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3,467,520

## PRODUCTION OF COLORED DIRECT POSITIVE PHOTOGRAPHIC IMAGES

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U.S. Cl. 96—53

4 Claims 10

### ABSTRACT OF THE DISCLOSURE

Direct color positives are produced using silver halide emulsion containing an amidrazone that reacts with a color coupler under silver bleaching conditions to form a dye sufficiently intense to be a primary image rather than a masking image. Amidrazone is caused to react with oxidation products of the developer during development and residual amidrazone left unreacted after development forms the color image during bleaching. The color coupler is kept from reacting during development either by adding the color coupler after the development, or by having the color coupler in a separate layer in non-diffusible form, the amidrazone being diffusible during bleaching, or when the color coupler is present in the emulsion layer during development, effecting the development with a black and white developer.

The invention relates to a process and photographic materials for the production of colored direct positive photographic images by the simultaneous use of conventional color couplers and of monohydrazone compounds that react with oxidized developers to form colorless stable products but react under oxidizing conditions to form dyes, the production of the colored positive image being so carried out that during the development of the exposed material, no colored image is formed.

British Patent No. 916,657 describes the reaction of dihydrazones of  $\alpha,\beta$ -dicarbonyl compounds with the oxidation products of color-forming developers in the production of direct positive pictures. These dihydrazones are practically colorless and, during the color photographic processing, they react at the light-struck areas with the developer oxidation products to form colorless compounds. Upon the bleaching of the silver image by means of an oxidizing bath, the remaining dihydrazones at the unexposed areas form compounds which have yellowish-orange color. It is possible in this way to produce colored direct positive images. These images are relatively weak in color but they are useful as colored masking images. A process for the preparation of colored direct positive images by the principle described hereinbefore would per se be extremely advantageous in comparison with the known direct positive processes.

Such a process would be superior to the known reversal processes, because the method of processing would be substantially simpler, as the second uniform exposure and the second development which are necessary in the conventional processes become superfluous.

In Belgian Patent No. 602,250, certain amidrazones are described for the production of colored masking images. These amidrazones have the property of coupling by oxidation with color couplers, so that after the color development in the bleaching bath, a colored positive image is formed at the unexposed and undeveloped areas.

This principle is utilized in the process described in German Auslegeschrift 1,146,751 for the production of colored direct positive images, in which use is made of

the difference in the acid sensitivity of the dyes formed by reaction of conventional color couplers with the oxidation products of conventional color developers and of the dyes formed by oxidative coupling of the amidrazones and color couplers. The process is performed in the usual way, by exposure followed by color development, bleaching and fixing, then followed by a chemical treatment with a strongly acid aqueous solution which destroys the so-called primary dyes formed upon reaction of the color coupler with the oxidation products of the color-forming developer, while the so-called secondary dyes formed by oxidative coupling of the amidrazones with the color couplers at the non-lightstruck areas are stable against strong acids. The process, however, is of limited utility, since the differences in the acid sensitivity of the dyes is not so great that one would be completely and irreversibly destroyed while the other is not affected at all.

The object of the present invention is to provide a direct positive color-photographic process which does not have the aforementioned disadvantages and which permits the production of colored direct positive images of satisfactory quality in a simple manner.

Other objects will be apparent from a consideration of the following description and examples.

We now have found, that direct positive color-photographic images can be obtained in a very simple manner if the conventional processing of light-sensitive materials with at least one light-sensitive silver halide emulsion layer which contains an effective amount of an amidrazone or its vinylene homologs, phenylene homologs or azavinylene homologs is performed in such a way that no dye image is formed upon development and that the bleaching is accomplished in effective contact with a color coupler customarily employed in conventional color-photographic processes.

The process of the present invention is based on the discovery that certain amidrazones or homologous compounds react with the oxidation products of conventional developers, and indeed of both color-forming developers and black-and-white developers, to form colorless products which are stable against oxidizing agents as employed in photographic bleaching baths.

The final color image formed in accordance with the process of the present invention consists of azo or azine dyes of the same type as the dyes formed in the final color image according to German Auslegeschrift 1,146,751. The process according to the present invention is in principle characterized in that the production of the direct positive image is performed in such a way that formation of negative color images in the exposed silver halide emulsion layer by reaction of conventional color couplers with the oxidation products of a color-forming developer is avoided. Upon development of the exposed silver halide layer the amidrazones react at the exposed areas with the oxidation product of the developer to form a colorless product which is stable against the oxidizing agent in bleaching baths and which is incapable of reacting with a conventional color coupler.

The following embodiments have been found suitable for the process of our invention:

(1) A supported light-sensitive silver halide emulsion layer containing amidrazones or vinylene homologs or phenylene homologs or azavinylene homologs is exposed to the object to be reproduced and developed, whereby the amidrazones are imagewise transformed at the exposed areas into colorless stable products. Conventional color couplers are thereafter introduced into the layer by treating it with a solution containing color couplers. The color couplers react with the amidrazone at the unexposed and undeveloped areas in the oxidizing bleaching bath to form a positive dye image. According to a pre-



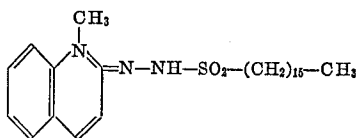
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pounds of the above general formula are oxidized. Attention is to be paid to this when choosing suitable amidrazones for the three embodiments of the process that are set out above. Thus, in the process in which diffusion-resistance is to be eliminated by the oxidation of the amidrazone, e.g., in embodiment (2), it is only possible to use those amidrazones or their vinylene, azavinylene or phenylene homologs which have long aliphatic radicals only in the substituents which can be split off, these being R<sub>3</sub> and R<sub>4</sub>. As regards the groups R<sub>1</sub> and R<sub>2</sub>, any alkyl radicals present in the amidrazones of embodiment (2) should have not more than 6 carbon atoms, and advantageously should have 1 to 3 carbon atoms.

Suitable compounds include the following:

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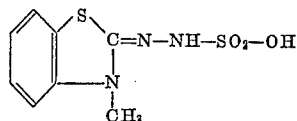
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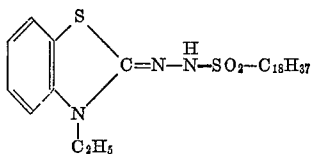
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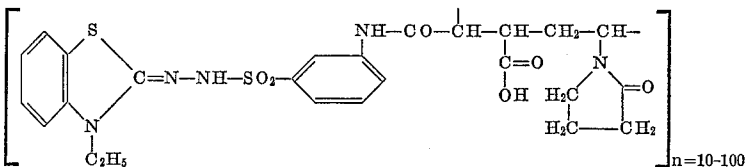
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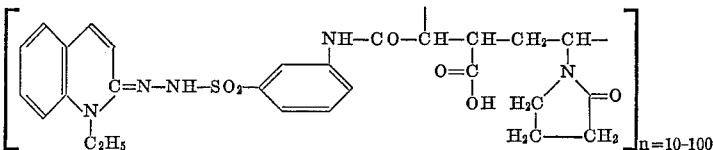
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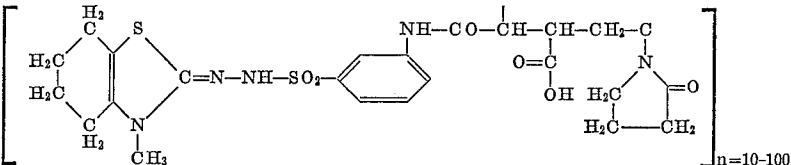
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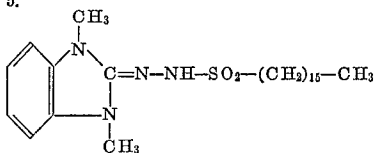
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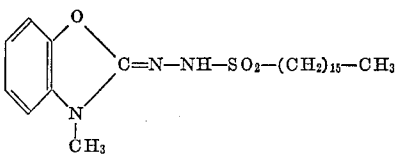
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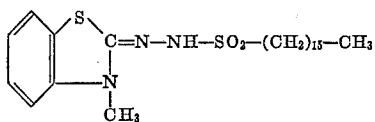
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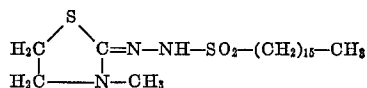
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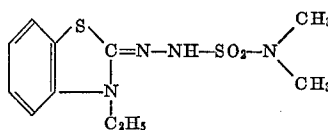


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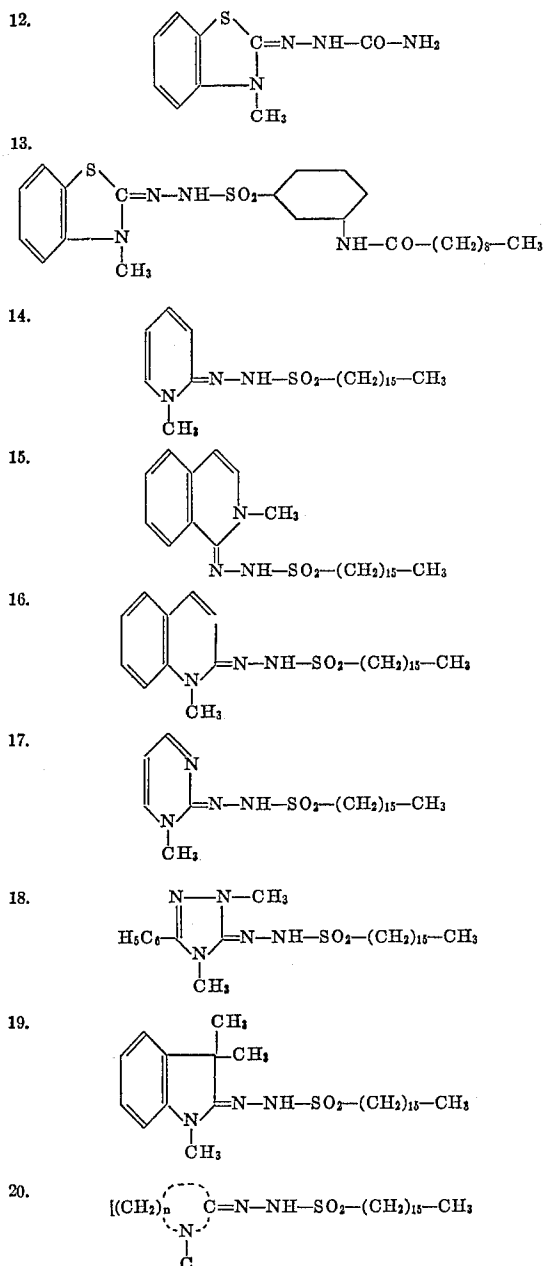
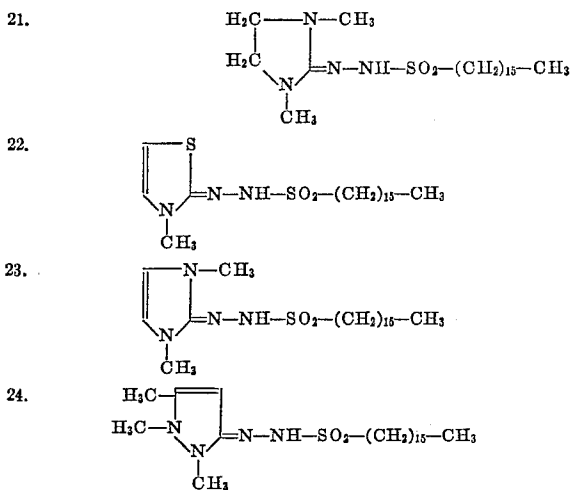
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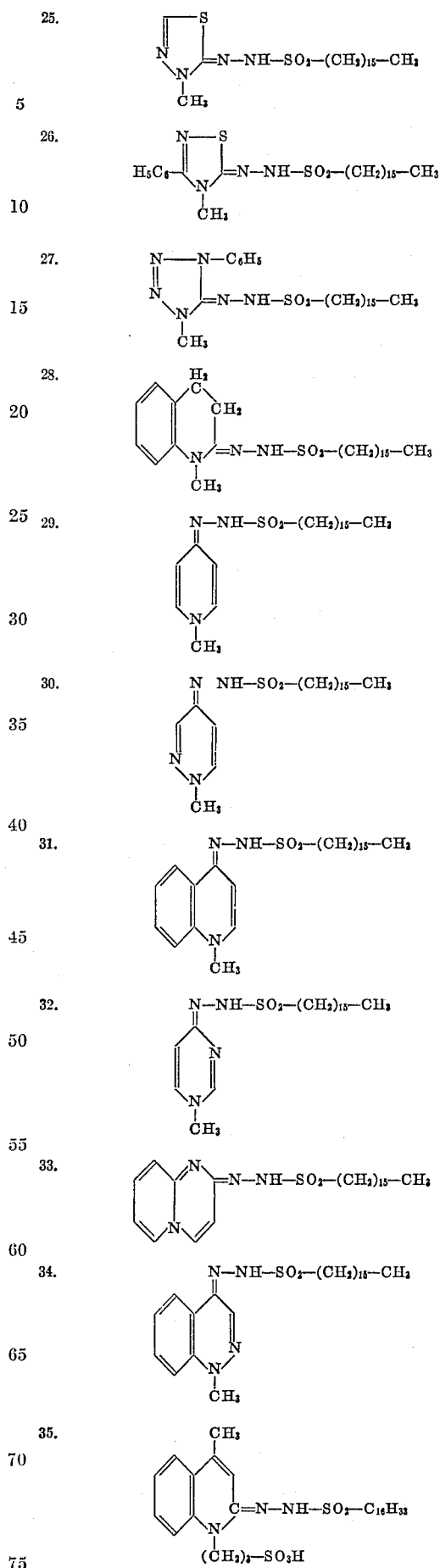


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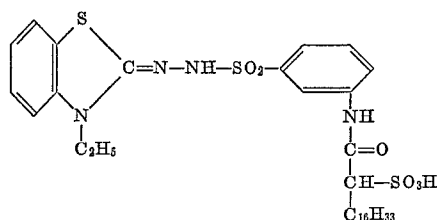
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wherein  $n=4, 5$  or  $6$ 

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36.



Further suitable anhydrazones and homologous compounds are described in Belgian Patent No. 602,250 in particular on pp. 11 to 18 and in German Auslegeschrift 1,146,751.

Preparation of the amidrazones.—Processes for the production of the amidrazones or their vinylene homologs or phenylene homologs or azaavinylene homologous are generally known and particularly described in the Belgian patent referred to hereinbefore. Some specific examples for the production of some of the compounds listed in the above table are given in the following:

#### Compound 1

20 g. of N-ethyl benzthiazolone hydrazone, 35 g. of octadecyl sulphonyl chloride and 8 g. of pyridine are boiled under reflux for 2 hours in 600 cc. of acetonitrile.

On cooling, 39 g. (69.1% of the theoretical yield) of 3-ethyl-2-benzthiazolone- $\beta$ -n-octadecyl sulfonyl hydrazone of melting point 111 to 114° C. crystallize out.

#### Compound 2

15 g. of a vinyl pyrrolidone-maleic anhydride copolymer as described in British patent specification 954,924 are dissolved at 90 to 100° C. in 100 cc. of glacial acetic acid.

In this solution there are introduced 20 g. of 3-amino phenyl sulfonyl hydrazone of N-ethyl-2-benzthiazolone, dissolved in 200 cc. of dimethylformamide.

The mixture is kept for 1 hour at 100° C. and poured into 4 liters of water, suction-filtered and dried in vacuo at room temperature. Yield: 30 g.

Compounds 3 and 4 can be prepared in an analogous manner.

The common photographic processing baths are suitable for the process of the present invention. Examples of some of the baths are set out below.

(A) Developer.—The color-forming or black-and-white developers may be of conventional composition. As color-forming developer the usual primary aromatic amino developer are preferred. For embodiment (3) as referred to hereinbefore ordinary black-and-white developers are used. It is sometimes advantageous to adapt the developer to the amidrazone used. The most suitable developer for any given amidrazone will be apparent to those skilled in the art upon making the tests customarily used in the art. Thus there can be used the following developer bath:

(1) 4-amino-N,N-diethyl aniline sulfate	g.	2.5
Anhydrous sodium sulfite	g.	1.0
Potassium bromide	g.	1.0
Potassium carbonate	g.	75.0
Water	liter	1

In the above composition the 4-amino-N,N-diethyl aniline sulfate can be replaced by:

(2) 4-amino-N,N-butyl butane sulfoaniline	g.	5.0
(3) 4-aminophenol	g.	5.0
(4) p-Methylamino phenol	g.	5.0
(5) Glycine	g.	15
(6) 1-phenyl-3-pyrazolidone	g.	3
(7) 1-p-amino-phenyl-3-amino - pyrazoline dihydrochloride	g.	5
(8) Hydroquinone	g.	5
(9) Pyrocatechol	g.	5

(B) Intermediate baths.—The following intermediate baths are to be applied for embodiment (1) of the process as referred to hereinbefore.

Conventional color-couplers can be employed.

The successive color-formation in each of the single layers of a multi-layer material during the bleaching is obtained by controlled penetration of the solution of the color couplers set out below. If the time of treatment with the following solution is carefully controlled it is possible, for example, that only the top layer of the multi-layer material contain the color coupler.

Such procedures are well-known from the so-called "Developing-in process" or the so-called "Successive Colorant Formation."

(1) 10% by weight aqueous solution of 1-phenyl-3-methyl-5-pyrazolone, which is dissolved at a pH of 8 by adding 2 N-sodium hydroxide solution.

(2) 3% by weight aqueous solution of 1-naphthol-4-sulfonic acid, which is dissolved at a pH of 8 by adding 2 N-sodium hydroxide solution.

(3) 3% by weight aqueous solution of 1-phenylamino naphthalene-8-sulfonic acid, which is dissolved at a pH of 8 by adding 2 N-sodium hydroxide solution.

(C) Bleaching bath.—In principle, it is possible to employ the conventional bleaching baths or combined bleaching and fixing baths, for example, aqueous solutions of complexes of trivalent iron or trivalent cobalt with aminopolycarboxylic acids such as ethylene diamine tetraacetic acid, nitrilo triacetic acid or the like as described, for example, in German patent specification 866,605, or aqueous solutions of potassium bichromate or potassium ferricyanide. Suitable baths are, for instance, a 20% by weight solution of potassium ferricyanide or for instance a 10% by weight aqueous solution of potassium bichromate. The required pH can be adjusted by adding the necessary amount of aqueous solution of acids or alkali metal hydroxides or carbonates.

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

Other conventional photographic processing baths can also be employed. In principle, they are, of course, not essential to the process, but they are often advantageous. They include, for example, stop baths which have a pH down to 3 or hardening baths.

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 silver halide emulsions are produced in accordance with common practice. The preparation involves 3 separate steps: (1) precipitation of the silver halide and physical ripening in the presence of gelatin, (2) freeing of the emulsion of excess water-soluble salt usually by washing, and (3) after-ripening or chemical ripening to obtain the desired speed or sensitivity.

The amidrazones can be added at any desired stage to the light-sensitive silver halide emulsion layer. In the preparation of the photographic emulsions of the present invention, the amidrazones are advantageously incorporated in the finished emulsion after the chemical ripening.

It is convenient to add the amidrazones of the present invention from solutions in appropriate solvents. The solvent should, of course, be completely free from any deleterious effect on the silver halide emulsion. Water or lower aliphatic alcohols or admixtures thereof has proven satisfactory as solvents for the majority of the amidrazones of the invention.

According to another method, the amidrazones and monohydrazone couplers are first dissolved in an oily or

ganic material, and this combination is dispersed in a finely divided state throughout the emulsion.

The concentration of the amidrazones in the emulsion can vary widely from about 2 to 50 g. per mol of silver halide, their specific concentration will vary according to the type of the light-sensitive emulsion and according to the effects desired. Preferred are concentrations of between 5 and 20 g. per mol of silver halide. The most suitable concentration for any given emulsion will be apparent upon making the test customarily used in the art.

As silver halides for the light-sensitive emulsions, it is possible to employ silver chloride or silver bromide, possibly with a few mol percent of silver iodide, or mixtures of these halides.

The usual hydrophilic colloids are suitable as binders, such as, advantageously, gelatin, although this can be wholly or partially replaced by other film-forming materials, such as carboxymethyl cellulose, polyvinyl alcohol, alginic acid or derivatives thereof, such as salts, esters or amides, polyvinyl pyrrolidone and the like.

The emulsions stabilized in accordance with the present invention can be chemically sensitized by any of the accepted procedures. The emulsions can be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum. Suitable compounds are well known in the art. The emulsions can also be sensitized with gold salts as described by R. Koslowsky, *Z. Wiss. Phot.*, 46, 65-72 (1951).

The emulsions can also be chemically sensitized with reducing agents such as stannous salts, polyamines, sulfur compounds, such as described in the U.S. Patent No. 1,574,944, polyethylene oxides and the like.

The emulsions can also be optically sensitized with the ordinary sensitizing dyes, cyanines or merocyanines. The emulsions can be stabilized with any of the known stabilizers such as mercury compounds, triazoles, azaindenes, such as disclosed by Birr in *Z. Wiss. Phot.*, vol. 47 (1952), pp. 2-28.

The emulsions may be hardened by any suitable hardener, such as formaldehyde and halogen substituted aliphatic acids such as mucobromic acid.

Conventional color couplers can be used for the oxidative coupling with the amidrazone, for example yellow couplers of the  $\beta$ -ketoanilide type as described, for example, by Glafkides, "Photographic Chemistry," vol. 2, pp. 597-600, published by Fountain Press, London, cyan couplers such as phenols or naphthols as described for instance by P. Glafkides, "Photographic Chemistry," vol. 2, pp. 596-597, published by Fountain Press, London, or magenta couplers as described by P. Glafkides, "Photographic Chemistry," vol. 2, pp. 600-603, published by Fountain Press, London, such as prazolones as described by O. Wahl, in "Angew. Chemie," 64 (1952), pp. 259-265, indazolones, couplers with cyanacetyl groupings or pyrazolobenzimidazoles such as disclosed in British Patent No. 918,128.

If the photographic material contains the color coupler, the compounds can be incorporated into the desired layer in a dissolved diffusion-resistant form. According to another method the coupler is first dissolved in an oily organic material and this combination is then dispersed in a finely divided state throughout the layer.

#### EXAMPLE 1

A silver bromide gelatin emulsion containing 1.5 g. of compound 1 per 100 cc. is applied to a suitable support (e.g. a foil of acetyl cellulose, polycarbonate of bis-hydroxy phenylalkanes or polyethylene terephthalate), exposed and developed for 5 minutes at 20° C. in developer A1. After an intermediate rinsing of 15 minutes, the developed material is placed in one of the intermediate baths B1 to B3 for two minutes and thereafter bleached and fixed in the baths C and D, respectively. When using intermediate bath B1 a yellow direct positive image is

obtained, while a red image is obtained with B2 and a blue image with B3.

The above material can be developed in the developers 2 to 9 under conventional processing conditions. In each instance, corresponding to the intermediate baths which are chosen, yellow, red or blue direct positive images are obtained.

#### EXAMPLE 2

The following photographic layers are applied to a support in the sequence as indicated:

(1) A layer applied from 5% by weight aqueous gelatin solution which contains per 100 ml. 8 g. of 4-sulfo-1-naphthol-2-carboxylic acid stearyl-anilide.

(2) A blue-sensitive silver bromide gelatine emulsion layer which contains 9 g. of compound 3 per kg. of emulsion. By developing in developer 3, the compound 3 reacts in layer 2 at the exposed areas with the oxidized developer to form compounds which are finally colorless and which are stable against the bleaching bath. Upon bleaching compound 3 is transformed at the unexposed and undeveloped areas into a compound capable of coupling. Since simultaneously the polymeric part of the molecule which rendered the compound fast to diffusion is split off at the sulfonyl-amidrazone linkage, the oxidized amidrazone can diffuse into layer 1 and react with the color coupler to form a direct positive red image of the exposed original.

#### EXAMPLE 3

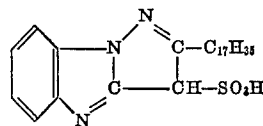
If the naphthol coupler in layer 1 of Example 2 is replaced by 1-(4'-sulfo-phenyl)-3-palmityl-5-pyrazolone and if the compound 3 in layer 2 is replaced by compound 2, and if this layer is processed in a manner analogous to Example 2 with developer 2, a direct positive, yellow image is obtained.

#### EXAMPLE 4

If the naphthol coupler in layer 1 of Example 2 is replaced by 1-naphtholcarboxylic acid-2(2'-N-stearyl-N-methylamine-4'-sulfoanilide) and the compound 3 in layer 2 is replaced by compound 4, processing taking place as indicated in Example 2, but using developer 2, then a direct positive, blue image is obtained.

#### EXAMPLE 5

A silver bromide emulsion, containing per 100 cc., 1.0 g. of the compound 2 and 1.0 g. of the compound of the following formula:



is applied to a suitable support, exposed, developed for 5 minutes at 20° C. in the developer 4 and thereafter bleached and fixed in the baths C and D. A yellow, direct positive is obtained.

#### EXAMPLE 6

The material described in Example 5 is developed in developer 5 while maintaining the other processing conditions. Here also, a yellow positive image is obtained.

#### EXAMPLE 7

In the material described in Example 5, the coupler is replaced by the compound 4-sulfo-1-naphthol-2-carboxylic acid stearyl-anilide. It is exposed, developed for 5 minutes at 20° C. in the developer 3 and thereafter bleached and fixed in the baths C and D. A red, direct positive image is obtained.

If the above material is developed in the developers 6, 8 and 9, in each instance, a red direct positive image is obtained.

What is claimed is:

1. In the preparation of a direct positive color image by exposing, developing and bleaching out the silver from a photographic silver halide emulsion layer containing an amidrazone that reacts with a color coupler under bleaching conditions to form a dye sufficiently intense to be a primary image, the improvement according to which the amidrazone is not protected by the color coupler during the development so that the exposed portion of the amidrazone reacts with the oxidation products of the developer during the development and is converted to material that does not provide color during the bleaching, and during the bleaching the color coupler is present at the exposed as well as unexposed portions but only the unexposed portion of the amidrazone reacts with the color coupler during the bleaching.

2. In the preparation of a direct positive color image by exposing, developing and bleaching out the silver from a photographic silver halide emulsion layer containing an amidrazone that reacts with a color coupler under bleaching conditions to form a dye sufficiently intense to be a primary image, the improvement according to which the color coupler is not added to the emulsion until after the developing is completed so that the exposed portion of the amidrazone reacts with the oxidation products of the developer during the development and is converted to material that does not provide color during the bleaching, and the unexposed portion of the amidrazone reacts with the color coupler during the bleaching.

3. In the preparation of a direct positive color image by exposing, developing and bleaching out the silver from a photographic silver halide emulsion layer containing an amidrazone and a color coupler that react with each other under bleaching conditions to form a dye sufficiently intense to be a primary image, the improvement according to which the development is effected with a

black-and-white developer so that the color coupler does not react during developing, the exposed portion of the amidrazone reacts with the oxidation products of the developer during the development and is converted to material that does not provide color during the bleaching, and the unexposed portion of the amidrazone reacts with the color coupler during the bleaching.

4. In the preparation of a direct positive color image by exposing, developing and bleaching out the silver from a photographic silver halide emulsion layer containing an amidrazone that reacts with a color coupler under bleaching conditions to form a dye sufficiently intense to be a primary image, the improvement according to which the color coupler is in diffusion-resistant form and is incorporated in a layer contiguous with but separate from the emulsion layer, and the amidrazone has at its reaction site a diffusion-resistant substituent that splits off during the bleaching to render the reactive portion of the amidrazone diffusible and cause it to diffuse to the color coupler layer where it forms the color image.

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