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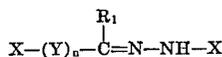
**SILVER HALIDE PHOTOGRAPHIC MATERIALS CONTAINING ORGANIC HYDRAZONE COMPOUNDS**

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 4 Claims. (Cl. 96—53)

**ABSTRACT OF THE DISCLOSURE**

The preparation of better color images with a relatively stable hydrazone, by improving contrast or color range or providing direct color images of good intensity. The hydrazones have the formula



where X is an organic group capable of mesomerism; Y is  $-C(R_2)_2-$  or  $-CR_2=CR_2-$ ;  $R_2$  is hydrogen, nitrile, alkyl or aryl; n is 1, 2 or 3;  $R_1$  is hydrogen, alkyl aryl, cyclohexyl, aralkyl, styryl or a heterocyclic radical; and X, Y and  $R_1$  can be combined to complete a heterocyclic ring. These hydrazones can be used with either a color developer or a black and white developer.

The invention relates to photographic materials which contain hydrazone compounds that couple with developer oxidation products.

The photographic use of organic compounds which react with oxidation products of developer compounds and which contain hydrazone groupings, is known per se. For example, German patent specification 1,083,125 describes dihydrazones of  $\alpha,\beta$ -dicarbonyl compounds for the production of direct positive images. These dihydrazones are practically colorless. At the exposed areas they form on color photographic processing colorless reaction products. They react with the oxidizing bath applied for bleaching out the silver image at the unexposed areas to form an orange-yellow compound. Thus, it is possible to produce colored direct positive images which are, however, of limited utility since the dyes produced by that process are only weakly colored. The color of those images suffices only for the production of color masks. A process for the production of colored direct positive images according to the principle described in the aforementioned German patent would per se be extremely advantageous in comparison with the known direct-positive processes. Such a process would be superior to the known reversal process because the processing would be much simpler; the second exposure and the second development would then be superfluous.

Another direct positive process is the so-called silver dye bleaching process. Layers which are colored with azo dyes are used for this purpose. Because of their absorption of light, the sensitivity of those layers does not meet practical requirements.

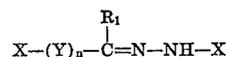
British Patent No. 590,637 also describes cyan acetyl color couplers which are substituted with a monohydrazone grouping and which react in known manner with oxidised color forming developers to form a dyestuff.

It is among the objects of the present invention to provide a photographic material for the production of direct positive color images, which material contains organic hydrazone compounds capable of reacting with the oxidation products of a photographic developer to form

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a colorless reaction product. A further object of the present invention is to provide photographic materials which contain usual color couplers which react with the oxidation product of color forming developers to form a dye, and which in addition contain an organic hydrazone compound which reacts with the oxidation product of the photographic developer to form a colorless compound, thus improving the quality of the resulting color image. Other objects and advantages of the photographic material, some of which are referred to specifically hereafter, will be known to those skilled in the art to which this invention pertains.

The objects have been attained by providing organic hydrazone compounds which react with the oxidation products of photographic developers to form colorless compounds. The properties of the hydrazone compounds of the present invention permit them to be widely used in color photographic materials. The organic hydrazone compounds have the following formula



wherein

X represents organic groups capable of mesomerism, e.g., aryl groups, preferably phenyl or naphthyl or aromatic heterocyclic radicals, such as furyl, furylidenyl, indolyl, pyridyl, thienyl, thiazolyl, benzthiazolyl, imidazolyl, oxazolyl, benzimidazolyl, benzoxazolyl, pyrazolyl or quinazolyl. These groups, particularly the phenyl or naphthyl, can in turn be substituted, for example with halogen, such as fluorine, chlorine or bromine, preferably chlorine; sulfo groups; alkyl radicals having up to 18 carbon atoms, preferably 5 carbon atoms; hydroxy groups; alkoxy groups the alkyl radical of which having up to 18 carbon atoms, preferably 5 carbon atoms; aryl groups, preferably phenyl; amino groups which can be substituted with alkyl having up to 18 carbon atoms or phenyl.

Y stands for the groupings  $-C(R_2)_2-$  or



in which

$R_2$  represents hydrogen, nitril, alkyl preferably methyl, ethyl or propyl, and aryl preferably phenyl.

n represents 0, 1, 2, or 3.

$R_1$  stands for hydrogen, alkyl preferably alkyl having up to 5 carbon atoms, aryl preferably phenyl, cyclohexyl, aralkyl preferably phenylalkyl such as benzyl, phenyl ethyl or styryl, or heterocyclic radicals such as furyl, furylidenyl, indolyl, pyridyl, thienyl, thiazolyl, benzthiazolyl, imidazolyl, oxazolyl, benzimidazolyl, benzoxazolyl, pyrazolyl or quinazolyl. The radicals and particularly the phenyl group can be substituted by halogen, such as fluorine, chlorine or bromine preferably chlorine, sulfo groups, alkyl radicals having up to 18 carbon atoms, preferably 5 carbon atoms, hydroxy groups, alkoxy groups the alkyl radical of which having up to 18 carbon atoms, preferably 5 carbon atoms, aryl groups preferably phenyl, amino groups which can be substituted with alkyl having up to 18 carbon atoms or phenyl; and

X, Y and  $R_1$  can be combined to represent the ring members necessary for completing a heterocyclic ring, such as those derived from quinolon, imidazolone, benzimidazolone, thiazolon, benzthiazolon, oxazolidon, or a carbocyclic ring for example a ring derived from cyclohexenone.

The compounds according to the invention can be classified into three groups, in accordance with their properties and the properties of their reaction products with the oxidation products of the developer or the oxidizing agent of the bleaching bath.

## 1.—COMPOUNDS OF GROUP 1

These hydrazones are yellow and stable with respect to oxidizing agents which are commonly used in color photographic processes. At the exposed areas, these substances react during the photographic processing to give colorless reaction products. A direct positive color image is obtained.

## 2.—COMPOUNDS OF GROUP 2

These hydrazones are almost colorless or at most pale yellow and react at the exposed areas with the oxidation products of a photographic developer to form colorless reaction products. In contrast to the compounds of Groups 1 and 3, they are, however, converted into dyes upon reaction with the oxidizing agent of an oxidizing bath, as commonly used in color photographic processes.

The hydrazones according to the invention have the outstanding advantage that depending on their chemical structure they yield dyes having different colors. Thus, it is possible to produce in a very simple manner not only direct positive yellow images, but also direct positive magenta and cyan images.

By utilizing the hydrazones of the present invention it is possible for the first time to produce a direct positive subtractive image in extremely simple manner.

To this end the photographic material includes at least three layers individually containing the colorless or almost colorless hydrazones of Group 2 which form yellow, magenta and cyan partial images.

## 3.—COMPOUNDS OF GROUP 3

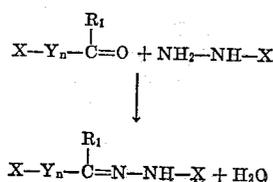
These hydrazones are colorless and also remain colorless after the photographic processing. It can, however, be concluded from their behaviour in the development step that they react with oxidized color developers to give colorless coupling products.

Because of their properties, the compounds of the present invention are of photographic interest in many respects. The compounds of Group 1 can, for example, be used for the production of integral masking images in color photographic materials or, in the same way as the compound of Group 2, for the production of colored direct positive images. They are less suitable for this purpose, however, than the compounds of Group 2, since their inherent color reduces their color sensitivity. The compounds of Group 3, which remain colorless throughout the entire processing, can be used for the prevention of color fogging and for better color separation as so-called white or colorless couplers. They correspond in function to the compounds described in British Patents Nos. 861,138 or 914,145.

A further advantage of the compounds of the invention is that they are substantially independent of the nature of the developer. Direct positive images are produced not only with conventional color forming primary aromatic amino developers such as N,N-diethylphenylene diamine, but also with black-and-white developers, e.g., p-methylaminophenol, p-aminophenol, hydroquinone or 1-phenylpyrazolidone-3.

## Preparation of the hydrazones

The compounds of the present invention can be prepared by reacting a carbonyl compound of the desired constitution with an aryl or heterocyclic hydrazine in weakly acid medium according to the following schematic equation:



The radicals X, Y and R<sub>1</sub> have the meaning as defined hereinbefore.

The preparation is described in the following in detail, by reference to some typical compounds.

## Preparation of Compound 1

5	4,4'-dihydrazinostilbene-2,2'-disulphonic acid	G.
	and	
10	Sodium acetate	2
	are dissolved in	

	Methanol	Cc.
	and	50
15	Water at boiling temperature	10

N-ethyl carbazole-3-aldehyde-6-sulphonic acid is added to the boiling solution, and this is boiled under reflux for 10 minutes. After cooling, the precipitated hydrazone is suction-filtered and dried.

## Preparation of Compound 8

	4,4'-dihydrazinostilbene-2,2'-disulphonic acid	G.
	and	4
25	Sodium acetate	10
	are dissolved in	

	Methanol	Cc.
	and	100
30	Water at boiling temperature	40

4 g. of N-ethyl-2-methylmercaptoquinolinium methyl sulphate are then added and the mixture is boiled for 2 hours. After cooling, the mixture is suction-filtered and the recovered solids dried.

## Preparation of Compound 10

	3-chloro-5-sulpho-6-hydroxy-phenylhydrazine	G.
	and	5
40	Sodium acetate	2
	are dissolved with heating in	Cc.
	Glacial acetic acid	80
	and	

45	Water	3
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6 g. of N-dodecyl-N-methyl-4-aminobenzaldehyde are added and the mixture is refluxed for 5 minutes. On cooling, the hydrazone crystallizes out. The precipitate is suction-filtered and dried.

In principle, all of the phenyl-hydrazones mentioned below can be prepared in accordance with the above methods.

The common photographic processing baths are suitable for the direct positive process according to the invention. Examples of some of the baths are set out below:

## Developer

## (A)

60	4-amino-N,N-diethylaniline	g--	2.5
	Anhydrous sodium sulphite	g--	1.0
	Potassium bromide	g--	1.0
	Potassium carbonate	g--	75.0
65	Water	liters--	1

## (B)

The 4-aminodiethylaniline of the solution specified in (A) is replaced by 5 g. of N-butyl-N-omega-sulfobutyl-p-phenylene diamine.

## (C)

The 4-aminodiethylaniline of the solution specified in (A) is replaced by 4 g. of 1-phenyl-4-aminopyrazolone-3-carboxylic acid amide.

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(D)

p-Methylaminophenol	-----g--	8.0
Anhydrous sodium sulphite	-----g--	2.0
Potassium carbonate	-----g--	50.0
Potassium bromide	-----g--	1.0
Water	-----liters--	1

(E)

1-phenyl pyrazolidon-3	-----g--	0.5
Hydroquinone	-----g--	4.0
Anhydrous sodium sulphite	-----g--	25.0
Anhydrous sodium carbonate	-----g--	25.0
Potassium bromide	-----g--	1.0
Water	-----liters--	1

Suitable are also p-aminophenol developers, for example, the developer Agfa 10 described in the book of Dr. Eduard Schloemann, published 1952 by Verlag "Photo-Blätter," Koeln-Thielenbruch. "Photochemikalien und ihre Anwendung."

## Oxidizing baths

The chemical structure of the oxidizing agent is not especially critical and is selected according to the properties of the monohydrazone compound with which the oxidizing agent is to be reacted. Preferred are those agents and baths which are commonly used in color photographic processes for bleaching silver images. Suitable agents are potassium ferricyanide, potassium bichromate or complex compounds of 3-valent iron or cobalt with aminopolycarboxylic acids such as ethylene diamine tetraacetic acid, nitrilo triacetic acid or the like, which are described, for example, in German Patent No. 866,605. Suitable baths are, for example, a 20% by weight aqueous solution of potassium ferricyanide or a 10% by weight aqueous solution of potassium bichromate.

It is also possible to apply combined bleach-fixing baths, such as described in Example 5 of German Patent No. 866,605.

## Fixing baths

Any desired photographic fixing baths can be used. The fixing agent, however, must not have reducing properties. Preferred are aqueous solutions of thiosulfate salts, e.g., sodium thiosulfate, potassium thiosulfate or ammonium thiosulfate. The fixing agents can be used as about 20% by weight aqueous solutions.

It might be advantageous in certain cases to rinse the photographic material between the different processing steps. After the final rinsing, drying can be performed by means of conventional dryers for photographic materials at slightly raised temperatures.

The hydrazones of the present invention are added to the light-sensitive halide emulsion layer in an amount of in between 5 and 50 g. per kg. of emulsion, preferably 10-30 g. They can be incorporated into the emulsion layer in a dissolvable diffusion resistant form. According to another method, the hydrazone couplers are first dissolved in an oily organic material, and this combination is dispersed in a finely divided state throughout the emulsion. The hydrazone compounds according to the invention can also be used in those processes in which the so-called "successive colorant formation" is applied. In this process the hydrazone is incorporated into the developer composition in an amount of between 5 and 40 g. per liter. The successive reaction with the oxidation product of the developer in each of single layers of the multi-layer material is obtained by controlled penetration of the processing solution. For example, in an integral tripack.

It is possible by means of such a solution to develop the top-layer of the material without affecting the lower emulsion layers if the time of development is carefully controlled.

The silver halide of the light-sensitive layer consists of silver chloride or silver bromide or mixtures thereof which may additionally contain a small amount of silver iodide

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of about up to 5 mol percent. The common hydrophilic layer-forming products can be used as binding agents for the silver halide emulsion layer, such as polyvinyl alcohol, polypyrrolidone, carboxymethylcellulose, starch, alginic acid and derivatives thereof such as salts, esters and amides, proteins such as albumin, casin or in particular gelatin. It is also possible to use a mixture of several binding agents.

The light-sensitive layer may further contain additives in accordance with special requirements, such as sensitizers or stabilizers. The silver halide emulsion can be optionally sensitized with the common methincyanine, rhodacyanine or merocyanine dyes. Furthermore it is possible to use silver halide emulsions which are chemically sensitized by sulfur compounds, complexes of noble metals, such as gold, palladium or iridium, or by polyethylene glycol or derivatives thereof.

## EXAMPLE 1

1.5 g. of Compound 1 are formed into a paste with 5 cc. of methanol and dissolved in 50 cc. of a 4% by weight sodium hydroxide solution. The solution is mixed with 100 cc. of a conventional silver halide gelatin emulsion which is then applied to a suitable support (e.g., a foil consisting of acetyl cellulose or polycarbonate or polyethylene terephthalate) to give a yellow layer. This layer is exposed to the object to be reproduced and developed in the previously described developer (A). After bleaching the image silver in a potassium ferricyanide bleaching bath and fixing, a direct positive yellow image is obtained. Similar results are obtained with Compounds 3 and 4.

## EXAMPLE 2

A light-sensitive silver halide gelatin emulsion layer is prepared as described in Example 1, using Compound 5. The resulting emulsion has an orange color. Development is performed with developer (B). The hydrazone reacts at the exposed areas with the oxidation product of the developer to form a colorless product. Thereafter the developed element is treated with the bleach and fixing bath as described in Example 1. An orange colored direct positive image is obtained. Similar direct positive images which are colored orange-yellow to orange-red can be produced by using compounds 7, 14, 15, 21, 22, 23, 24, 34, 35, 37, 38, 39, 40, 41, 43, 44, 45, 46, 48, 49 or 50 instead of Compound 5.

## EXAMPLE 3

1.5 g. of Compound 2 are added to a silver halide gelatin emulsion layer as indicated in Example 1. The silver halide of that emulsion consists essentially of silver bromide. The emulsion is cast on a cellulose acetobutyrate support and dried.

The material is exposed to an object to be reproduced and thereafter developer in developer (B). The original colorless layer contains only a negative silver image formed upon development since the hydrazone at the exposed areas reacts with the oxidation products of the developer to form a compound which is colorless. The exposed and developed element is treated with an aqueous potassium ferricyanide bleaching bath followed by a treatment with a fixing bath. Upon bleaching the negative image is converted into a colorless image of silver compounds and the hydrazone at the unexposed and undeveloped areas is oxidized to form a direct positive red image. The reaction products of the original hydrazones with the oxidation products of the developer at the exposed areas is stable against the oxidizing action of the bleaching bath and remains colorless.

Direct positive images of a similar color are obtained if Compound 31 is used instead of Compound 2.

Blue to blue-green direct positive images are obtained if Compounds 9, 10, 25, 26, 27, 28, 29, 42 or 47 are used instead of Compound 2.

Compounds 16, 17, 18, 19, 20, 30, 32, 33 or 36 yield yellow direct positive images.

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## EXAMPLE 4

A light-sensitive photographic element containing in a silver halide emulsion layer Compound 11, 12 or 13 is prepared as described in Example 1. The resulting photographic material which contains a yellow colored light-sensitive layer, is imagewise exposed, developed in developer (B) and bleached with a 10% aqueous sodium bichromate solution. A direct positive image is obtained having the yellow color of the original light-sensitive layer since the yellow hydrazone compounds at the exposed areas have reacted with the oxidation product of the developer to form a colorless product.

## EXAMPLE 5

The colorless compound 8 is processed according to Example 2, but bleaching is effected in a 10% potassium ferricyanide solution, the pH of which has been adjusted to 10 with 2 N-sodium carbonate solution. A direct positive image is obtained which is magenta in color.

## EXAMPLE 6

The procedure according to Example 1 is carried out with the colored Compound 6, but bleaching takes place in a combined bleaching and fixing bath according to German Patent No. 866,605. A direct positive red brown image is obtained.

## EXAMPLE 7

The procedure according to Example 1 is carried out with the colored Compounds 4, 18 and 19 but using developer (C) for the development. In this way, direct positive yellow images are obtained.

## EXAMPLE 8

A light-sensitive photographic material is prepared as described in Example 3 containing 2 g. of Compound 26 is imagewise exposed and developed in developer solution E. The bleaching is performed with aqueous potassium ferricyanide solution. A direct positive cyan image is obtained.

## EXAMPLE 9

A light-sensitive material is prepared as described in Example 1, the silver halide of which consists of silver bromide with a small content of silver iodide. Compounds 4, 18, 19 or 20 are used instead of Compound 1. The materials are exposed to the object to be reproduced and developed with a p-aminophenol developer of the type of the "Agfa 10 developer." Thereafter it is bleached in a potassium ferricyanide bleaching bath and fixed. Direct positive yellow images are obtained.

## EXAMPLE 10

The process according to Example 2 is carried out with Compound 26, but with development in the developer (D). A direct positive cyan image is obtained.

## EXAMPLE 11

A color photographic element is prepared as described in Example 3 with the exception that Compound 2 is replaced by one of the Compounds 51, 53 and 54.

The material is imagewise exposed and developed in developer (A). The bleaching is performed with a 10% aqueous sodium bichromate solution. The fixed material shows no colored image, but the exposed areas are slightly more opaque than the unexposed areas.

A similar result is obtained if developer (B) is used instead of developer (A).

Onto a sheet-like support of cellulose acetobutyrate are coated the following silver halide emulsion layers:

- (a) a silver halide emulsion layer the silver halide of which consists essentially of silver bromide. The emulsion contains per kg. 9 g. of the magenta coupler 1-(4-sulfophenyl)-3-palmityl-pyrazolone-(5) and 50 g. of silver halide,
- (b) an intermediate layer of gelatin which contains 9 g. of Compound 51 per kg. of the 5% aqueous gelatin solution,

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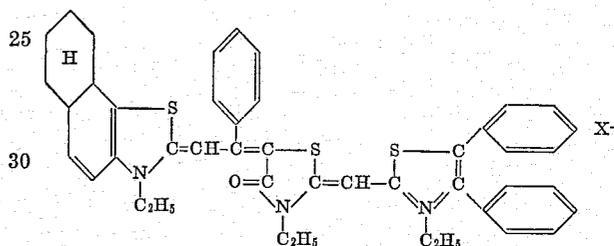
- (c) a silver halide gelatin emulsion layer the silver halide of which consists essentially of silver bromide. The emulsion contains per kg. 10 g. of the cyan coupler N-stearyl-4-sulfo-1-hydroxy-2-naphthoylanilide and 50 g. of silver halide.

The above material is imagewise exposed developed in developer bath (A), bleached in a 20% aqueous potassium ferricyanide solution and fixed in a 20% aqueous sodium thiosulfate solution. A photographic color image showing an excellent color separation is obtained. The excellent color separation is due to the presence of Compound 51 in the intermediate layer, which compound reacts with the oxidation products of the developer which are diffusing from layer (a) to layer (c) and vice versa and thereby prevent migration of images.

## EXAMPLE 12

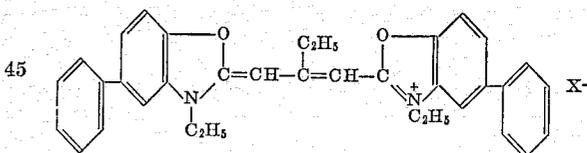
Onto a sheet-like support of cellulose acetate are coated the following silver halide gelatin emulsions in the sequence indicated below:

- (a) a red sensitive layer containing as sensitizing dye the rhodacyanine of the following formula:



and 10 g. of Compound 42 per kg. of emulsion the silver halide of the gelatin emulsion consisting essentially of silver bromide. Compound 42 yields after processing as described in Example 3 a direct positive cyan partial image.

- (b) an intermediate layer of gelatin,  
 (c) a green sensitive layer containing as a sensitizing dye the carbocyanine of the following formula:



and 9 g. of Compound 8 per kg. of emulsion, the silver halide of the gelatin emulsion consisting essentially of silver bromide. Compound 8 yields after processing as described in Example 3 a direct positive magenta partial image,

- (d) an intermediate layer consisting of gelatin,  
 (e) a blue sensitive layer which contains 10 g. of Compound 43 per kilogram of emulsion, the silver halide of this gelatin layer consisting essentially of silver bromide.

The blue sensitive layer acts simultaneously as a yellow filter layer since Compound 43 is originally yellow colored. On processing as described in Example 3, a yellow partial image is obtained.

The above described color photographic multilayer material is exposed to the object to be reproduced and developed in the following developer:

4-diethylamino-2-ethoxyaniline	g	2.5
Anhydrous sodium sulphite	g	1.0
Potassium bromide	g	1.0
Potassium carbonate	g	75.0
Water	liter	1

The developed material is bleached in a 10% aqueous sodium bichromate solution and fixed in a common fixing bath containing sodium thiosulfate.

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A subtractive direct positive color image of the original in true colors is obtained.

## EXAMPLE 13

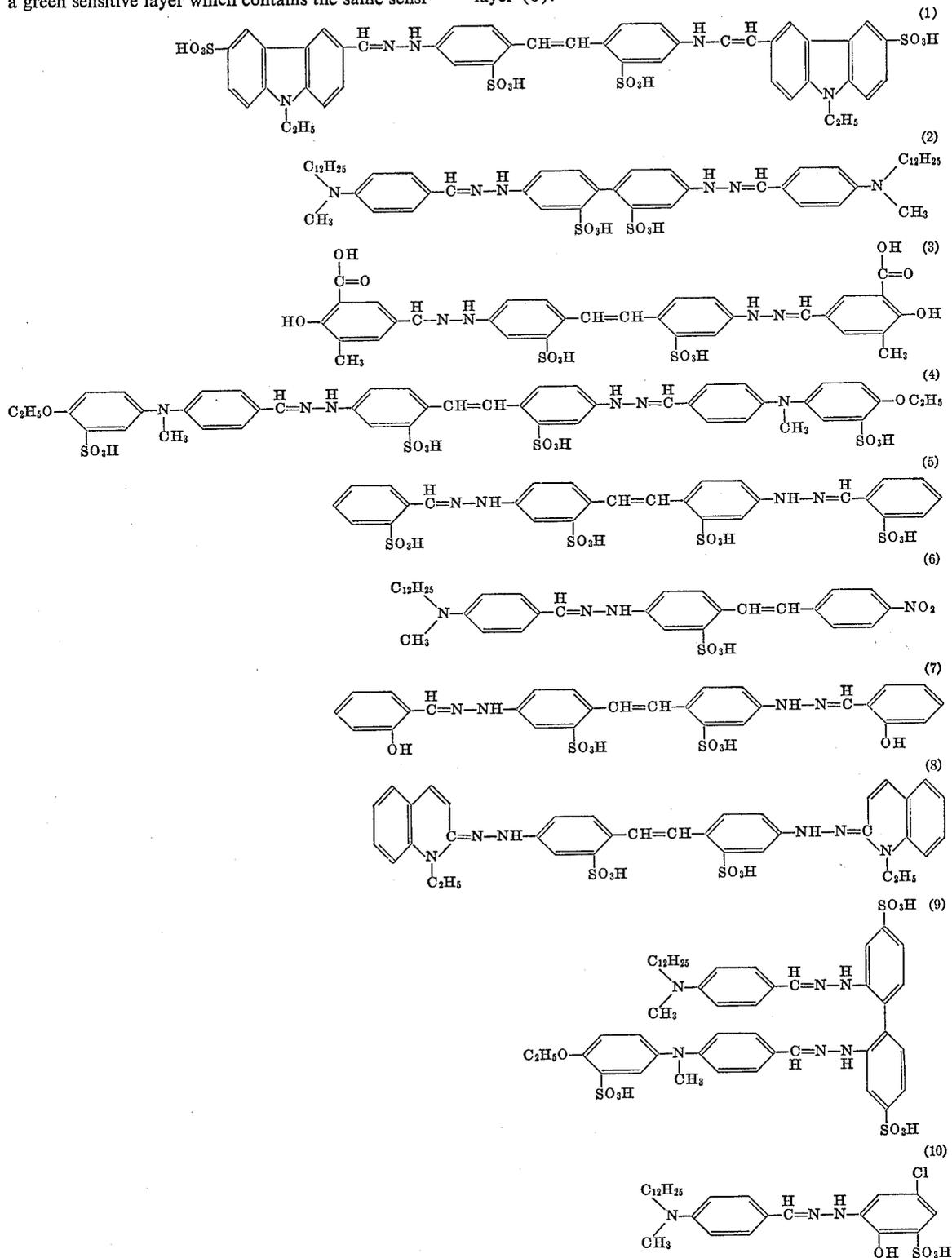
Onto a sheet-like support of polyethylene terephthalate are cast the following silver halide gelatin emulsion layers

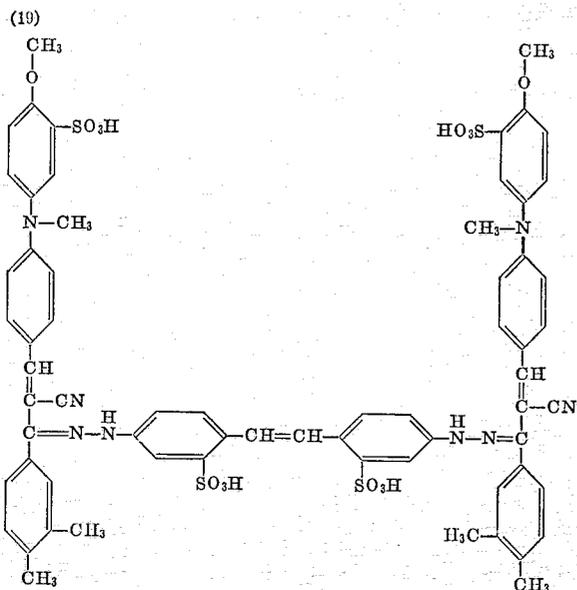
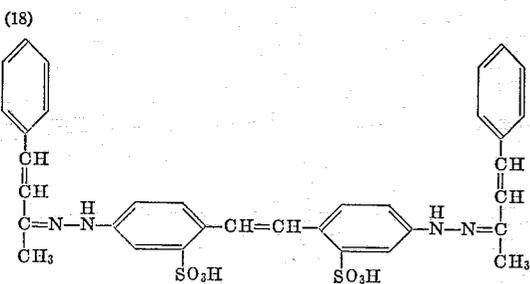
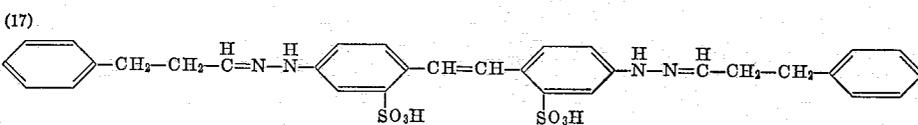
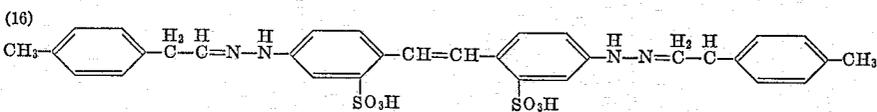
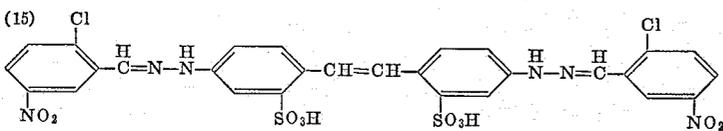
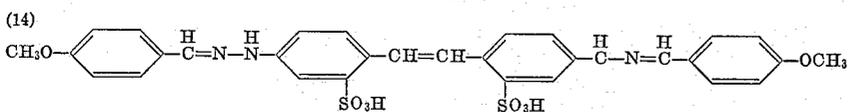
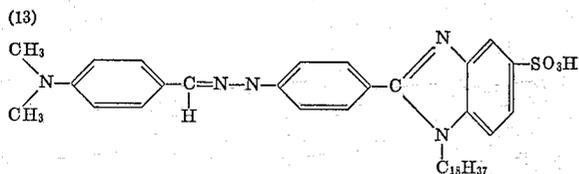
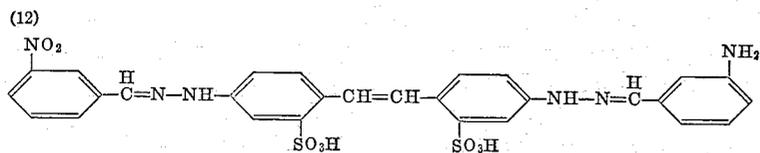
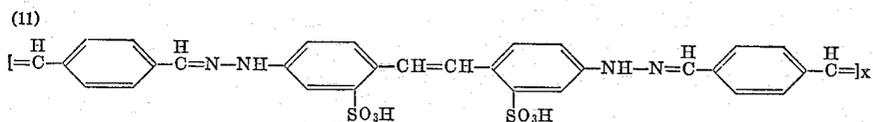
- (a) a green sensitive layer which contains the sensitizing dye of layer (c) of Example 12 and a magenta coupler 1-(4-sulfophenyl) - 3-palmitylpyrazolone-5, the silver halide of the layer consisting essentially of silver bromide,  
 (b) a green sensitive layer which contains the same sensi-

5 tizing dye and 8 g. of Compound 43 per kg. of the emulsion.

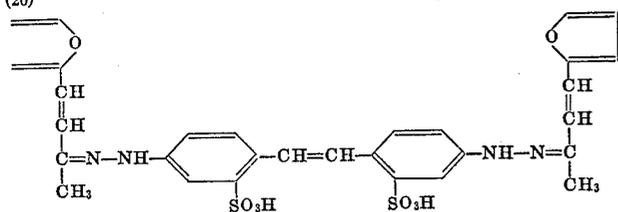
The above material is exposed, developed with developer bath (B) and bleached and fixed by using the common bleach and fixing baths.

A negative magenta image is obtained in layer (a) and a direct positive yellow image in layer (b). The undesired negative yellow image in layer (a) which is produced because of the yellow density of the magenta dye is eliminated by the positive yellow masking image of layer (b).

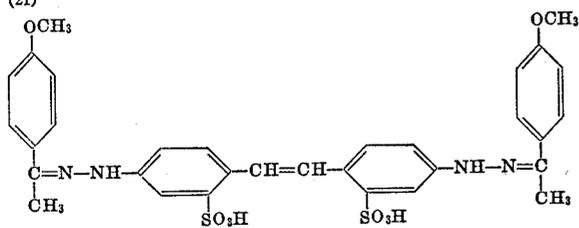




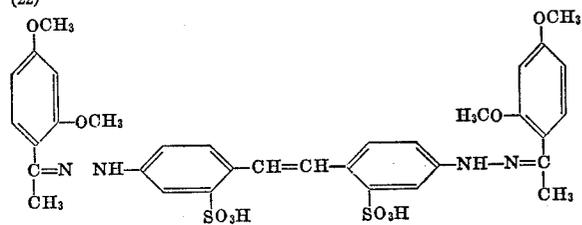
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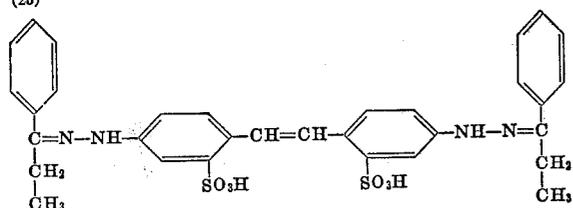
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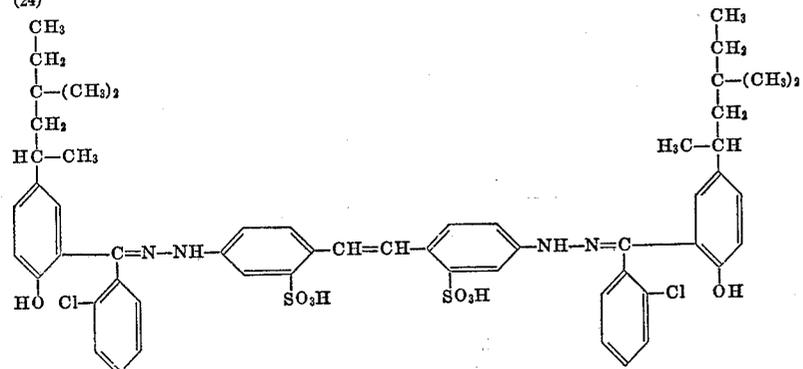
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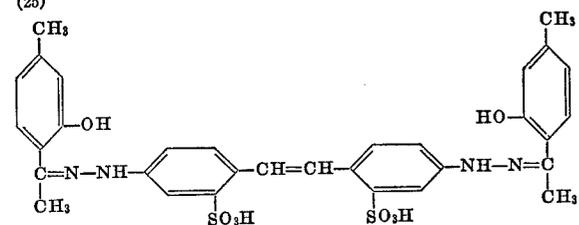
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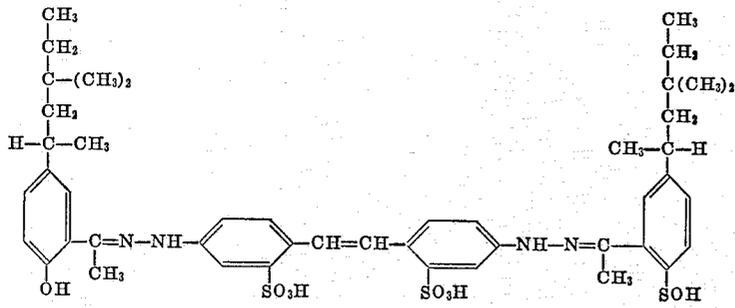
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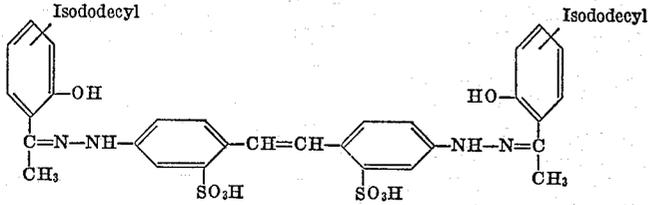
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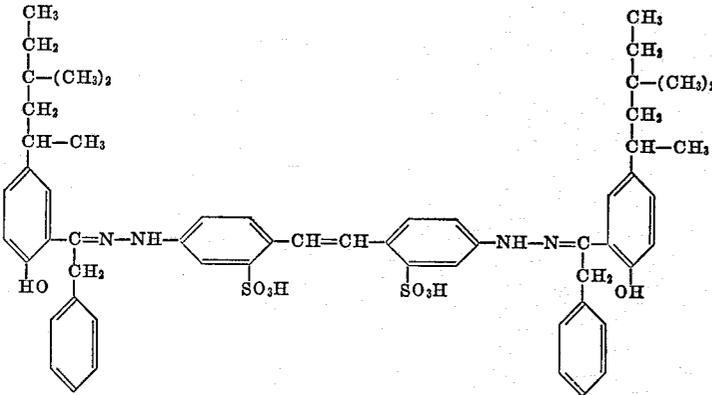
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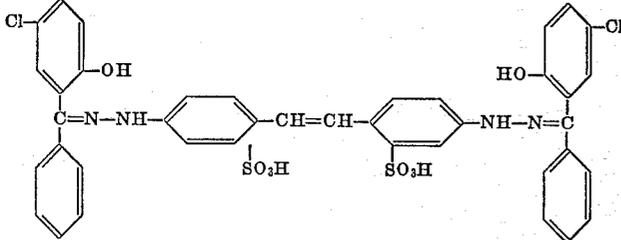
(27)



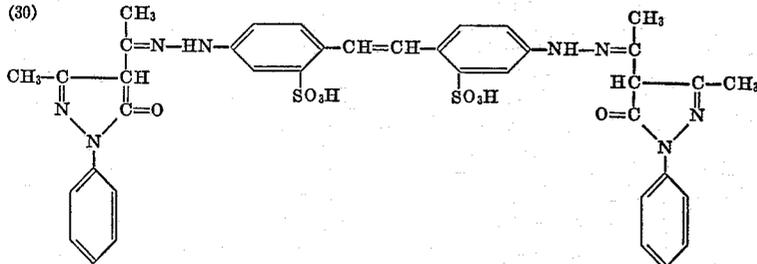
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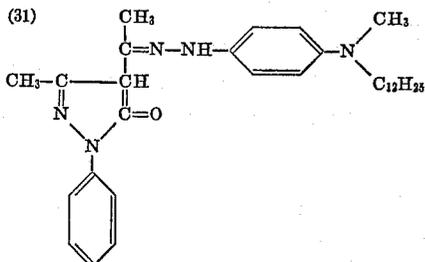
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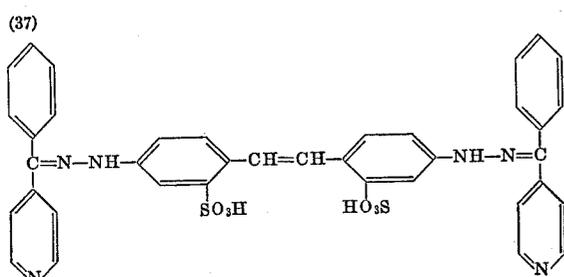
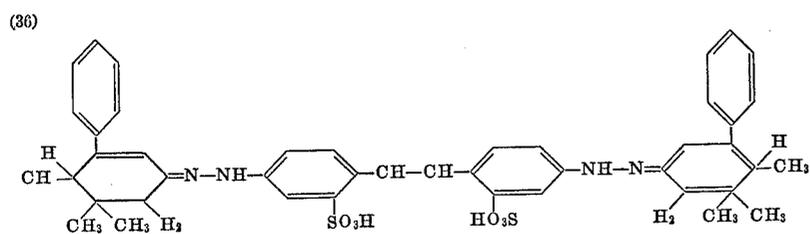
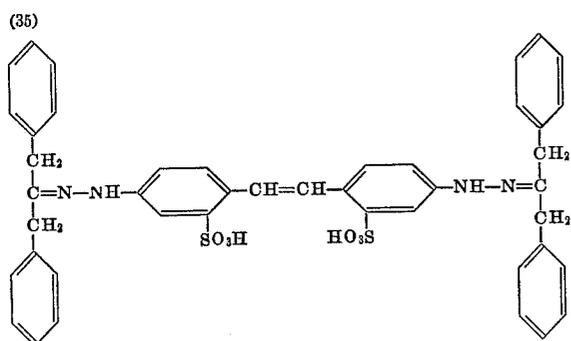
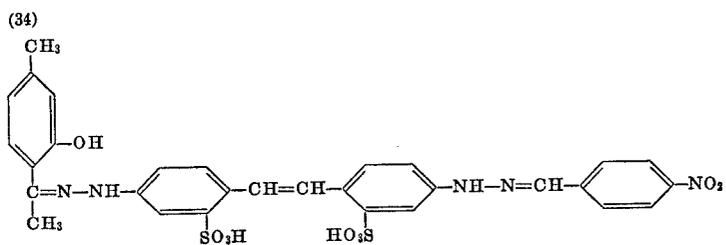
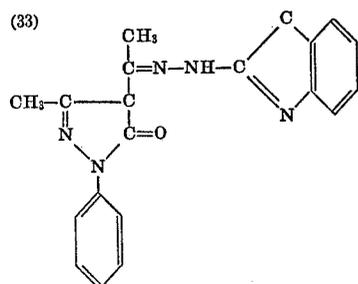
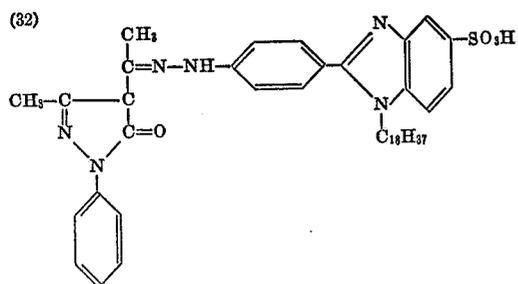
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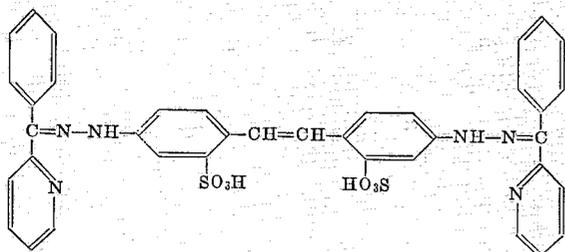
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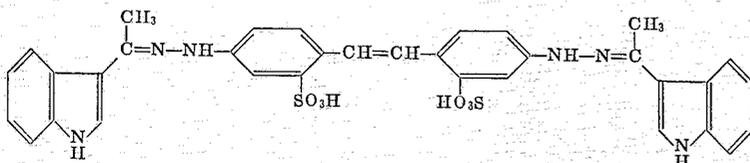
17



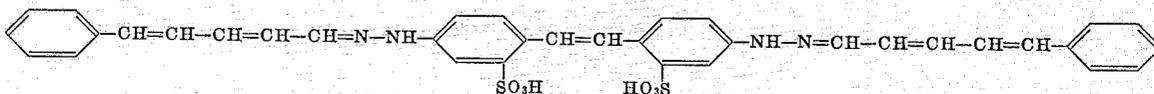
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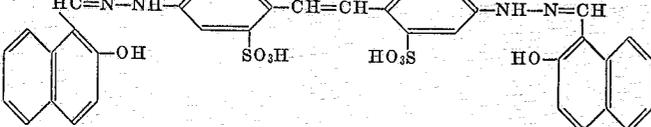
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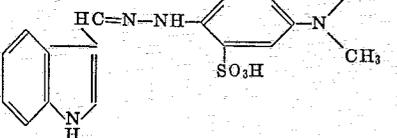
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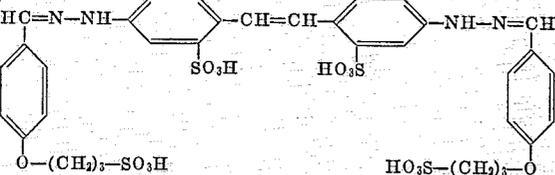
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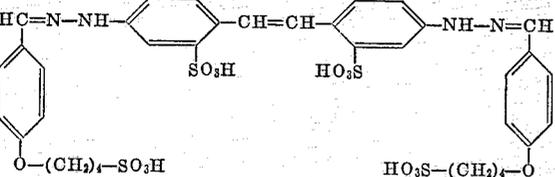
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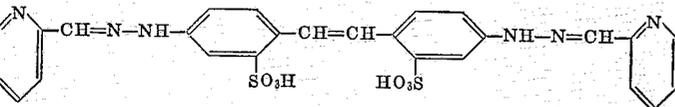
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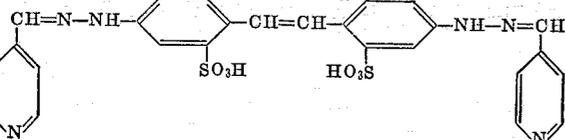
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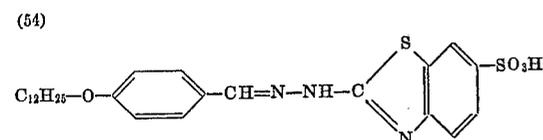
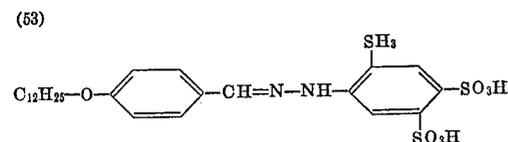
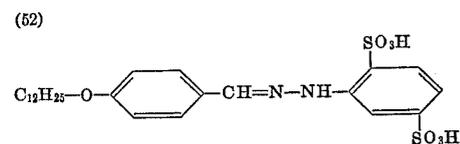
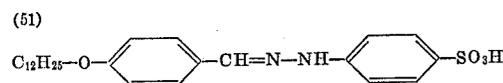
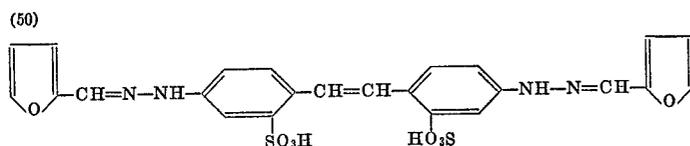
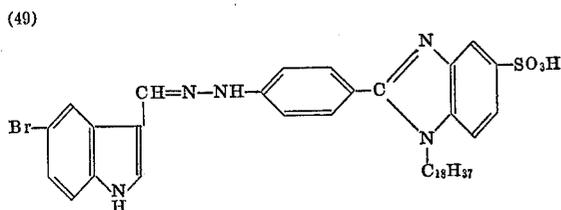
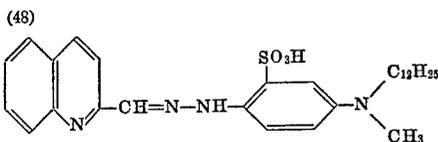
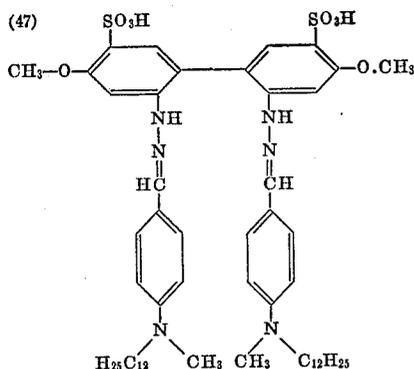
(45)



(46)

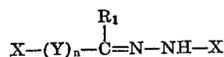


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We claim:

1. A photographic element with at least one supported light-sensitive silver halide emulsion layer containing an organic hydrazone which reacts with the oxidation products of a photographic developer to form only colorless material, and has the following formula



wherein

X represents a member of the group consisting of a phenyl, a naphthyl, a 5-membered heterocyclic radical and a 6-membered heterocyclic radical,

Y stands for a radical of the group consisting of  $-\text{C}(\text{R}_2)_2-$  and  $-\text{CR}_2=\text{CR}_2-$ ,

$\text{R}_1$  represents a group substituent of the class consisting of hydrogen, alkyl, phenyl, cyclohexyl, phenyl-alkyl, a 5-membered heterocyclic radical and a 6-membered heterocyclic radical,

$\text{R}_2$  stands for a substituent of the group consisting of hydrogen, nitril, alkyl and phenyl, and

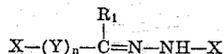
$n$  is an integer between 0 and 3.

2. A photographic element as defined in claim 1 wherein X is a phenyl radical.

3. In a photographic process for the production of color photographic images by exposing to an object to be reproduced a photographic element containing at least one light-sensitive silver halide emulsion layer, developing, bleaching and fixing the exposed photographic element, the improvement which comprises developing the

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exposed photographic element in effective contact with an organic hydrazone which reacts with the oxidation products of the developer to form only colorless materials, and has the following formula



wherein

X represents a member of the group consisting of a phenyl, a naphthyl, a 5-membered heterocyclic radical and a 6-membered heterocyclic radical,

Y stands for a radical of the group consisting of  $-\text{C}(\text{R}_2)_2-$  and  $-\text{CR}_2=\text{CR}_2-$ ,

R<sub>1</sub> represents a substituent of the class consisting of hydrogen, alkyl, phenyl, cyclohexyl, phenylalkyl, a 5-membered heterocyclic radical and a 6-membered heterocyclic radical,

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R<sub>2</sub> stands for a substituent of the group consisting of hydrogen, nitril, alkyl and phenyl, and n is an integer between 0 and 3.

4. A photographic process as defined in claim 3, wherein X is a phenyl radical.

#### References Cited

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10	3,186,840	6/1965	Puschel et al. ....	96-9
	3,245,787	4/1966	Willems et al. ....	96-9
	3,293,032	12/1966	Jaeken et al. ....	96-9

##### FOREIGN PATENTS

15	810,459	8/1951	Germany.
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J. TRAVIS BROWN, *Primary Examiner.*

UNITED STATES PATENT OFFICE  
**CERTIFICATE OF CORRECTION**

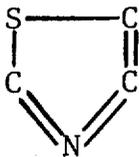
Patent No. 3,384,484

May 21, 1968

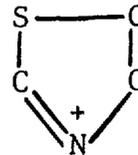
Karl Wilhelm Schranz et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

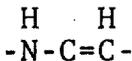
Column 2, line 58, "aliky1" should read -- alkyl --. Column 8, first formula, the portion of the formula reading



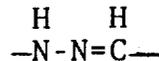
should read



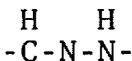
Columns 9 and 10, formula (1), the portion of the formula reading



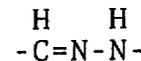
should read



same columns, formula (3), the portion of the formula reading



should read



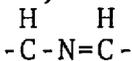
Columns 11 and 12, formula (12), the portion of the formula reading



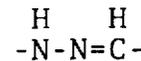
should read



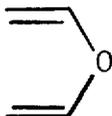
same columns, formula (14), the portion of the formula reading



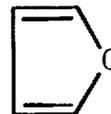
should read



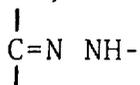
Columns 13 and 14, formula (20), the portion of the formula reading



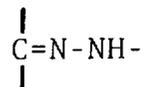
should read



same columns, formula (22), the portion of the formula reading

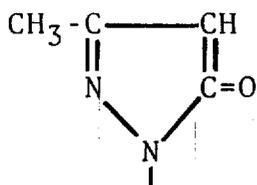


should read

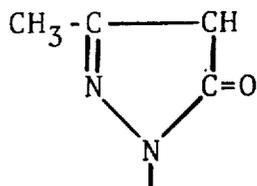


Columns 15 and 16, formulas (30) and (31), the portion of each formula reading

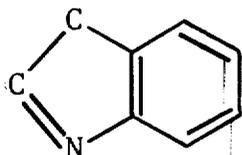
(2)



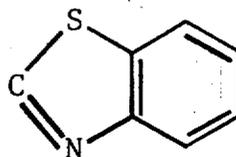
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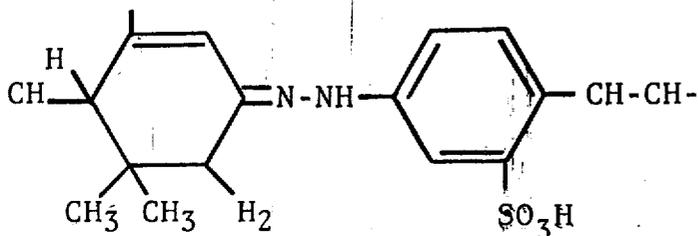
Columns 17 and 18, formula (33), the portion of the formula reading



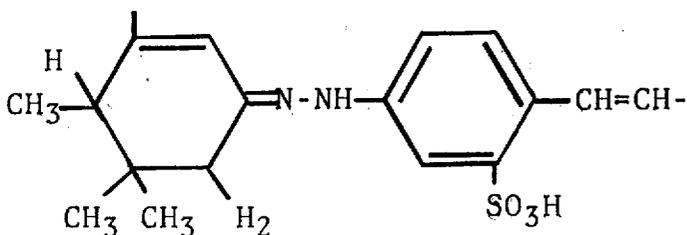
should read



same columns, formula (36), the portion of the formula reading



should read



Columns 21 and 22, formula (53), the portion of the formula reading



should read



Signed and sealed this 25th day of November 1969.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents