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COLOR PHOTOGRAPHIC SILVER HALIDE EMULSION

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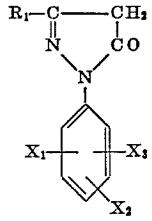
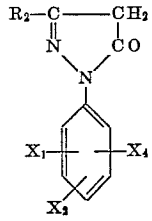
U.S. Cl. 96—100 3 Claims

ABSTRACT OF THE DISCLOSURE

A color photographic silver halide emulsion containing at least a color former having the general formula:



wherein R_1 represents a member selected from the class consisting of an alkyl group, a substituted alkyl group, an acylamino group and a sulfamido group and X_1, X_2 and X_3 each represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, an acylamino group, an alkylcarbamoyl group, a sulfamoyl group, a substituted sulfamoyl group, an alkoxy group, and an aryloxy group, and at least a member selected from the class consisting of a color former having the general formula:



wherein R_2 repersents a member selected from the class consisting of an alkyl group, a substituted alkyl group, an acylamino group, a sulfamido group, an amino group, and an arylamino group; X_1 and X_2 are the same as previously defined; and X_4 represents a member selected from the class consisting of a sulfonic acid group and a carboxyl group, alkali metal salts thereof, and an ammonium salt thereof.

This invention relates to a color photographic silver halide emulsion forming color images by coupling and particularly to a color photographic silver halide emulsion containing pyrazolone derivatives as color formers.

Many studies have been published about color photographic silver halide emulsions containing color formers and it has been known that in the development using a p-phenylenediamine derivative as a color developer, the developing speed is largely influenced by the properties of the color formers contained in the photographic emulsion to be treated.

When a light-sensitive material using a photographic silver halide emulsion which contains only a color former having a low color coupling rate is developed by using a p-phenylenediamine derivative as a color developer, a linear gradation can be easily obtained in general but the developing speed is reduced due to the low color-coupling rate and, therefore, a sufficient optical density cannot be obtained and the gradation tends to become soft. This tendency is particularly remarkable when the amount of the color former is small. In order to overcome such troubles, there have hitherto been proposed a method using increased amounts of a color former and a silver halide and a method using a photographic material having an emulsion of an increased thickness. However, there are drawbacks in the former method in that the viscosity of the emulsion is extremely increased or the setting point of the emulsion is lowered, as well as the emulsion is easily fogged. Further, in the former method, the amount of the color former in proportion to gelatin is increased and the selection of color former is limited in accordance with the compatibility of the color former with gelatin. On the other hand, in the latter method, there is a drawback that the sharpness of thus obtained image is reduced.

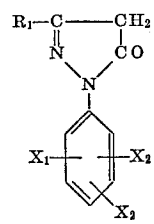
When a light-sensitive material using a photographic silver halide emulsion which contains only a color former having a high color coupling rate is developed by using a p-phenylenediamine derivative as a color developer, the development proceeds too much to obtain a linear gradation in contrast with the former case using a color former having a low color coupling rate.

An object of this invention is to provide a color photographic silver halide emulsion having no drawbacks as mentioned above.

Another object of this invention is to provide a color photographic element having the improved silver halide photographic emulsion layer containing specific color formers.

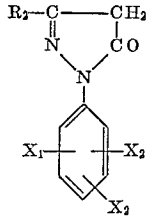
The above objects of this invention can be achieved by incorporating in a silver halide emulsion at least a color former shown below having a high coupling rate and at least a color former shown below having a low coupling rate.

According to the present invention, the color photographic silver halide emulsion contains therein at least a color former having the general formula:



(I)

wherein R_1 represents an alkyl group, a substituted alkyl group and acylamino group, or a sulfamido group, and X_1, X_2, and X_3 each represents a hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, an acylamino group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group, a sulfamido group, a sulfamoyl group, a substituted sulfamoyl group, an alkoxy group, or an aryloxy group; and at least a color former having the general formula



(II)

wherein R_2 represents an alkyl group, a substituted alkyl group, an acylamino group, a sulfamido group, or an arylamino group; X_1 and X_2 are the same as previously defined; and X_4 represents a sulfonic acid group or a carboxyl group. The compound shown by Formula II may by an alkali metal salt or an ammonium salt thereof.

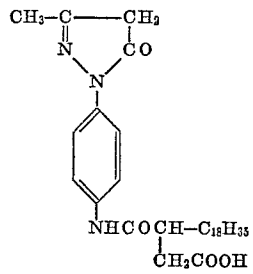
The structural feature of color former (II) is that water-solubilizing group X_4 is directly bonded to the phenyl nucleus having the pyrazolone ring at the 1-position.

The color coupling rate of the color former shown by general Formula II with the oxide of a p-phenylenediamine derivative is higher than that of color former (I). Accordingly, when color former (I) is present together with color former (II) in a photographic emulsion, the coupling of color former (II) with the oxide of a p-phenlyenediamine precedes that of color former (I). Therefore, when both color former (I) and color former (II) are present in a photographic emulsion, the development can be remarkably accelerated and an effective optical density can be obtained as compared with the case where only color former (I) is present. The present invention is particularly effective in case where a color photographic emulsion of a type containing a small proportion of color former (I) and the development proceeds slowly.

In accordance with the present invention, it is possible to use color formers that have not been used up to the present time because of their low color coupling speed in spite of their excellence in hue and color fastness. Further, it is possible to reduce the amount of color formers without lowering color forming density.

Examples of color former (I) used in this invention are as follows:

Example (1-1)



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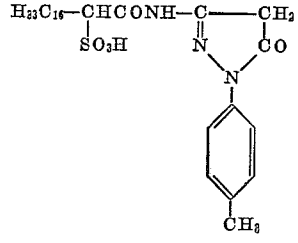
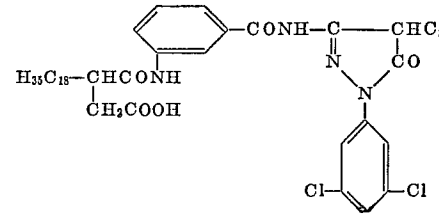


(1-3)



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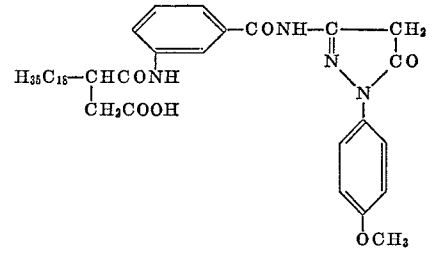

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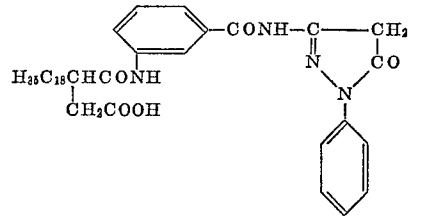

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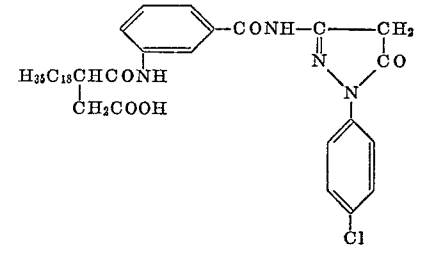

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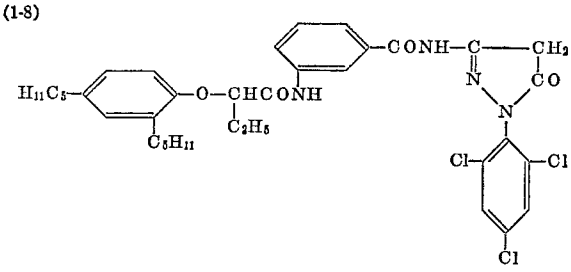

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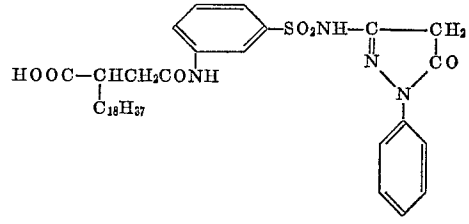

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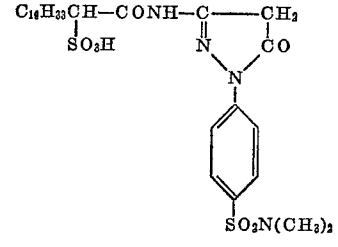

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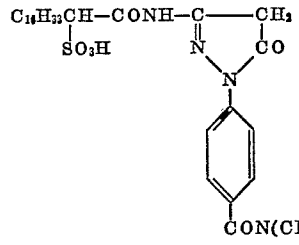
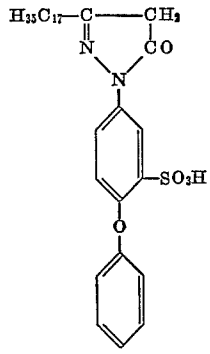


Examples of color former (II) used in this invention are as follows:

Example (2-1)



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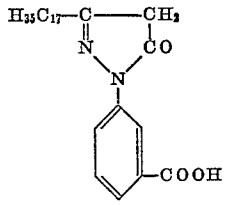
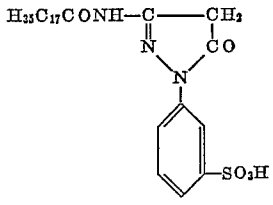


(2-3)



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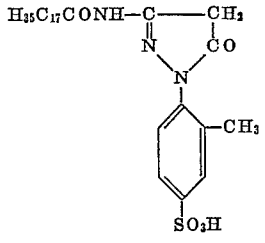

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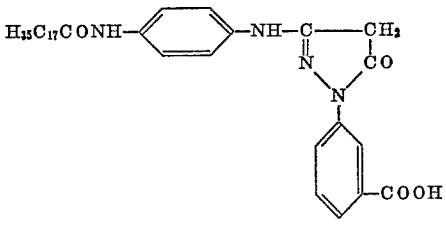

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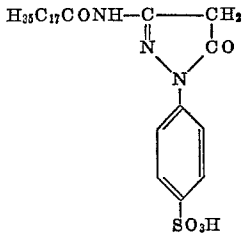

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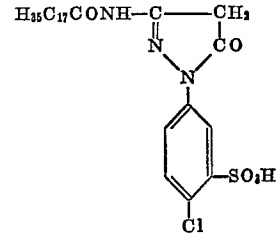

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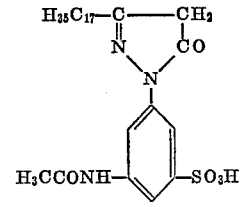

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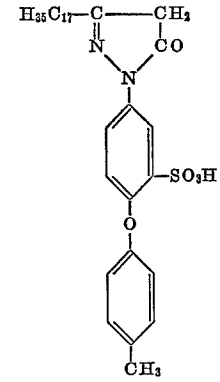


In the above examples are shown color former (I) or (II) as a form of an acid having a carboxyl group or a sulfonic acid group, but it may be an alkali metal salt or an ammonium salt. Color former (II) for increasing the density should be added in a proportion of 1–50% by weight of all the color formers, preferably, 6–20% by weight.

Silver halide incorporated in the emulsion in this invention may be silver bromide, silver iodide or mixed silver halide such as silver iodobromide, silver chlorobromide, etc.

This emulsion may be mixed with a chemical sensitizer, for example, a sulfur sensitizer, such as, allyl isothiocyanate, allylthiourea, sodium thiosulfate and potassium selenocyanide, and a reduction sensitizer such as imino-aminoethane-sulfinic acid, its derivatives and salts of noble metal such as gold, platinum and palladium, and a natural sensitizer present in gelatin.

Moreover, this emulsion may be mixed with optical sensitizer for imparting the green sensitive property, such as,

3-β-carboxyethyl-5,5'-diphenyl-9-ethyl-3'-β-sulfoethyl-oxacorbocyanine,

1,1'-diethyl-3,3'-di-sulfopropyl-5,5'-tetrachloroimidacarbocyanine and

3-carboxymethyl-5-((3-methyl-2(3)-thiazolinylidene) ethylidene)-rhodanine.

The emulsion may include the conventional additives, for example, a fog inhibitor or stabilizer (such as benzenesulfinic acid derivative and various azaindene compounds disclosed in British Patent 748,745), an anti-stain agent (such as hydroquinone derivatives disclosed in U.S. Patent 2,360,290 and U.S. Patent 2,701,197, and ascorbic acid ester disclosed in U.S. Patent 2,728,661), a development promoter (such as condensate of alkylene oxide disclosed in British Patent 592,676), a hardening agent (such as mucobromic acid, vinyl compounds disclosed in British Patent report 64,987 (8,403–8,407), ethyleneimino com-

pounds disclosed in Japanese Patent 37/8,790 and dichlorotriazine disclosed in Belgium Patent 641,044) and a coating aid (such as lauryl- or oleyl ether of polyethylene glycol, sulfated or alkylated polyethylene glycol and alkylbenzenesulfonic acid).

When two emulsion layers having optical sensitivities in the same zone are applied, the present invention may be adapted for either or both of the emulsion layers.

The following examples are given in order to illustrate the present invention, in which all parts and percent are to be taken by weight.

Example 1

An optical sensitizer for imparting the green sensitive property, 20 parts of 5% aqueous alkaline solution of the color former (I) (22 parts when color former (II) is not added) and 2 parts of 5% aqueous alkaline solution of color former (II) were added to 100 parts of a photographic silver bromoiodide emulsion prepared by the conventional manner and the resulting solution was applied to a subbed film. Then, the film thus obtained was treated with a developing solution containing N,N-diethyl-p-phenylenediamine as a color developer at 20° C. for 10 minutes and subjected to the bleaching and fixing step. The increase in the optical density was shown in Table 1 by the gamma values of the characteristic curve of green light:

TABLE 1

Color former (I)	Color former (II)	Gamma value
1-3	No	0.28
1-3	2-1	0.40
1-3	2-4	0.35
1-3	2-5	0.32
1-3	2-6	0.43
1-3	2-7	0.41
1-6	No	0.36
1-6	2-1	0.43
1-6	2-2	0.45
1-6	2-3	0.45
1-6	2-6	0.50
1-6	2-7	0.53
1-1	No	0.30
1-1	2-1	0.37
1-2	No	0.35
1-2	2-1	0.38
1-4	No	0.28
1-4	2-1	0.35
1-5	No	0.26
1-5	2-1	0.31
1-7	No	0.24
1-7	2-7	0.38

Example 2

27 parts of a 5% aqueous alkaline solution of color former (1-7) or 12 parts of the same and 0-12 parts of a 5% aqueous alkaline solution of color former (2-1) were added to the emulsion as in Example 1. The resulting solution was applied to a film and treated similarly to Example 1 to give gamma values as shown in Table 2:

TABLE 2

Amount of (2-7) added	Amount of (2-1) added						
	No	0.3 part	0.8 part	2 part	3 part	6 part	12 part
27 parts	0.35	0.40	0.44	0.49	0.52	----	----
12 parts	0.20	0.25	0.30	0.34	0.37	0.46	0.64

Example 3

5 g. of the color former (1-8) in place of 20 parts of a 5% eqeous alkaline solution of color former (I) in Example 1 was dissolved in 10 g. of dibutyl phthalate and dispersed with a dispersion aid in 100 g. of 10% aqueous gelatin solution. 26 parts of the dispersion (29 parts when color former (II) is not added) and 2 parts of a 5% aqueous alkaline solution of color former (II) were mixed to prepare a coating solution. The solution was applied to a film and treated similarly to Example 1 to give gamma values as shown in Table 3:

TABLE 3

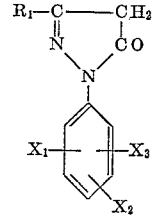
Color former (I)	Color former (II)	Gamma values
1-8	No	0.28
1-8	2-1	0.41
1-8	2-3	0.45
1-8	2-7	0.42

The above examples refers to only the case using one color former (I) and one color former (II) but the almost same results were obtained when more than one color former (I) and/or color former (II) were used, for example, when color former (1-6) was used together with color former (2-1) and color former (2-3).

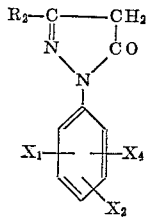
The invention was described about the specific examples in detail but it should be understood that the invention is not limited to the specific cases.

What is claimed is:

1. A color photographic silver halide emulsion containing at least one color former having the general Formula I:

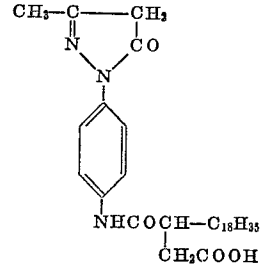


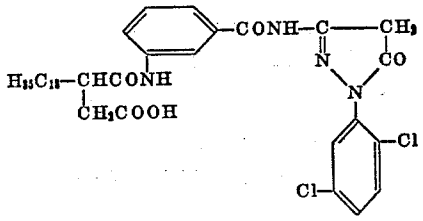
wherein R_1 represents a member selected from the class consisting of an alkyl group, a substituted alkyl group, an acylamino group containing an aryl radical, and a sulfamido group and X_1, X_2 and X_3 each represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, an acylamino group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group, a sulfamido group, a sulfamoyl group, a substituted sulfamoyl group, an alkoxy group, and at least one member selected from the class consisting of a color former having the general Formula II:

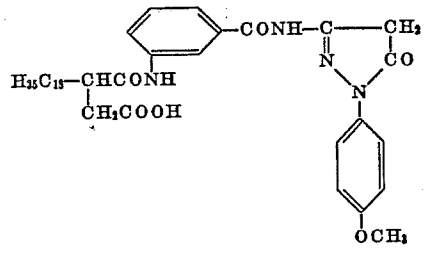


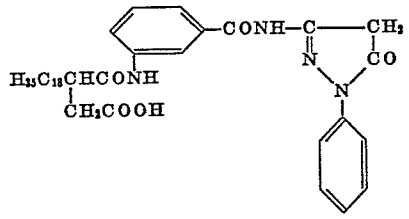
wherein R_2 represents a member selected from the class consisting of an alkyl group, a substituted alkyl group, an acylamino group, a sulfamido group, an amino group, and an arylamino group; X_1 and X_2 are the same as defined above; and X_4 represents a member selected from the class consisting of a sulfonic acid group and a carboxyl group, alkali metal salts thereof, and an ammonium salt thereof.

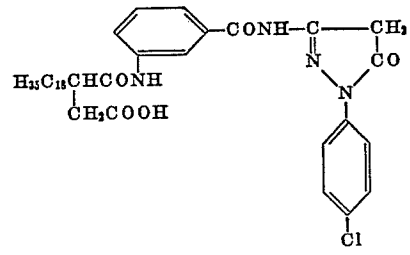
2. The emulsion according to claim **1**, wherein the color former of Formula I is a member selected from the group consisting of

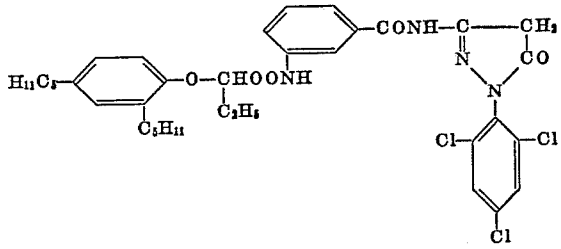


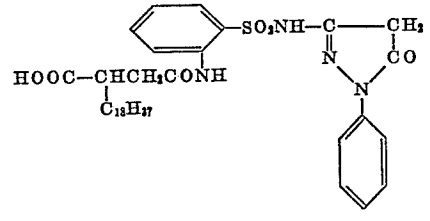




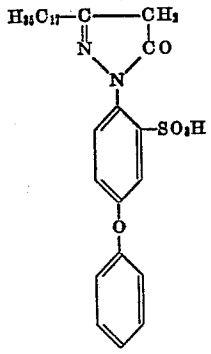


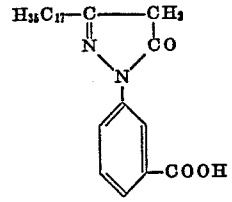


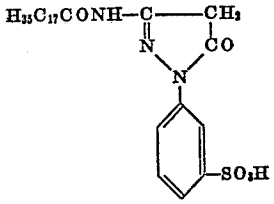


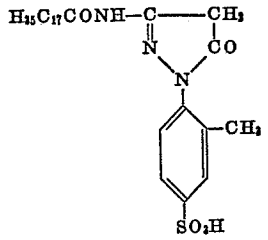


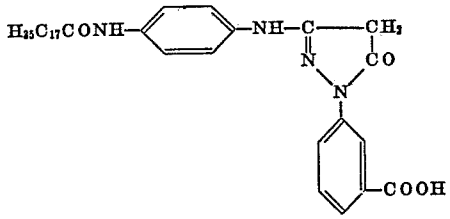
3. The emulsion according to claim 1, wherein the color former of Formula II is a member selected from the group consisting of

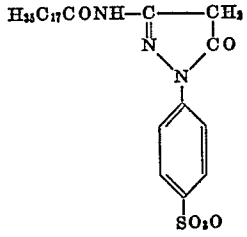


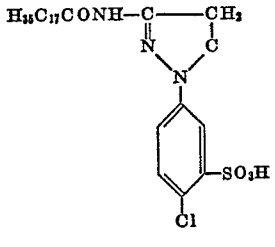


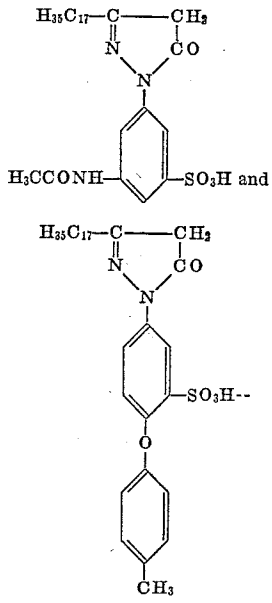












and

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U.S. Cl. X.R.

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