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2,860,974

PHOTOGRAPHIC COLOR CORRECTION PROCESS

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No Drawing. Application August 15, 1955
Serial No. 528,516

8 Claims. (Cl. 96—9)

This invention relates to color photography and more particularly to the correction of color in color photography by means of masking images.

The use of masks to compensate for the deficiencies of dyes comprising colored images in color photography is well known. Neutral as well as colored masks have been used for this purpose. In the Hanson U. S. Patent 2,449,966, granted September 21, 1948, is described the use in emulsion layers of non-diffusing colored color-forming coupler compounds to provide masking images, the coupler compounds having the property of coupling to form a dye image in the exposed regions while the original coupler remains in the unexposed regions as a masking image. In the Vittum et al. U. S. Patent 2,428,054, granted September 30, 1947, is described the use in emulsion layers of such non-diffusing colored color-forming coupler compounds in conjunction with varying amounts of non-diffusing colorless color-forming coupler compounds to obtain masking images imparting the desired degree of color correction. In that process during color development the color of the colored coupler is destroyed in the exposed areas while at the same time and in the same area the colorless coupler forms the dye image, the unreacted colored coupler remaining as a masking image in the unexposed areas. That process has some limitations such as the requirement that the colored couplers produce on development, dyes of the same hue as produced by the uncolored coupler.

In the Weller et al. U. S. Patent 2,689,793, granted September 21, 1954, is described the use of colorless non-diffusing image-forming couplers in conjunction with colorless non-image-forming couplers which compete with the image-forming couplers in the development reaction and form soluble dyes which wash out of the emulsion layers. Accordingly, emulsion layers can be employed containing considerably more silver halide than is usually possible in color processes without obtaining undesirably high contrast dye images. In the Whitmore U. S. patent application Serial No. 470,499, filed November 22, 1954, now U. S. Patent 2,808,329, granted October 1, 1957, is described the use, in conjunction with non-diffusing image-forming couplers, of colored non-image-forming couplers which have the property of coupling in the exposed region to form soluble dyes which can be washed out of the emulsion leaving a colored masking image in the unexposed region of the emulsion composed of the original colored coupler and being of the same color as the original colored coupler. Thus, it is possible, as in the process of Weller et al., to employ emulsions of comparatively high silver halide content and still maintain the contrast of the process at the desired level.

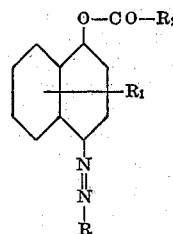
I have discovered certain green and red light-transmitting non-image-forming couplers which may be employed in color development processes in conjunction with non-diffusing image-forming couplers in the manner of the Whitmore invention, which also have the property of coupling in the exposed region of an emulsion layer to

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form a soluble dye which washes out of the emulsion layer, leaving the non-image-forming coupler remaining in the unexposed regions as a colored masking image. In addition, my coupler compounds have the further property that their color is changed to a different color by a simple manipulation in the color process in which they are employed. That is, my non-image-forming coupler compounds are initially light colored, e. g. yellow in color and by removal of a masking group on an auxochrome of the coupler molecule, the color may be readily changed to a green light-absorbing color such as magenta. This property is especially advantageous as will be apparent since it is possible to employ the couplers in, for example, the blue-sensitive emulsion layer of a multilayer color film without the couplers interfering with the exposure by red or green light of underlying red or green-sensitive emulsion layers. After exposure of the film, the coupler can then be changed to the green light absorbing form.

The novel coupler compounds of the invention can be described as color-forming coupler compounds which react with the oxidation products of primary aromatic amine silver halide developing agents to form dyes but further, they have attached to their molecule in a non-coupling position, a solubilizing group which allows the dye formed therefrom to be washed out of an emulsion layer. Furthermore, attached in the coupling position of the molecule is an azo chromophore group which renders the couplers nondiffusing in emulsion layers and to which chromophoric group can be attributed the green light absorbing coloration of the coupler compound. Also, in another non-coupling position of the coupler molecule is present an auxochrome group which is made less effective, as far as light absorption is concerned, by esterification; and to which in combination with the azo chromophore entity can be attributed the initial color of the coupler compound.

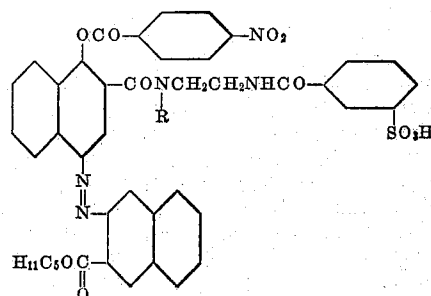
The coupler compounds of the invention have the general formula



wherein R represents an aromatic group which renders the coupler non-diffusing such as a naphthalene or substituted naphthalene group, R₁ represents a solubilizing group such as a sulfophenyl group suitably linked to the naphthyl nucleus and R₂ is either a nitrophenyl or cyanophenyl group comprising the auxochrome entity.

Representative colored coupler compounds having this general formula are as follows:

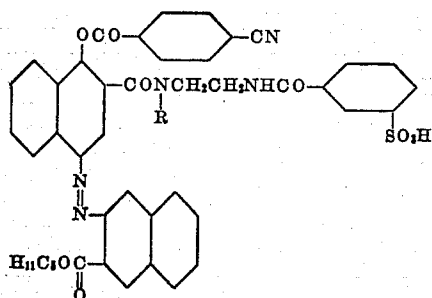
I.



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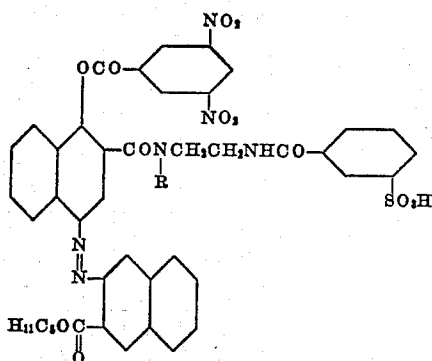
wherein R represents a member of the class consisting of hydrogen and p-nitrobenzoyl.

II.



wherein R represents a member of the class consisting of hydrogen and p-cyanobenzoyl.

III.



wherein R represents a member of the class consisting of hydrogen and 3,5-dinitrobenzoyl.

The couplers can be used in the free acid form given above or as their alkali metal or ammonium salts.

The coupler compounds having the particular structures above are yellow in color and can be treated with simple aqueous alkaline solutions to hydrolyze the nitrobenzoyl or cyanobenzoyl groups and thus release the magenta colored phenolic form of the coupler. Accordingly, after exposure of an emulsion layer containing the couplers, it is possible to merely develop the emulsion layer with the usual alkaline color developing solutions with the result that the phenolic magenta-colored form of the coupler couples in the exposed regions with the color developing agent to yield a dye which washes out of the film, whereas the hydrolyzed magenta-colored coupler remains in the unexposed regions. It is possible to vary the color of the masking image remaining in the unexposed regions by hydrolyzing only a portion of the yellow coupler therein. Thus, a masking image of color ranging from yellow to magenta can be obtained. Similar effects can be obtained by employing the above yellow-colored coupler compounds of the invention in conjunction with the image-forming colored couplers, for example, of the Vittum et al. U. S. Patent 2,428,054 which couple in the exposed regions to give non-diffusing dye images of color different from the original coupler. A preferred method of using the coupler compounds of the invention illustrated in the following examples is to hydrolyze the couplers from the yellow form to the magenta-colored form by means of an alkaline bath applied after exposure of the emulsion layer and prior to the color development step. This procedure is desirable when all of the colored coupler is to be hydrolyzed. Alternately or in addition to the above procedures, an alkaline bath may be applied following color development for the same purpose.

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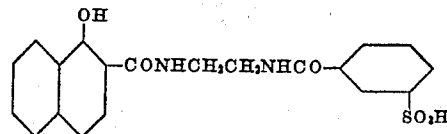
EXAMPLE 1

Coupler I is prepared as follows:

Intermediate A

Two molecular equivalents of 1-hydroxy-2-β-aminoethyl-naphthamide were dissolved in dioxane and one equivalent of m-sulfobenzoyldichloride dissolved in dioxane is added. The precipitated amine hydrochloride is separated by filtration. The filtrate is drowned in water and the precipitate collected. This is then refluxed in a 50-50 water and alcohol solution, the excess alcohol removed and the aqueous residue filtered. The filtrate is chilled and the product collected which has the structure

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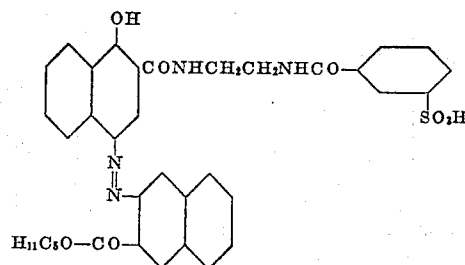
Intermediate B

3-amino-2-naphthoic acid is dissolved in an excess of n-amyl alcohol and dry hydrogen chloride is passed into the mixture. After refluxing several hours, the excess alcohol is removed by vacuum distillation and the residue stirred in a sodium carbonate solution. The product n-amyl-3-amino-2-naphthoate is collected on a filter and dried.

Intermediate B is then diazotized and coupled in basic medium such as pyridine, sodium hydroxide or acetic acid and sodium acetate, with the naphthol Intermediate A to obtain the magenta-colored azo dye of structure

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IV.



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To obtain the final coupler I, the resulting magenta-colored azo dye is then reacted with p-nitrobenzoyl chloride in pyridine at room temperature and the solution drowned out in ice and hydrochloric acid. The solid is purified. Melting point sinters 136° C.

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EXAMPLE 2

Coupler II is prepared in the manner of Example I except in the final step p-cyanobenzoyl chloride being substituted for p-nitrobenzoyl chloride. Yield is 62 percent; melting point: sinters 90° C.

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EXAMPLE 3

Coupler III is prepared as above using 3,5-dinitrobenzoyl chloride in the final step of the synthesis. Yield is 85 percent; melting point: sinters 160° C.

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The couplers prepared according to Examples 1, 2 and 3 have been assigned the general Formulas I, II and III above inasmuch as it has been difficult to determine with the desired degree of accuracy whether they are obtained in the form of the mono- or di-acylated compounds or a mixture of both, although the preponderance of evidence is that the di-acylated compounds predominates in the reaction mixtures. My invention therefore contemplates the use of the compounds in either form obtained as described by reaction of the azo dye IV above with the indicated nitro and cyanobenzoyl halides. These

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Chemical structure of a sulfonated polyimide. The main chain consists of a 1,2,3,4-tetrahydronaphthalene-1,4-dione unit linked to a 4,4'-biphenylene unit via imide bonds. The biphenylene unit is substituted with a long alkyl chain (H₁₁C₆-O-CO-) and a sulfonate group (-SO₃H). The tetrahydronaphthalene unit is substituted with a side chain: -CONCH₂CH₂NHCO- linked to a 1,4-cyclohexadiene ring with a sulfonate group (-SO₃H). The side chain also has an R₁ group and an R group on the nitrogen atoms.

EXAMPLE 4

	Grams
Sodium hexametaphosphate -----	1.0
2-amino-5-diethylaminotoluene hydrochloride -----	2.0
Sodium sulfite (anhydrous) -----	2.0
Potassium bromide -----	2.0
Sodium carbonate (monohydrate) -----	20.0
Water to make up a volume of 1000 cc.	

Rinsing -----	15 seconds.
Fixing -----	2 minutes.
Washing -----	3 minutes.
Bleaching -----	2 minutes in 50 grams of potassium ferricyanide, 20 grams of potassium bromide per liter.

The processed element contained a yellow image derived from the colorless yellow coupler in the exposed area and a low-contrast magenta masking image of the hydrolyzed yellow coupler remained in the unexposed area.

The colored couplers II and III above were coated and processed in an identical manner and also were found to yield magenta masking images, in all cases the yellow colored couplers coupled to a soluble dye in the exposed areas which washed out of the film during processing.

Other colorless non-diffusing couplers which can be used with the mentioned colored diffusing non-image-forming couplers of the inventions are, for example, those described in Weissberger U. S. Patent 2,298,443, granted October 13, 1942.

This example illustrates the preparation of a multilayer film containing the coupler compounds of the invention. In this example a multilayer film was prepared as follows:

The other colored couplers of the invention can be used in multilayer films in the same manner.

30 The use of the yellow colored couplers of the invention in the outer blue-sensitive layer of the multilayer film as described above thus takes advantage of the outstanding feature of the couplers residing in the fact that since the couplers transmit green and red light, they do not interfere with exposure of the underlying green and red-sensitive emulsion layers of the multilayer film.

35 As mentioned previously, in the above examples the couplers of the invention can be hydrolyzed to the green light-absorbing form at any stage of the process before or after color development and to the extent desired.

The above examples illustrate the formation of a masking image in a negative-positive color reproduction process. The novel couplers of the invention are equally useful in reversal processes of color photography. In such processes, the negative image is developed with the usual black-and-white developers and the residual silver halide is then developed with a color-forming developer to obtain a positive dye image from the image-forming couplers and the coupler of the invention forms a negative dye masking image in the other areas of the photographic element.

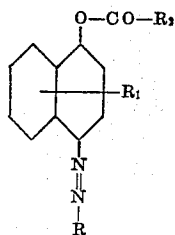
50 In accordance with the invention, I prepare color photographic elements by coating in any order two or more differently sensitized silver halide emulsions, for example, sensitized to the blue, green and red, over one another, and, if desired, separated by inert or colored gelatin layers, 55 onto a suitable photographic support material such as films or sheets of cellulose acetate, cellulose mixed esters, cellulose nitrate, cellulose ether, synthetic resin materials such as polyesters, polyamides, etc., paper materials, glass plates, and the like. The preferred photographic color 60 element contains three differently sensitized silver halide emulsion layers in the order; a bottom red-sensitized layer next to the support, a middle green-sensitized layer and a top blue-sensitized layer. While combinations of the couplers of the invention and uncolored couplers may be 65 incorporated in any one or all of these layers, a preferred form of my invention is to include a suitable yellow colored coupler together with a suitable uncolored magenta forming coupler in the green-sensitized layer, a suitable 70 yellow colored coupler of the invention with an uncolored yellow forming coupler in the blue-sensitive layer and a suitable orange colored coupler with an uncolored cyan forming coupler in the red-sensitized layer. In such elements the green and red light-transmitting couplers of the invention which become magenta colored on hydrolysis 75

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naturally are of use in the blue-sensitive emulsion layer. Various other combinations of the couplers of the invention with other colored or colorless couplers which either form soluble or insoluble dye images in the exposed areas of emulsion layers may be used to good advantage in forming masking images.

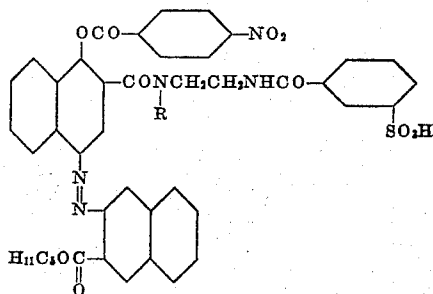
What I claim is:

1. The method of producing a masking image in a multilayer photographic element, at least one of which layers is a silver halide emulsion layer containing at least one uncolored color-forming coupler which is reactive with the oxidation product of a primary aromatic amino silver halide developing agent to form a non-diffusing dye in said layer and said layer further containing a yellow colored color-forming coupler having the general formula



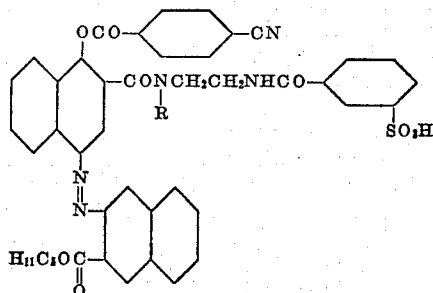
wherein R represents an aromatic group which renders the coupler non-diffusing in said layer, R₁ represents a strongly acidic alkali-solubilizing group and R₂ represents a member of the class consisting of cyanophenyl and nitrophenyl groups, which comprises exposing said element, hydrolyzing said coupler at the ester group to change its color to magenta, and developing the exposed element with said developing agent to split off the azo group of the hydrolyzed colored coupler and to form color images from said uncolored coupler and the hydrolyzed colored coupler in the exposed portions, thus forming a soluble dye from the hydrolyzed coupler which is removed from the emulsion layer leaving the uncoupled portion of said yellow-colored coupler in the emulsion layer as a magenta masking image.

2. The process of claim 1 wherein the yellow colored color-forming coupler has the formula



wherein R represents a member of the class consisting of hydrogen and p-nitrobenzoyl.

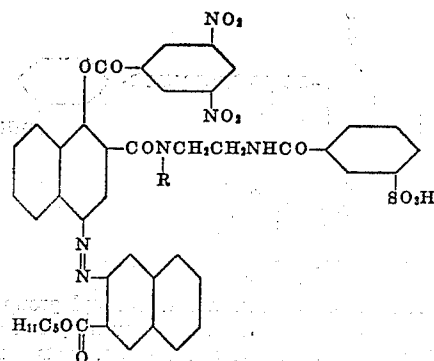
3. The process of claim 1 wherein the yellow colored color-forming coupler has the formula



wherein R represents a member of the class consisting of hydrogen and p-cyanobenzoyl.

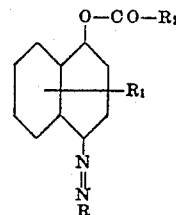
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4. The process of claim 1 wherein the yellow colored color-forming coupler has the formula



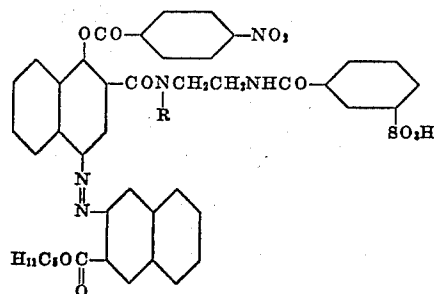
wherein R represents a member of the class consisting of hydrogen and 3,5-dinitrobenzoyl.

5. A multilayer photographic element at least one of which layers is a silver halide emulsion layer containing at least one uncolored color-forming coupler which is reactive with the oxidation product of a primary aromatic amino silver halide developing agent to form a non-diffusing dye in said layer, and a yellow colored color-forming coupler having the general formula



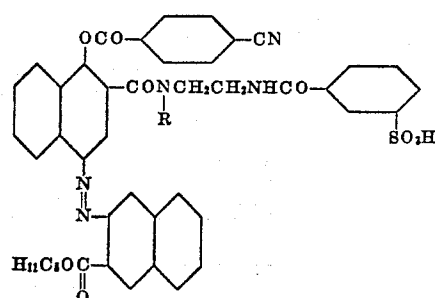
wherein R represents an aromatic group which renders the coupler non-diffusing in said layer, R₁ represents a strongly acidic alkali-solubilizing group and R₂ represents a member of the class consisting of cyanophenyl and nitrophenyl groups.

6. The element of claim 5 wherein the colored color-forming coupler has the formula



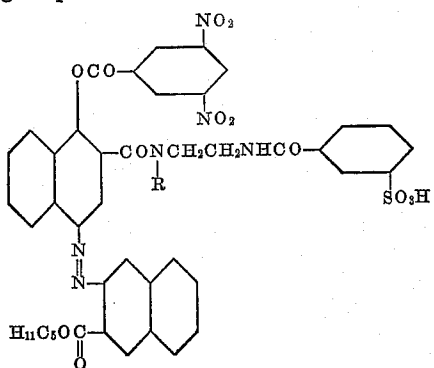
wherein R represents a member of the class consisting of hydrogen and p-nitrobenzoyl.

7. The element of claim 5 wherein the colored color-forming coupler has the formula



wherein R represents a member of the class consisting of hydrogen and p-cyanobenzoyl.

8. The element of claim 5 wherein the colored color-forming coupler has the formula



wherein R represents a member of the class consisting of hydrogen and 3,5-dinitrobenzoyl.

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