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3,476,560

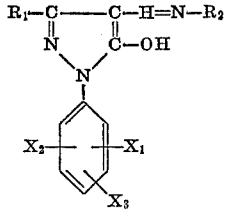
INHIBITING FOGGING ACTION DURING COLOR DEVELOPMENT

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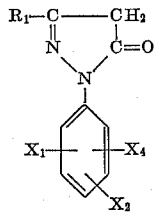
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Claims priority, application Japan, July 28, 1964, 39/42,578
Int. Cl. G03c 7/16, 1/34
U.S. Cl. 96—22 6 Claims

ABSTRACT OF THE DISCLOSURE

A silver halide photographic emulsion layer adapted to be color developed with a p-phenylenediamine derivative, comprising a colored coupler represented by the general formula (I)



wherein R_1 represents a member selected from the group consisting of an alkyl group, an acylamino group, an N-arylamino group and a sulfonamido group; R_2 represents a member selected from the group consisting of a phenyl group, an alkyl-substituted phenyl group, an acylamino-substituted phenyl group, an alkoxy-substituted phenyl group, a sulfo-substituted phenyl group, a naphthyl group, an alkyl-substituted naphthyl group, an acylamino-substituted naphthyl group, an alkoxy-substituted naphthyl group, a sulfo-substituted naphthyl group and a pyrazolyl group; and X_1, X_2 and X_3 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a halogen atom, an acylamino group, an alkylcarbamoyl group, a sulfonamido group, an alkoxy group, an aryloxy group, a sulfonic acid group, an alkali metal salt of said sulfonic acid group, an ammonium salt of said sulfonic acid group, a carboxyl group, an alkali metal salt of said carboxyl group and an ammonium salt of said carboxyl group, and a colorless coupler represented by the general formula (II)



wherein R_1, X_1 and X_2 have the same significance as in the above mentioned formula (I) and X_4 represents a member selected from the group consisting of a sulfonic acid group, an alkali metal salt of said sulfonic acid group, an ammonium salt of said sulfonic acid group, a carboxyl group, an alkali metal salt of said carboxyl group and an ammonium salt of said carboxyl group.

The present invention relates to a process for inhibiting a fogging action during color development and more particularly to a process for preventing color fogging in developing a silver halide photographic emulsion containing a coupler having —N=N—R group (wherein R represents a substituted or unsubstittued aryl group or heterocyclic residual group) into the 4th position of pyrazolone or a pyrazolone derivative using a p-phenylenediamine derivative as a color developing agent.

It has been well known that the distortion of color reproduction in a color negative-positive process by subtractive color process is caused by undesirable spectral absorption characteristics of dyes formed by the color development. As a process for compensating for such undesirable absorption characteristics of the dyes, masking has been generally adopted and for this purpose the use of a yellow-colored coupler prepared by introducing the —N=N—R group (wherein R is a substituted or unsubstituted aryl group or heterocyclic residual group) into the 4th position of pyrazolone derivative was disclosed by U.S. Patent 2,455,170. When a photographic sensitive layer prepared by adding such a coupler in a silver halide photographic emulsion is exposed and color-developed with a p-phenylenediamine derivative, a magenta dye is formed from the coupler at the exposed portions as a negative image while the remaining coupler forms at the unexposed portions a yellow positive image.

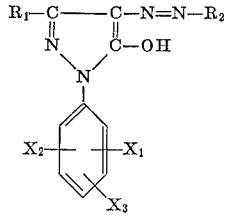
When the exposed silver halide is developed using a p-phenylenediamine derivative as the color developing agent, the oxidation product of it is coupled with these couplers in 4-position of them and also the azo group is liberated at the same time. However, the use of the colored coupler in this case is accompanied with the following two difficulties. The first point is that since the extinction coefficient of the colored coupler having the —N=N—R group (where R is a substituted or unsubstituted aryl group or heterocyclic residual group) is too high, the masking effect is liable to become excessive. Hence, it is necessary to control masking and as the methods, for example, the following two methods are known. One of them is shown by U.S. Patent 2,428,054 in which the colored coupler is incorporated in one emulsion layer together with a colorless coupler. The other is disclosed by U.S. Patent 2,688,539 in which two emulsion layers having the same color sensitivity are formed, one of them being incorporated with the colored coupler and another being incorporated with a colorless coupler.

The 2nd problem is that when a silver halide photographic emulsion layer containing a colored coupler in which the hydrogen of the active methylene group has been substituted with an azo group is developed using a p-phenylenediamine derivative as color developing agent, a remarkable fogging action occurs as the development proceeds. In spite of the fact that the prevention of the formation of such fogging is very important, almost no methods have been known about the prevention thereof. The formation of fogging by such an azo-substituted colored coupler occurs only when the p-phenylenediamine derivative is used as the color developing agent but no fogged silver image is formed when the same emulsion layer is processed with a developing agent for black and white photographic materials, such as, Metol or hydroquinone. However, when a silver halide photographic emulsion layer is processed with a p-phenylenediamine derivative as the developing agent under the presence of a diazonium compound, remarkable fogging is observed. From these facts it can be considered that the formation of fogging at color development of a colored coupler with a p-phenylenediamine derivative is markedly increased by the liberated diazonium compound by-produced when the oxidation product of the color developing agent formed by fogging peculiar to the silver halide emulsion at unexposed portions is coupled with a colored coupler. The formation of such a kind of fogging can scarcely be prevented by conventional

fog inhibitors or stabilizers for silver halide photographic emulsions.

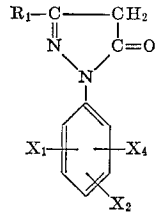
The present invention is concerned with an improved process for preventing the formation of fogging at color development with a p-phenylenediamine derivative which comprises incorporating as a colorless coupler, a pyrazolone derivative substituted at the 1st position by a phenyl group having a carboxyl group or a sulfonic acid group, or an alkali metal salt or an ammonium salt of them in a silver halide photographic emulsion layer containing as a colored coupler, a pyrazolone or a derivative thereof in which the 4th position is substituted with —N=N—R group (where R represents a substituted or unsubstituted aryl group or a heterocyclic residual group).

That is, in accordance with the process of this invention, the formation of fogging at development with a p-phenylenediamine derivative as the color developing agent is prevented effectively by incorporating in a silver halide photographic emulsion layer contaiinng as a colored coupler a compound shown by the following general formula



(I)

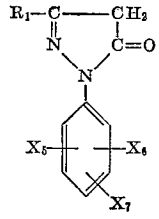
(wherein R_1 represents an alkyl group, a substituted alkyl group, an acylamino group, an N-arylamino group, an N-substituted arylamino group, or a sulfonamido group; R_2 represents a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, or a heterocyclic residual group; and X_1, X_2, and X_3 each represents a hydrogen atom, an alkyl group, a halogen atom, a substituted alkyl group, acylamino group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group, a sulfoamide group, an alkoxy group, an aryloxy group, a sulfonic acid group, or a carboxyl group), or an alkali metal salt or an ammonium salt of the compound, and containing as a colorless coupler, a compound having the general formula



(II)

(wherein R_1, X_1 and X_2 have the same significance as in the above-mentioned formula (I) and X_4 represents a sulfonic acid group or a carboxyl group) or an alkali metal salt or an ammonia salt thereof.

Further, in the process of this invention, a colorless coupler having the following general formula



(III)

wherein R_1 has the same significance as in the above-mentioned formula (I), and X_5, X_6 and X_7 each represents a hydrogen atom, a halogen atom, an alkyl group, a substituted alkyl group, an acylamino group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group, a sulfoamide group, an alkoxy group or an aryloxy group may be used as a masking controlling agent in combination with the above-mentioned colored coupler of general formula (I) and the colorless coupler of the general formula (II) for anti-fogging.

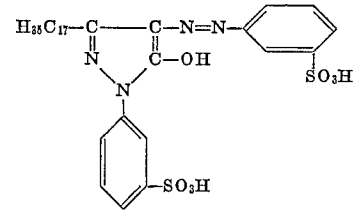
The main structural feature of the coupler (II) for anti-fogging is that the 1st position of the pyrazolone is substituted with a phenyl nucleus having the directly substituted water-solubilizable group X_4. The coupling rate of the colorless coupler shown by the general formula (II) with the oxidation product of a p-phenylenediamine derivative is very much higher than that of the coupler (I) or coupler (III). Therefore, in the case where the three couplers (I), (II), and (III) are present together, the coupler of the type of formula (II) can be coupled with the oxidation product of the p-phenylenediamine derivative more predominantly than the couplers (I) and (III). Further, since the coupling rate of the colored coupler (I) with the oxidation product is almost the same as that of the colorless coupler (III), masking can be controlled suitably.

The colorless coupler (II) cannot be used for controlling masking since in this case coupling of the colorless coupler (II) occurs predominantly, which cannot control the masking or gives partial masking only. However, there occurs no fog formation by the colored coupler (I). When a small amount of the colorless coupler (II) is added with the colored coupler (I) or a small amount of the colorless coupler (II) is added with the colored coupler (I) and a suitable amount of the colorless coupler (III), the small amount of the colorless coupler (II) is first consumed by color development and then coupling of the couplers (I) and (III) occurs. Therefore, if the coupler (II) is added in a suitable amount necessary for preventing color fogging that is determined by the silver halide emulsion to be used and the developing conditions to be adopted, the fog formation can be prevented without giving substantially any effect on masking. The suitable amount of the colorless coupler (II) for anti-fogging is about 4–50% by weight based on the amount of the colored coupler (I).

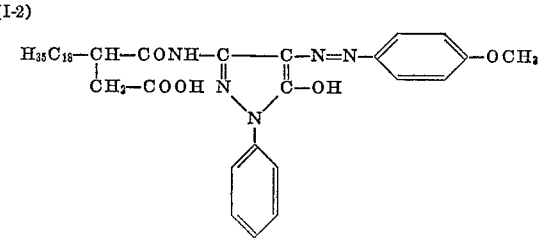
The colored couplers (I) can be prepared by the same methods described in U.S. Patents 2,455,170, 2,983,608 and 3,005,712.

The typical examples of the colored coupler (I) that can be generally used in this invention are as follows:

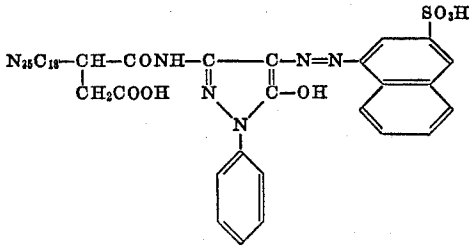
(I-1)



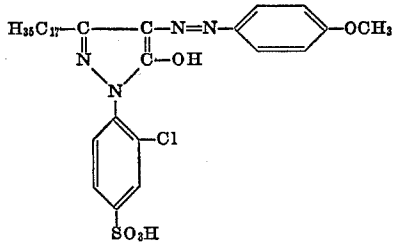
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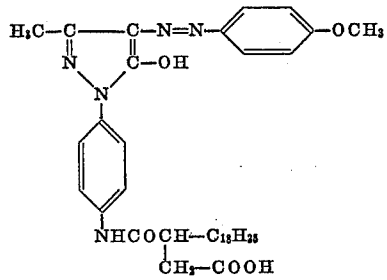
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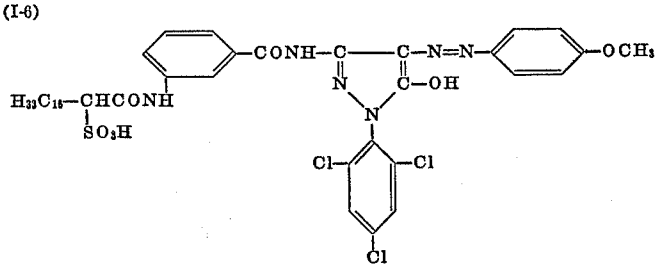
(I-4)



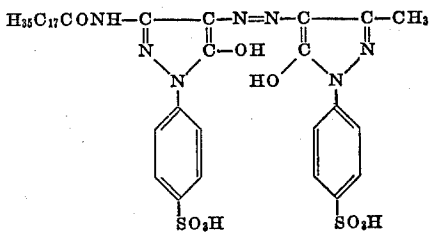
(I-5)



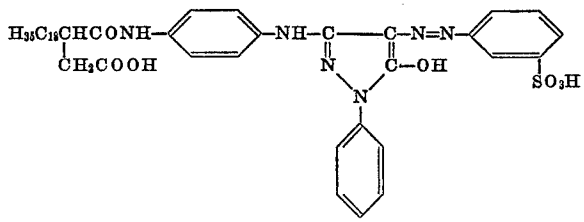
(I-6)



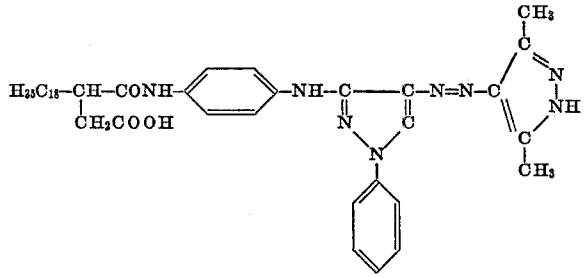
(I-7)



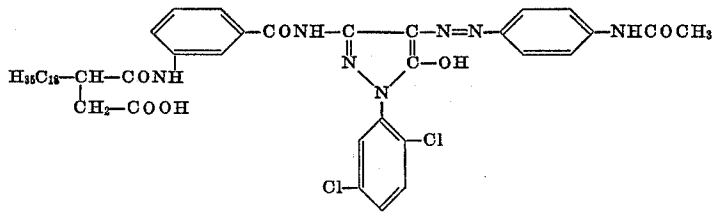
(I-8)



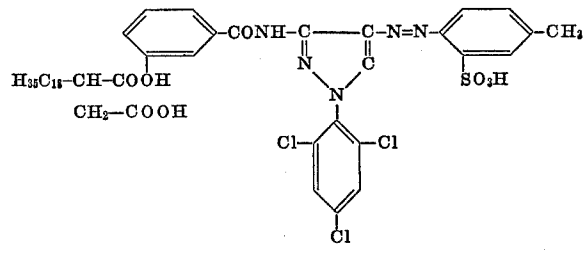
(I-9)



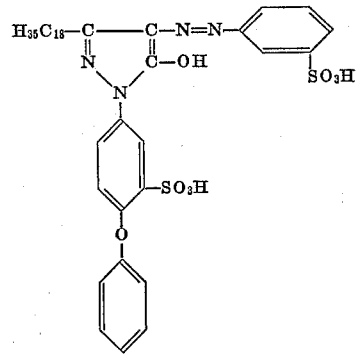
(I-10)



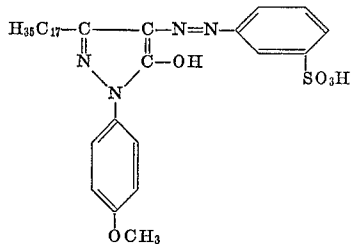
(I-11)



(I-12)

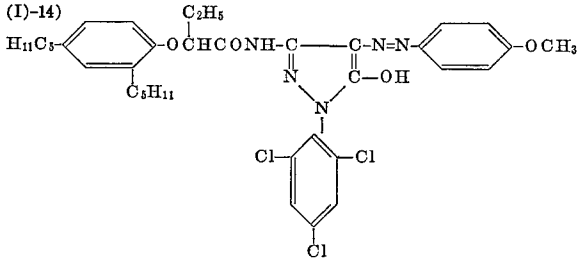


(I-13)



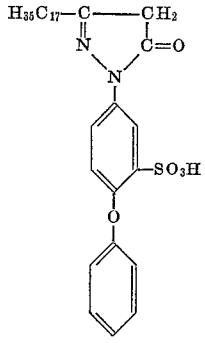
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(I)-14)

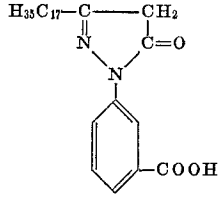


The typical examples of the colorless coupler (II) for anti-fogging that can be generally used in this invention are as follows;

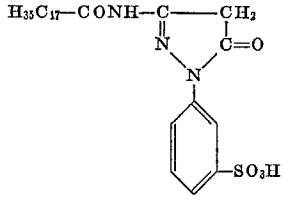
(II-1)



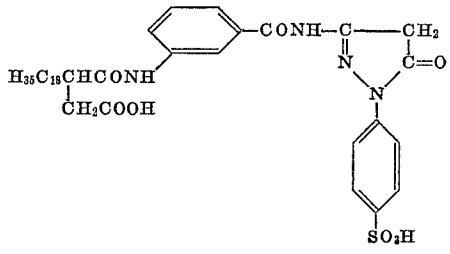
(II-2)



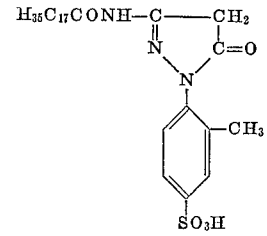
(II-3)



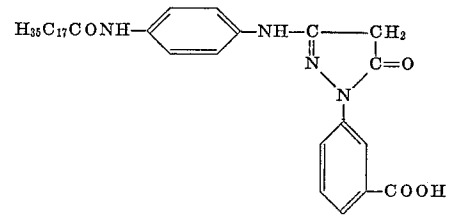
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(II-5)

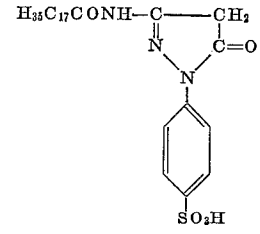


(II-6)



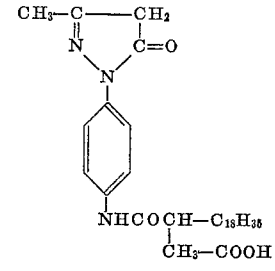
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(II-7)

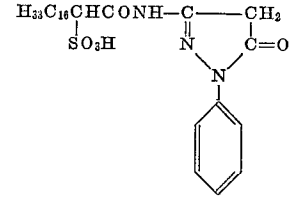


The typical examples of the colorless coupler (III) for masking control that can be generally used in this invention are as follows;

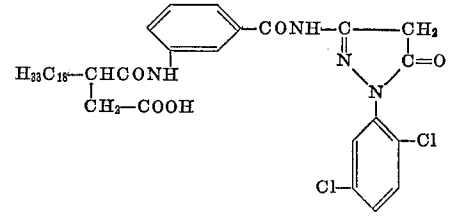
(III-1)



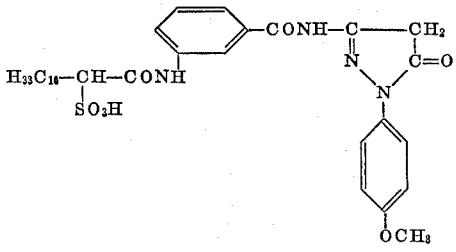
(III-2)



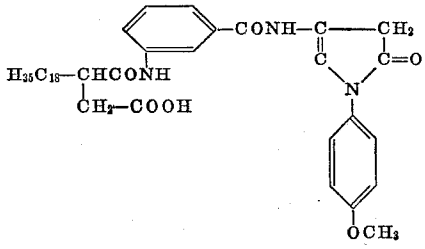
(III-3)



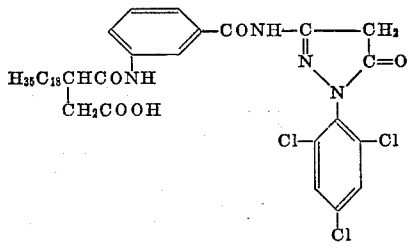
(III-4)



(III-5)

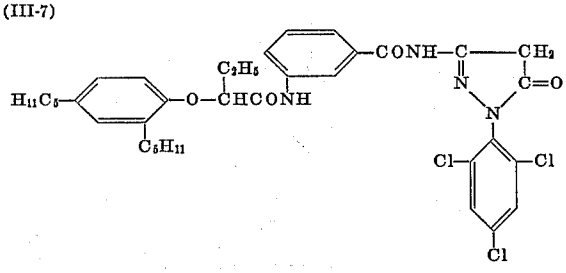


(III-6)



and

(III-7)



The invention will be further illustrated by the following examples in which the term "part" means "part by weight."

Example 1

A color sensitizing agent for giving green sensitivity was added 100 parts of a silver iodobromide photographic emulsion prepared by a conventional method. The emulsion was then added with 20 parts of a 5% alkaline aqueous solution of colored coupler (I) and 3 parts of a 5% alkaline aqueous solution of colorless coupler (II) for anti-fogging and coated onto a substratum-coated film base. Thus obtained film sample was processed for 10–15 minutes at 20° C. in a developing solution using as the color developing agent N,N - diethyl - p - aminoaniline and then subjected to bleaching and fixing. The processed sample measurement is taken as the green-light density of color fog, the results being as follows:

TABLE 1

	Colorless coupler (II)	Color fog density 10 minutes	Color fog density 15 minutes [1]
Colored coupler (I):			
I-6	None	0.44	0.88
I-6	II-1	0.15	0.21
I-6	II-2	0.11	0.14
I-6	II-3	0.14	0.21
I-6	II-4	0.20	0.29
I-1	None	0.24	0.38
I-1	II-1	0.12	0.14
I-1	II-2	0.10	0.14
I-1	II-5	0.14	0.20
I-1	II-6	0.08	0.11
I-1	II-7	0.13	0.15
I-2	None	0.38	0.65
I-2	II-1	0.16	0.24
I-3	None	0.30	0.44
I-3	II-1	0.14	0.21
I-4	None	0.27	0.40
I-4	II-1	0.09	0.14
I-5	None	0.39	0.77
I-5	II-1	0.16	0.26
I-7	None	0.20	0.31
I-7	II-1	0.11	0.14
I-8	None	0.35	0.56
I-8	II-1	0.14	0.19
I-9	None	0.41	0.74
I-9	II-1	0.17	0.25
I-10	None	0.33	0.51
I-10	II-1	0.12	0.18
I-11	None	0.22	0.34
I-11	II-1	0.10	0.14

[1] Developing time.

Example 2

Five grams (5 g.) of colored coupler (I–14) was dissolved in 10 g. of dibutyl phthalate and the solution was dispersed in 100 g. of a 10% aqueous gelatin solution together with a dispersing agent. Example 1 was repeated with the exception that 23 parts of thus obtained dispersion was used instead of 20 parts of the 5% alkaline aqueous solution of colored coupler (I). The results of the fog density obtained by color development are shown in the following table.

TABLE 2

	Colorless coupler (II)	Color fog density 10 minutes	Color fog density 15 minutes
Colored coupler (I):			
I-14	None	0.28	0.43
I-14	II-1	0.12	0.16
I-14	II-3	0.11	0.17
I-14	II-4	0.15	0.22

Example 3

A color sensitizer for giving green sensitivity was added in 100 parts of a silver iodobromide photographic emulsion prepared by a conventional method, the emulsion was added with 10 parts of a 5% alkaline aqueous solution of colored coupler (I), 15 parts of 5% alkaline aqueous solution of colorless coupler (III) for masking control, and 2 parts of a 5% alkaline solution of colorless coupler (II) for anti-fogging, and coated onto a substratum-coated film base followed by drying. The film sample was color-developed as in Example 1 and the color fog density of the unexposed portions was detected. The results are shown in Table 3.

TABLE 3

	Colorless coupler (II)	Colorless coupler (III)	Color fog density (10 min. develop.)
Colored coupler (I):			
I-2	None	III-5	0.34
I-2	II-1	III-5	0.15
I-9	None	III-2	0.48
I-9	II-1	III-2	0.27
I-9	II-2	III-2	0.16
I-6	None	III-3	0.28
I-6	II-2	III-3	0.14

Example 4

Into 10 g. of dibutyl phthalate were dissolved 1.0 g. of colored coupler (I) and 2.0 g. of colorless coupler

(III) for masking control, and the solution was dispersed in 100 g. of a 10% aqueous gelatin solution together with a dispersing assistance. Example 3 was repeated with the exception that 30 parts of the dispersion was used instead of the alkaline aqueous solution of colored coupler (I) and colorless coupler (III). The procedure was also repeated by using the dispersion added with 2 parts of a 5% alkaline aqueous solution of colorless coupler (II) for anti-fogging. When the samples were color-developed as in Example 1, the fog density of the unexposed portion was as follows:

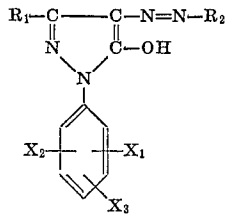
TABLE 4

	Colorless coupler (II)	Colorless coupler (III)	Color fog density (10 min. dev.)
Colored coupler (I):			
I-14	None	III-7	0.28
I-14	II-1	III-7	0.12
I-14	II-2	III-7	0.09

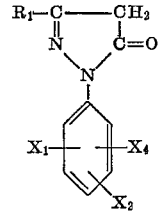
As shown the above examples, by carrying out the color development of a silver halide photographic emulsion layer containing colored coupler (I) while incorporating in the emulsion layer colorless coupler (II), the formation of color fog can be remarkably prevented.

What is claimed is:

1. A silver halide photographic emulsion layer adapted to be color developed with a p-phenylenediamine derivative, comprising a colored coupler represented by the general formula (I)



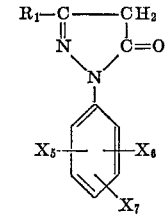
wherein R_1 represents a member selected from the group consisting of an alkyl group, an acylamino group, an N-arylamino group and a sulfonamido group; R_2 represents a member selected from the group consisting of a phenyl group, an alkyl-substituted phenyl group, an acylamino-substituted phenyl group, an alkoxy-substituted phenyl group, a sulfo-substituted phenyl group, a naphthyl group, an alkyl-substituted naphtyl group, an acylamino-substituted naphthyl group, an alkoxy-substituted naphthyl group, a sulfo-substituted naphthyl group and a alkyl-substituted pyrazolyl group; and X_1, X_2 and X_3 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a halogen atom, an acylamino group, an alkylcarbamoyl group, a sulfonamido group, an alkoxy group, an aryloxy group, a sulfonic acid group, an alkali metal salt of said sulfonic acid group, an ammonium salt of said sulfonic acid group, a carboxyl group, an alkali metal salt of said carboxyl group and an ammonium salt of said carboxyl group, and a colorless coupler represented by the general formula (II)



wherein R_1, X_1 and X_2 have the same significance as in the above mentioned formula (I) and X_4 represents a member selected from the group consisting of a sulfonic acid group, an alkali metal salt of said sulfonic acid group, an ammonium salt of said sulfonic acid group, a carboxyl group, an alkali metal salt of said carboxyl group and an ammonium salt of said carboxyl group.

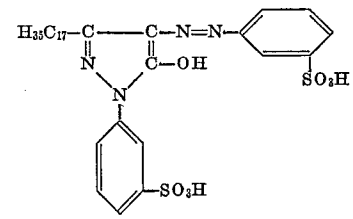
2. The emulsion layer according to claim **1** wherein the amount of said colorless coupler is about 4–50% by weight of the amount of said colored coupler.

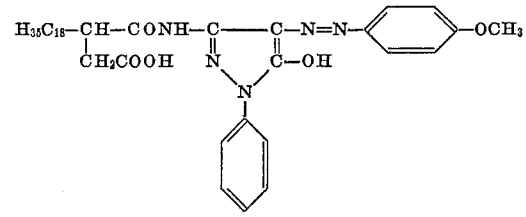
3. The emulsion according to claim **1** wherein silver halide photographic emulsion further contains a colorless coupler for masking control represented by the general formula (III)

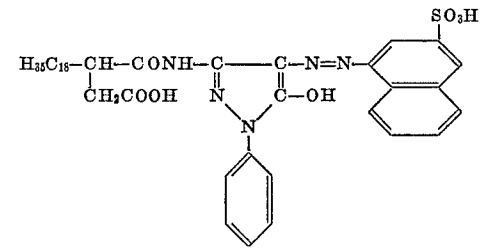


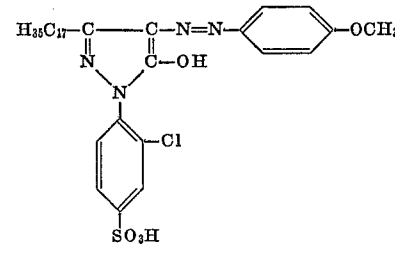
wherein R_1 has the same significance as in the formula (I) shown in claim **6** and X_5, X_6, and X_7 each represents a member selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group, an acylamino group, an alkylcarbamoyl group, a sulfonamido group, an alkoxy group, and an aryloxy group.

4. The emulsion layer according to claim **1** wherein the colored coupler of the formula (I) is a compound selected from the group consisting of:

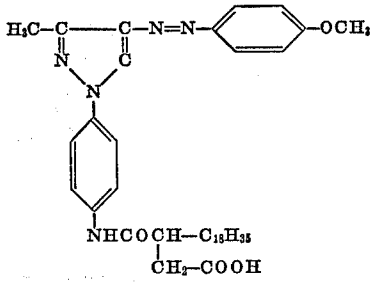


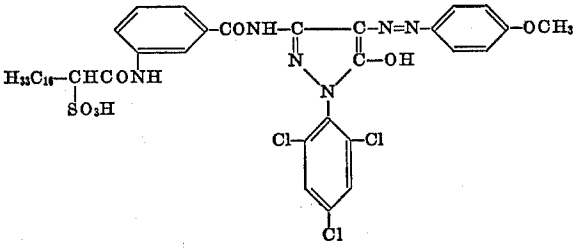


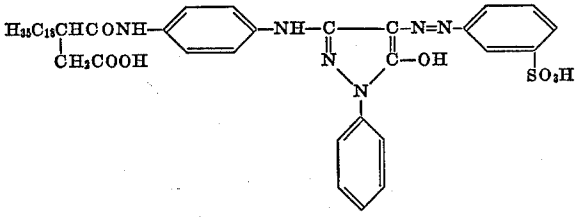


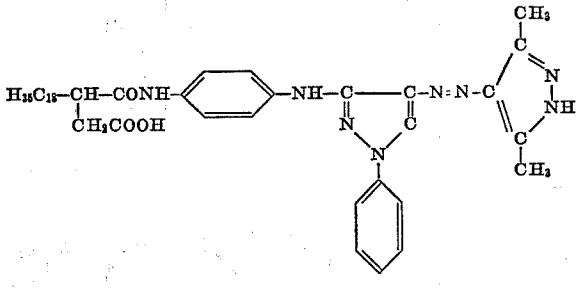


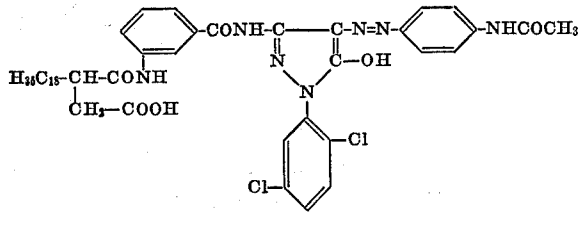
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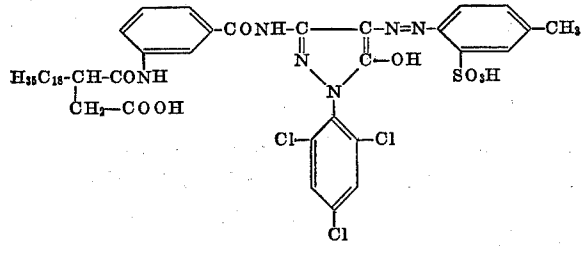




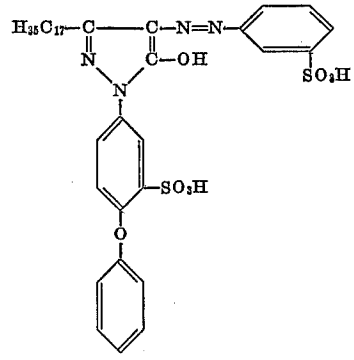


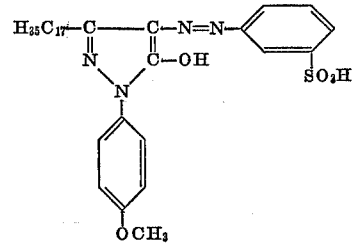




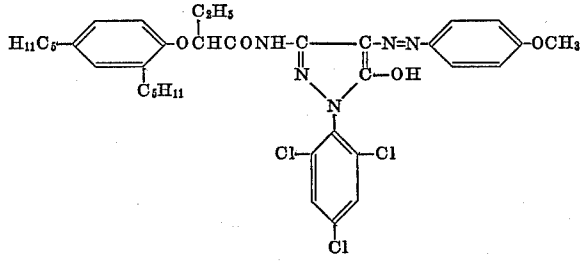


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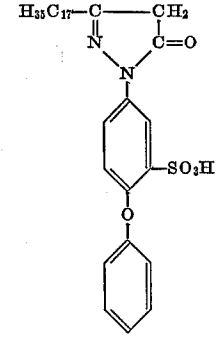


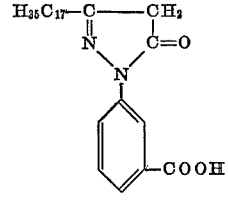


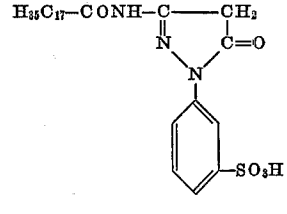
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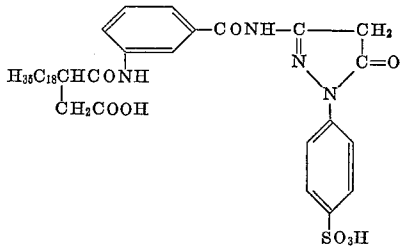
5. The emulsion layer according to claim **1** wherein the colorless coupler of the formula (II) is a compound selected from the group consisting of:

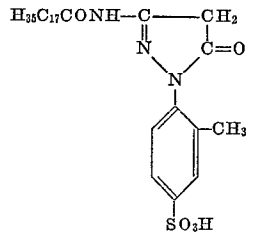


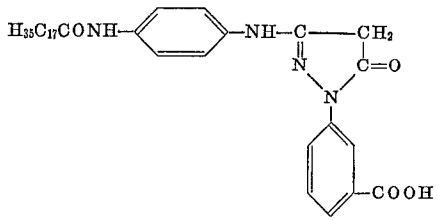




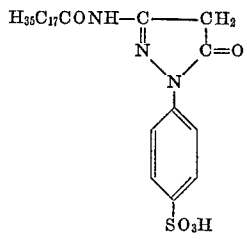
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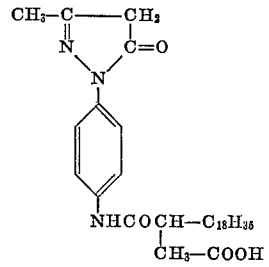


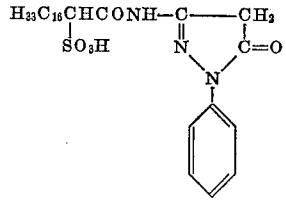


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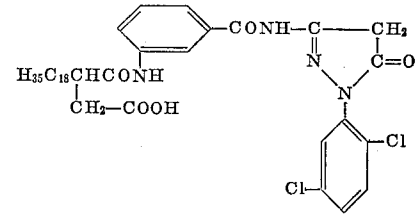


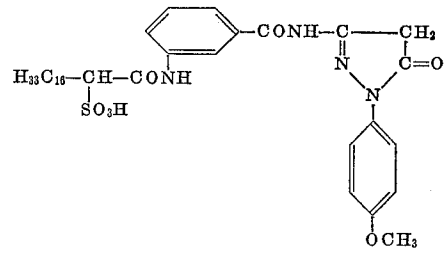
6. The emulsion layer according to claim 3 wherein the colorless coupler of the formula (III) is a compound selected from the group consisting of:

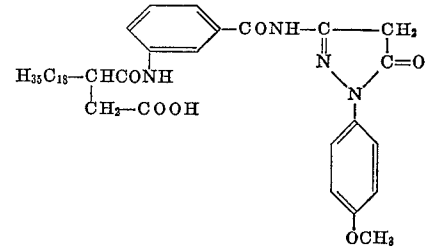


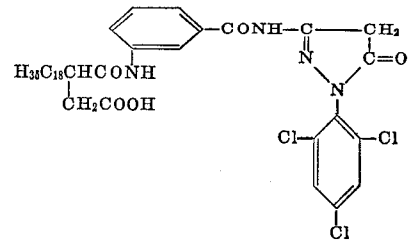


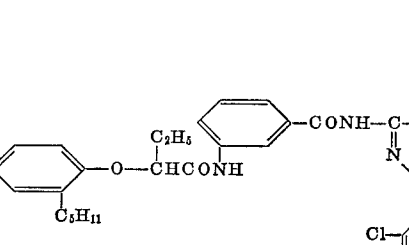
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U.S. Cl. X.R.

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