanilide (structural Formula VII)

Into 120 ml. of water 25 ml. of 36% hydrochloric acid was added. Then, 126 g. of 3,5-dicarbomethyloxyaniline was suspended therein, added with about 30 g. of broken ice. Under maintaining the temperature of the solution below 5° C., 6 g. of sodium nitrite was dissolved in 30 ml. of water and the resulting solution was dropped. On the other hand, 31.7 g. of sodium salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthoanilide was added in 400 ml. of water together with 20 g. of sodium hydroxide, and heated at about 50° C. to dissolve. Thereafter, the solution was cooled to 5° C. The solution of diazonium salt previously prepared was dropped maintaining the temperature of the solution below 8° C., while stirring. Then, stirring was carried out further for about 30 minutes. 40 ml. of 36% hydrochloric acid was added to the solution. Red precipitates separated were collected, washed with about 200 ml. of water, dried, boiled with a mixture solution containing 50 ml. of dimethylformamide and 250 ml. of methanol, and washed with 250 ml. of methanol. After filtering at a high temperature, the precipitates were washed with 100 ml. of methanol, and dried to yield 1 - hydroxy - 4 - (3,5-dicarbomethyloxyphenylazo)-2-(2-octadecyloxy-5-sulfo)naphthoanilide. The yield was 28.5 g. (69%) and the melting point was 281–283° C.

(3).—1 - hydroxy - 4 - (2 - sulfophenylazo)-2-(octadecyloxy-5-sulfo)naphthoanilide (structural Formula VIII)

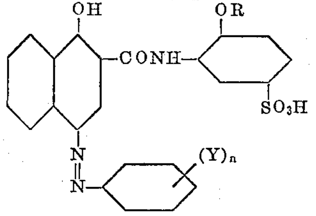
In (1–c), 2-aminobenzenesulfonic acid was urged in place of 3-amino benzoic acid. The sodium salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthoanilide was used instead of triethylamine salt of 1-hydroxy-2-(2-octadecyloxy-5-sulfo)naphthoanilide. By the same treatment except using the above substances and recrystallized from dimethylformamide 1 - hydroxy-4-(2-sulfophenylazo)-2-(2-octadecyloxy-5-sulfo)naphthoanilide was obtained. The yield was 55% and the melting point was 290° C.

(4).—1 - hydroxy - 4 - (4 - sulfophenylazo)-2-(2-dodecyloxy-5-sulfo)naphthoanilide (structural Formula X)

In (1–a), triethylamine salt of 3-amino-4-dodecyloxybenzene sulfonic acid was prepared by the same treatment except dodecyl bromide was used instead of octadecylbromide. By the same treatment with (1–b), triethylamine salt of 1-hydroxy-2-(2-dodecyloxy-5-sulfo)naphthoanilide was obtained, and treated by the same manner as in (2–a) to prepare the sodium salt thereof. When the same treatment with (3) was carried out, 1-hydroxy-4-(4-sulfophenylazo)-2-(2-dodecyloxy-5-sulfo)naphthoanilide was prepared. The yield was 53% and the melting point was more than 290° C.

With regard to concrete examples of couplers to be used in the present invention, the melting points and the results of nitrogen analysis are shown by the following table.

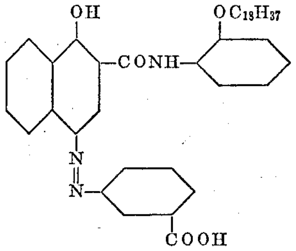
TABLE I



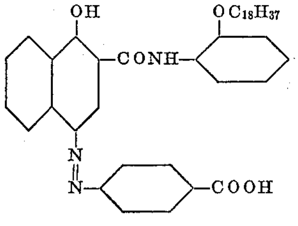
Structural formula	R	(Y)n	Melting point (° C.)	Nitrogen analysis	
				Calculated	Observed
III	$C_{18}H_{37}$	2-COOH	272–3	5.53	5.65
IV	$C_{18}H_{37}$	3-COOH	275–6	5.53	5.28
V	$C_{18}H_{37}$	4-COOH	280–2	5.53	5.55
VI	$C_{13}H_{37}$	3,5-COOH	>290	5.20	5.09
VII	$C_{18}H_{37}$	3,5-COOCH$_3$	281–3	5.06	5.39
VIII	$C_{13}H_{37}$	2-SO$_3$H	>290	5.29	5.59
IX	$C_{18}H_{37}$	4-SO$_3$H	>290	5.29	5.52
X	$C_{12}H_{25}$	4-SO$_3$H	>290	5.91	6.16

For comparing the coupler to be used in the present invention with a coupler which has no sulfo group in anilide group at 2-position of naphthol nucleus in respect to efficiency, the latter is represented by the following formula.

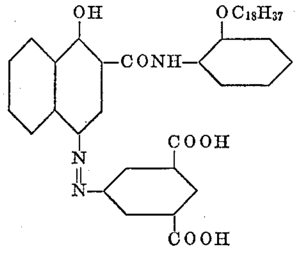
(IV')



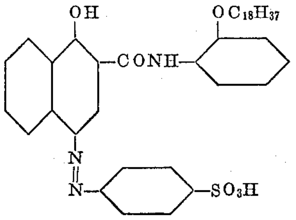
(V')



(VI')



(IX')



The saturated excess amounts of the couplers represented by the general formula of IV, IV', V, V', VI, VI', IX and IX' respectively are measured, added in a sodium hydroxide solution at pH 10 and stirred at 35.0° C. for 6 days. The amount of the coupler remaining in the saturated solution is measured by spectroscopic analysis. The solubilities are shown in Table 2 by molar ratio.

TABLE 2

Structural formula:	Molar ratio
IV	1.0
IV'	3.0×10^{-3}
V	1.0
V'	6.0×10^{-3}
VI	1.0
VI'	4.5×10^{-5} or below.
IX	1.0
IX'	1.1×10^{-2}

That is to say, it is clear that the coupler to be used in the present invention is more soluble in alkali than the comparative coupler.

Couplers represented by the structural formula of IV, IV', V, V', VI, VI', IX and IX', respectively are dissolved in a definite amount of pyridine and spectral absorption curve is measured. The maximum optical density at visible region is adjusted at 1.0, and shown in the accompanying drawings, i.e. FIG. 2, FIG. 4, FIG. 6 and FIG. 8. That is to say, it is understood that the coupler to be used in the present invention is almost same with the comparative coupler in pyridine solution in respect to the position of the absorption maximum value and shape of the absorption curve.

EXAMPLE 1

Into 100 parts by weight of red sensitive silver iodobromide emulsion is added 5 parts by weight of a 5% sodium hydroxide aqueous solution of the coupler prepared by the synthetic example (1–c); structural Formula IV, wherein 2.6 ml. of 1 N sodium hydroxide aqueous solution per gram of the coupler is used. The pH value of the emulsion is adjusted at 7.0 by use of citric acid solution, coated on a film base, and dried to produce red-sensitive materials.

On the other hand, a saturated solution of a comparative coupler represented by the structural formula of IV', wherein 1 N sodium hydroxide aqueous solution at 70° C. is used, is prepared and added in 100 parts by weight of red-sensitive silver iodobromide emulsion to be equivalent to the amount of the above-mentioned coupler represented by the structural Formula IV. The pH value is adjusted at 7.0 by use of citric acid solution. By the same treatment with the above, red-sensitive materials are produced.

The said two color sensitive materials are exposed to red light by light wedge, and developed by a conventional method by use of the following developer containing N·N-diethylparaaminoaniline.

Color developer:	G.
N·N-diethylparaaminoaniline sulfate	20
Sodium sulfite	2.0
Sodium carbonate monohydrate	50.0
Hydroxylamine chloride	1.5
Potassium bromide	1.0
Wate (makes up to 1000 ml.).	

pH 10.8±0.1.

Moreover, the following bleaching solution and the fixing solution are used for bleaching and fixing. Undeveloped silver halide and reduced silver formed are removed.

Bleaching solution:	G.
Sodium ferricyanide	100
Potassium bromide	20
Water (makes up to 1000 ml. as a whole).	

pH 6.9±0.3.

Fixing solution:	
Sodium thiosulfate	200
Sodium sulfite	20
Acetic acid (2.8%)	45
Boric acid	7.5
Potassium alum	20
Water (makes up to 1000 ml.).	

pH 4.5±0.2.

A negative image developed in cyan and a red image consisted of residual colored coupler are obtained at the same time from color sensitive materials employing the coupler represented by the structural Formula IV. Transparency of the film is very excellent. However, haze of unreacted colored coupler are observed in the film produced from color sensitive materials employing the comparative coupler represented by the structural Formula IV', and transparency of the film is inferior.

When the absorption maximum wave length of the film produced by bleaching and fixing said two kinds of color sensitive materials is measured, it is 520 mμ in case of the coupler represented by the structural Formula IV and 493 mμ in case of the comparative coupled represented by the structural Formula IV'. That is to say, in case of the coupler represented by the structural Formula IV, this absorption maximum wave length in the film is long by about 27 mμ, and quite desirable color is shown (refer to FIG. 1).

The relative speeds of said two kinds of color sensitive materials are shown by the following table. The coupler to be used in the present invention is at high speed by about 10%.

TABLE 3

Structural formula:	Relative speed of negatives
IV	100
IV'	89

Example 2

The same treatment as in Example 1 is carried out, except that the couplers corresponding to the structural Formulae P, VI and IX, respectievly, are used in place of the coupler corresponding to the structural Formula IV, and that the comparative couplers represented by the structural Formulae V', VI' and IX', respectively, are employed instead of the comparative coupler represented by the structural Formula IV', whereby each film is produced.

The film produced from the color sensitive materials employing the coupler corresponding to the structural Formulae V, VI or IX, are quite excellent in respect to spectral absorption and transparency, as in Example 1.

On the other hand, when the couplers for comparison corresponding to the structural Formula V', VI' or IX' is used, as in Example 1, haze of unreacted color coupler is observed and spectral absorption and transparency of the produced film are inferior. Each of spectral absorption curve of the film produced by bleaching and fixing the above-mentioned color sensitive materials are illustrated in FIGS. 3, 5 and 7, and the absorption maximum wave length is shown in the following table.

TABLE 4

Structural formula:	Absorption maximum wave length ($m\mu$)
V	525
V'	500
VI	520
VI'	470
IX	515
IX'	485

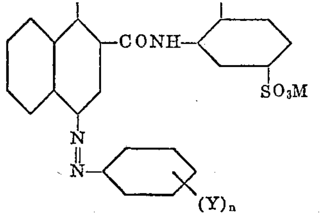
The relative speeds of color sensitive materials produced are shown in Table 5.

TABLE 5

Structural formula:	Relative speed of negatives
V	100
V'	76
VI	100
VI'	98
IX	100
IX'	74

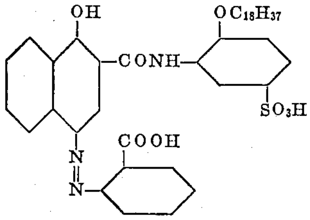
What we claim is:

1. A color photographic silver halide emulsion containing the color coupler having the following general formula:

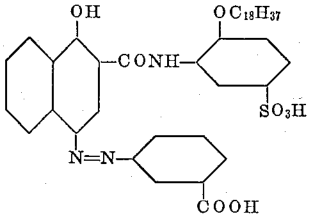


wherein R is alkyl group having more than 10 carbon atoms; M is a member selected from the group consisting of a hydrogen atom, an alkali metal, an ammonium group and $—H\cdot NH_p(R'')_q$, wherein $p+q=3$; p, q are 0–3, and R'' is a lower alkyl group; Y is a member selected from the group consisting of —COOM, $—SO_3M$, and a carboalkoxy group; and n is 1 or 2.

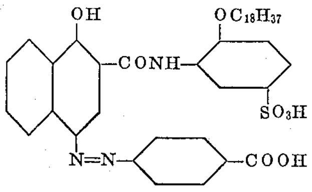
2. The color photographic silver haide emulsion as claimed in claim 1, wherein said color coupler is



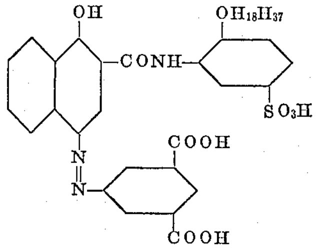
3. The color photographic silver halide emulsion as claimed in claim 1 wherein said color coupler is



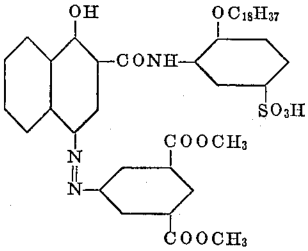
4. The color photographic silver halide emulsion as claimed in claim 1 wherein said color coupler is



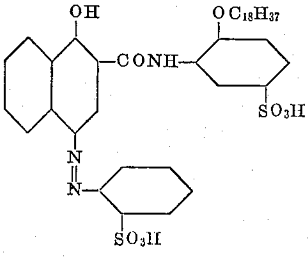
5. The color photographic silver halide emulsion as claimed in claim 1 wherein said color coupler is



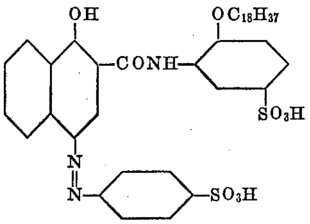
6. The color photographic silver halide emulsion as claimed in claim 1 wherein said color coupler is



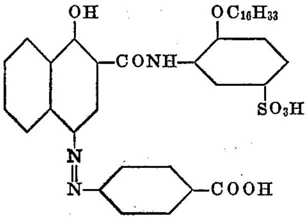
7. The color photographic silver halide emulsion as claimed in claim 1 wherein said color coupler is



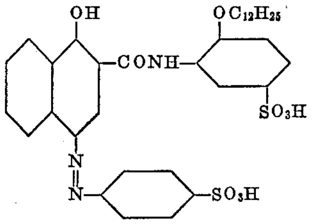
8. The color photographic silver halide emulsion as claimed in claim **1** wherein said color coupler is



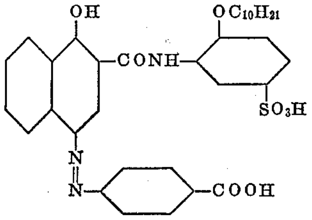
9. The color photographic silver halide emulsion as claimed in claim **1** wherein said color coupler is



10. The color photographic silver halide emulsion as claimed in claim **1** wherein said color coupler is



11. The color photographic silver halide emulsion as claimed in claim **1** wherein said color coupler is



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