

[54] **DIFFUSION-RESISTANT PURPLE COLOR COUPLERS FOR THE PREPARATION OF PHOTOGRAPHIC COLOR PICTURES**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **96/100**

[51] **Int. Cl.**..... **G03c 1/40**

[58] **Field of Search**..... **96/100, 56.5**

[56] **References Cited**

UNITED STATES PATENTS

3,677,764	7/1972	Glockner et al.	96/56.5
2,983,608	5/1961	Beavers.....	96/100
3,127,269	3/1964	Greenhalgh et al.	96/100

FOREIGN PATENTS OR APPLICATIONS

1,035,959	7/1966	Great Britain.....	96/100
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[57] **ABSTRACT**

A color photographic material having a layer sensitized for green and containing developers for forming the purple image and containing an anilino-pyrazolone coupler.

2 Claims, No Drawings

DIFFUSION-RESISTANT PURPLE COLOR COUPLERS FOR THE PREPARATION OF PHOTOGRAPHIC COLOR PICTURES

BACKGROUND OF THE INVENTION

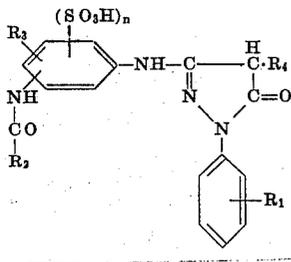
This invention relates to novel diffusion-resistant color components or couplers which react with oxidation products of developers of the p-phenylene diamine type to purple dyestuffs. They are employed in the green-sensitive layer of photographic materials, especially multi-layer color materials.

It is known that for purple components it is possible to use derivatives of 1-phenyl-3-anilino-pyrazolone (5), such as are disclosed in the U.S. Pat. Nos. 2,983,608 and 3,127,269, in the commonly owned U.S. application Ser. No. 849,498 filed Dec. 8, 1969, now U.S. Pat. No. 3,677,764, by Hans Glockner, Ernst Meier and Walter Puschel and in the Netherlands Pat. No. 6,413,277.

These patents disclose water-soluble and water-insoluble components. The water-insoluble couplers contain a diffusion-preventing radical, mostly bound by an acylamino grouping. According to known methods, such couplers are dispersed with the aid of wetting agents and if necessary oil formers into gelatin and in this form are added to the silver halide emulsion. The Netherlands Patent No. 6,413,277 discloses anilino-pyrazolone couplers wherein the diffusion-preventing radical is directly bound to the phenyl radical of the aniline group. In addition the couplers contain a sulfo group in the aniline radical. Such couplers may be added to the emulsion in the form of the aqueous solution of an alkali salt.

SUMMARY OF THE INVENTION

It has now been determined, according to the invention, that anilino-pyrazolones of the general formula:



are very well suited as color components for the preparation of purple color formers. In the above formula

R₁ is H or one or several substituents, customary to 1-phenyl-pyrazolones, such as alkyl-, alkoxy-, al-

kylothio-, phenoxy-, halogen-, carboxy-, sulfo acid-, alkylsulfonyl-, carbalkoxy-, carbamido-, sulfofluorido-, cyano-, nitro groups;

R₂ is alkyl, aryl, O-alkyl, O-aryl, NH-alkyl, NH-aryl, where alkyl and aryl may be substituted if necessary, and R₂ contains particularly a diffusion-preventing group in the form of one or several straight, branched or cyclic hydrocarbon radicals with collectively at least eight carbon atoms;

R₃ is H or halogen-, alkyl-, alkoxy-, alkylthio group; R₄ is H or a radical, separable in the developing, such as Cl, SO₃H or a substituted phenylazo group, as the case may be;

n is 1 or 2.

The novel purple components are advantageously distinguished over the known anilino-pyrazolone components in many respects. They contain an acylamino grouping which advantageously affects the photographic properties and by means of which the diffusion-preventing radical may be introduced in particular abundance. The sulfo group enables the introduction of the components into the photographic emulsion without special dispersion steps and without the aid of special dispersing additives. In this manner a high degree of dispersion is achieved with these couplers. In addition, the sulfo group affects exactly in the aniline radical in the advantageous manner the spectral properties of the purple coloring substances: Undesired secondary absorptions, in comparison to the unsulfonated components, are lessened, and the position of the absorption maximum may be affected depending at which point in the aniline radical the sulfo group is introduced. This last-named advantage shows up less in the absorption in solvents than in the use in the photographic layer.

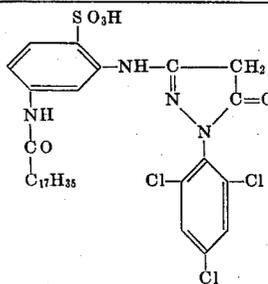
DETAILED DESCRIPTION OF THE INVENTION

As examples for the novel color components, the following are cited. The figures given signify the absorption maximum in mμ with N,N-diethyl-3-methyl-p-phenylene diamine in butanol.

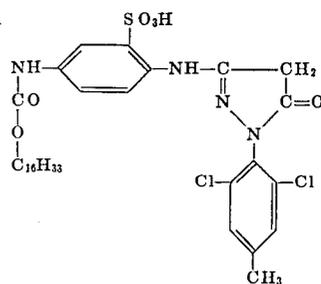
The novel purple components react very well with the oxidation product of all customary developers of the p-phenylene diamine type, such as for example N,N-diethyl-p-phenylene diamine, N,N-diethyl-3-methyl-p-phenylene diamine, 4-amino-3-methyl-N-ethyl-N-methane sulfonamidoethyl aniline, N-ethyl-N-β-oxyethyl-3-methyl-p-phenylene diamine, N-butyl-N-γ-sulfobutyl-p-phenylene diamine. The same holds true also for the instance of using the novel couplers in the form of phenylazo derivatives (masking coupler for negative materials, see U.S. Pat. No. 2,449,966).

The inventive couplers are found to be particularly advantageous when the acylamino grouping is present in the form of a derivative of carbamic acid.

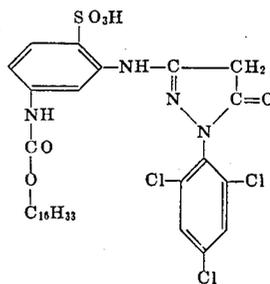
..... Absorptions, maximum: 535 mμ.....



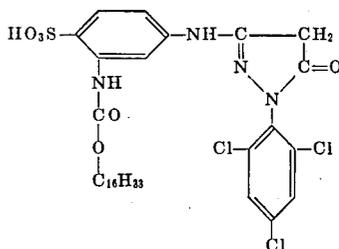
II..... Absorptions, maximum: 530 m μ



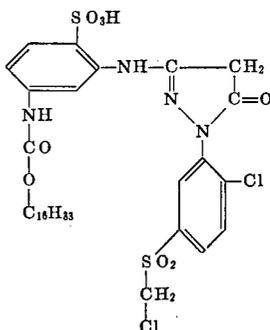
III..... Absorptions, maximum: 536 m μ



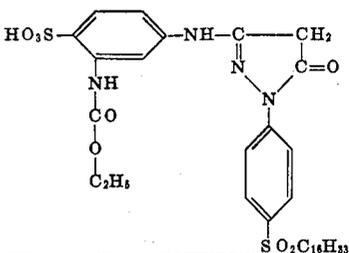
IV..... Absorptions, maximum: 534 m μ



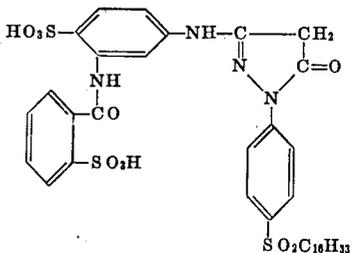
V..... Absorptions, maximum: 537 m μ



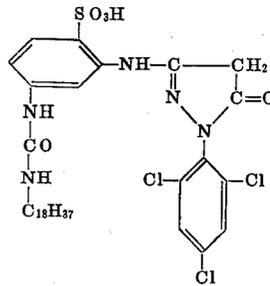
VI..... Absorptions, maximum: 543 m μ



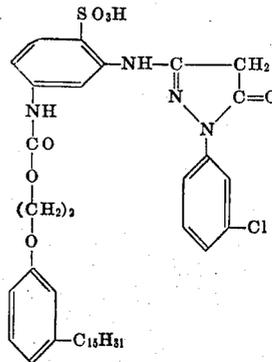
VII..... Absorptions, maximum: 536 m μ



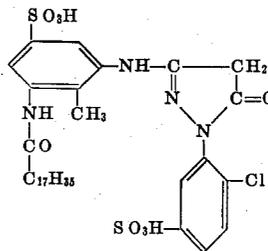
VIII..... Absorptions, maximum: 534.5 m μ



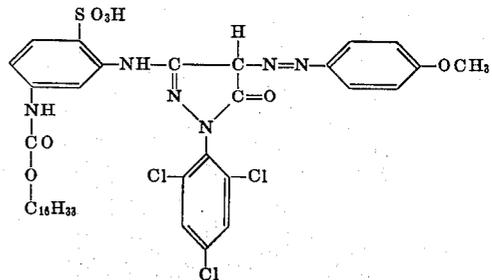
IX..... Absorptions, maximum: 530.5 m μ



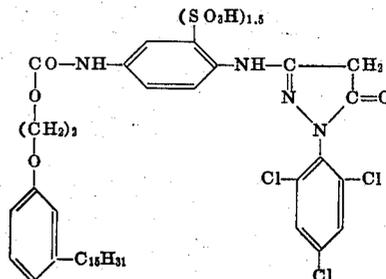
X..... Absorptions, maximum: 538 m μ



XI..... Absorptions, maximum: 536 m μ . Absorptions, maximum: 424 m μ (prior to uncoupling).



XII..... Absorptions, maximum: 532 m μ . Component contains 1.5 equivalent sulfo groups and is a mixture of mono- and disulfo acid.



The components of the invention may be used both in the negative/positive process as well as in the reverse process. The base for the layers may be both film as well as paper.

The preparation of the novel couplers may take place in accordance with known processes. For example, the unsulfonated couplers may be prepared first for which preparation there is a line of effective methods, as described in the British Patent Nos. 1,129,333, 1,129,334 and 1,134,329 and the commonly owned U.S. application Ser. No. 849,498 filed Dec. 8, 1969 by Hans Glockner, Ernst Meier and Walter Puschel.

These couplers are made by reacting an amino anilino pyrazolone with a chloroformic acid ester. Examples of suitable esters of the chloroformic acid are for instance the following: ethylester, 2-hexylnonylester, hexadecylester, 4-bromobutylester; cyclohexylester, tetrahydrofurfurylester; phenylester, p-

nitrophenylester, p-dodecylphenylester, n-pentadecylphenylester, 2,4-dichloro-6-tetradecylphenylester, octadecyloxyphenylester, p-chloro-o-tetradecylphenylester; p-butylphenoxyethylester, 2-butyl-4-nonylphenylester, m-pentadecylphenoxyethylester, p-dodecylphenoxypropylester, 4-chloro-3-methyl-6-tetradecylphenoxypropylester.

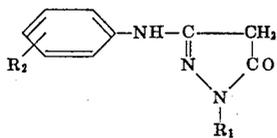
For example, 7.4 g of 1-(2',4',6'-trichlorophenyl)-3-(4''-aminoanilino)pyrazolone-(5) which has been described in U.S. Pat. No. 2,983,608, were dissolved while stirring in 35 ml pyridine and then reacted at 20°C with 8 g of 4-chloro-2-tetradecylphenylchloroformate. The temperature during this step rose to 40°C. Stirring was continued for 40 minutes without application of heat. The mass was then poured into a mixture of 50 ml of concentrated hydrochloric acid, 80 ml methanol and 80 ml ethylacetate and was stirred for 5 minutes. After adding 100 ml water, the ethylacetate layer was separated and shaken out with dilute hydrochloric acid and water. The solvent was removed by evaporation and the oily residue was taken up in petroleum ether, and the residue precipitated after cooling.

These couplers are then subjected in a known manner to a sulfonation process. Sulfonation agents, for example, are concentrated sulfuric acid or chlorosulfonic acid. In this connection, the sulfonation agent may be added to the unsulfonated coupler or also in reverse. Analytical investigation shows that the sulfonation preferably takes place in the aniline portion of the molecule. A sulfo group initially set in the 4-position of the molecule (coupling point) is again separated in the working up.

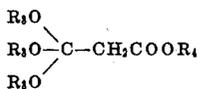
With this method of subsequent sulfonation, one obtains no homogeneous products but instead mixtures of position-isomeric mono- and disulfo acids. These mixtures may be separated into the individual constituents, by chromatography, for example. This separation process, however, is cumbersome and is mostly not required in the practice for employment of the components.

If homogeneous components according to the present invention are to be prepared wherein the placing of the components of the sulfo groups is clear, one must start with defined intermediate sulfonation products with respect to the pyrazolone synthesis. Unfortunately, in this instance, most of the known methods for the preparation of anilinopyrazolones fail. However, the reaction of aniline sulfo acids with β,β,β -trialkoxypropionic acid esters well achieves its goal.

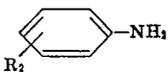
3-anilino-pyrazolone-(5) of the general formula



may be prepared by reacting a β,β,β -trialkoxy propionic acid alkyl ester of the general formula



with an aniline of the formula



and condensation of the intermediate product obtained with a hydrazine of the formula



In these formulae

R_1 is alkyl, aralkyl, aryl, if necessary substituted by one or several alkyl-, alkoxy-, alkylthio-, phenoxy-, halogen-, carboxy-, sulfo acid-, alkylsulfonic-, carbalkoxy-, carbamido-, sulfofluoride-, cyano-, nitro groups

R_2 is H or one or several substituents such as an alkyl-, alkoxy-, alkylthio-, halogen-, carboxy-, sulfo acid-, alkylsulfonic-, carbamido-, acylamino-, sulfofluorido-, cyano-, nitro group R_3 is short-chain alkyl with one to four carbon atoms, alike or R_4 different.

The β,β,β -trialkoxy propionic acid esters, used according to the invention, may also be designated chemically as semi-orthoesters of malonic acid. A compound of this sort of β,β,β -triethoxypropionates is described by McElvain, Schroeder, Am. Soc. 71, 1949, pp. 44-45. The corresponding trimethoxy propionic acid ethyl ester is very stable in pure form and may be employed particularly well according to the invention.

The particular advantage of the new process is that with the aid of such ortho esters, even acid anilines, such as sulfanilines for example, may be called upon with good yield for the synthesis of 3-anilinopyrazolones-(5).

Quite generally, the following anilines may for example be reacted with the orthoesters: Aniline, 4-chloroaniline, 2,4-dichloroaniline, m-toluidine, p-dodecylaniline, m-nitroaniline, sulfanilic acid, 2-amino-4-nitrobenzene sulfonic acid, 2-nitro-4-aminobenzene sulfonic acid, 2-nitro-4-chloro-5-aminobenzene sulfonic acid.

The reaction of the aniline with the orthoester takes place at temperatures between 20° and 100°C, preferably in the presence of glacial acetic acid. The yields of the intermediate product obtained, β -alkoxy- β -anilino acrylic acid ester, are nearly quantitative. In most instances, a purification with hydrazine prior to the reaction is eliminated.

Suitable hydrazines for a pyrazone synthesis are, for example, phenyl hydrazine, m-chlorophenyl hydrazine, 2,4,6-trichlorophenyl hydrazine, p-nitrophenyl hydrazine, 2-nitro-4-trifluoromethylphenyl hydrazine, 2-cetyloxyphenyl hydrazine, 4-hydrazino-phenylcetylfulfone, 4-chloro-5-hydrazino-phenylchloromethylsulfone, phenylhydrazine-m-sulfonic acid, ethyl-hydrazine, benzyl hydrazine, 2-chlorobenzyl hydrazine.

EXAMPLE 1

Purple Components of Formula III
First Step

1-(2',4',6'-trichlorophenyl)-3(3''-nitro-6''-sulfoanilino)-pyrazolone-(5) Na salt

A mixture of 48 g (0.2 mol) 2-amino-4-nitrobenzene-sulfonic acid sodium (dry and finely pulverized), 8.2 g (0.1 mol) sodium acetate (dry), 100 ml glacial acetic acid and 66 g (0.34 mol.) β,β,β -trimethoxy propionic acid ethyl ester were stirred at 80°C bath temperature until dissolved. Then the glacial acetic acid was distilled off under reduced pressure. The viscous residue was dissolved in 850 ml methanol and heated on a water bath with 42.3 g 2,4,6-trichlorophenyl-hydrazine.

After nearly everything is dissolved, 40 ml glacial acetic acid are added. After 15 minutes, the contents of the flask solidified to a thick crystal paste. The precipitate was drawn off after cooling and washed with methanol.

At the end of the pyrazolone cycle, the moist filter cake was mixed into 200 ml methanol and after addition of 2.5 mol-equivalent Na methylate was stirred for 90 minutes at room temperature. From the red solution, after acidifying with glacial acetic acid, there were precipitated 50 g nitroprazolone = 50 percent of the theoretical.

Second Step

1-(2',4',6'-trichlorophenyl)-3-(3''-amino-6''-sulfoanilino)-prazolone-(5)

50 g Nitro compound from Step 1 were introduced into 100 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with 200 ml HCl concentrated at 85°-100°C during stirring. The stirring was continued at 95°C for another 15 minutes after the completion of the reaction. The white precipitate was drawn off upon cooling and washed with 20 percent HCl. The moist crude product was mixed with methanol and again drawn off. The free amine was obtained by dissolving in water/alkali and precipitating with an excess of glacial acetic acid.

Yield: 36 g = 80 percent of the theoretical.

Third Step

Purple Component Formula III

To a solution of 22.5 g aminopyrazolone in 80 ml pyridine there were added while stirring 18 g of chloro-formic-acidcetyl-ester and heated to 50°C for one hour. The pyridine solution was poured over 300 ml 12 percent HCl, the precipitated deposit drawn off and washed with thinned HCl and water. The dried crude product was dissolved in methanol with the addition of pyridine. The filtered solution was acidified with hydrochloric acid to pH 1. The precipitated coupler was drawn off and washed with methanol.

Yield: 23.5 g.

Photographic Application of the Color Component

First, a solution of the coupler was prepared in the customary manner in that it was suspended in methanol and mixed with thinned soda lye. This solution was added to a silver halide emulsion. Thereupon, it was poured on a carrier and dried. The photographic film obtained was illuminated under a stepped photometric absorption wedge and was subjected to a color negative developing process. The developing substance was N,N-diethyl-3-methyl-p-phenylenediamine. Thereupon, the film was treated in a bleaching solution and in a fixing solution and dried. Obtained was a negative purple picture. Absorption maximum 540 m μ .

If the film is subjected to a color reversal process after exposure, there is obtained a corresponding positive purple picture.

EXAMPLE 2

The color component of Formula IV is obtained if in the preparation process of Example 1 the compound 2-amino-4-nitrobenzenesulfonic acid is replaced by the isomeric 4-amino-2-nitrobenzenesulfonic acid. The component obtained may be employed accordingly.

After the development of both color components III and IV in a photographic silver halide film, the following absorption maxima were measured with various color developing substances:

Developing substance	Component III	Component IV
N,N-diethyl-p-phenylene diamine	533 m μ	520 m μ
N,N-diethyl-3-methyl-p-phenylenediamine	540 m μ	527 m μ
4-amino-3-methyl-N-ethyl-N-methane sulfonamidoethyl anilin	539 m μ	515 m μ

As shown by this table, the absorptions with respect to component IV as compared to the position-isomeric component III have a shift toward shorter waves.

EXAMPLE 3

Purple Component of Formula XII

160 g Unsulfonated purple component according to Example 3 of the U.S. Appln. Ser. No. 849,498 referred to above were finely ground and introduced in 96 percent into 400 ml sulfuric acid at 20°C during stirring. After stirring at room temperature for 4 hours, the solution was stirred into 4.5 l water. The precipitated deposit was separated and dissolved in 4 l hot water. By the addition of 400 ml HCl conc., the component is again precipitated. After repeated dissolving and reprecipitating, no further SO_4 ions could be detected. The separated precipitate was dried and finely ground. After another drying under reduced pressure, 170 g of the component were obtained.

By analytical investigation it was determined that the sulfonation had taken place in the aniline radical of the molecule and that a mixture exists consisting of mono- and disulfonic acids. The SO_3H content was yielded in 14.7%; this corresponds to about 1.5 SO_3H equivalents.

The components may be dissolved in water in the customary manner with the aid of alkali. Added to a silver halide emulsion and further treated as described in Example 1, with the color developer 2-amino-5-diethylaminotoluol obtained is a purple picture with absorption maximum 530 m μ .

EXAMPLE 4

Screened Component of Formula XI

12.3 g (0.1 mol) p-anisidin, 150 ml HCl 5n and 60 ml H_2O were diazotized at 0°C with 6.9 g (0.1 mol) NaNO_2 and 20 ml H_2O . The diazonium solution was allowed during stirring to flow into a solution of 82.5 g components of Example 1 (Formula III) in 1400 ml pyridine. After 30 minutes at room temperature, it was stirred into a mixture of 2000 ml HCl conc. and 3 kg ice. The precipitate was drawn off and washed well with thinned HCl and H_2O . The dry crude product was stirred for purification with methanol at a water bath. Yield: 65 g

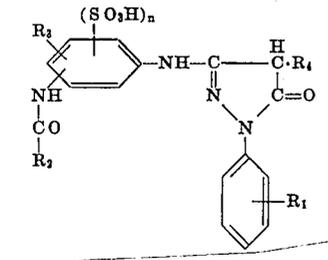
The component, a yellow-colored azo dyestuff, has an absorption maximum of 424 m μ (screened component).

For photographic application, the screened component was dissolved in water as lithium salt and incorporated in a green-sensitive negative emulsion. The emulsion was poured as a partial layer of a multi-film negative material. Dried and pictorially illuminated with green light; after customary processing in a color negative process - using 4-amino-3-methyl-N-ethyl-N-methane sulfonamidoethyl aniline as the developing substance - obtained was a negative purple picture. Absorption maximum: 539 m μ . At the same time there remains a positive yellow image which gradation is counter-current to the gradation of the purple image thus

eliminating the blue absorption of the corresponding purple dye image. It is noteworthy the good coupling of the masking coupler as well as the good stability of the mask in the bleaching bath.

What is claimed is:

1. In a photographic silver halide emulsion layer optically sensitized to the green region of the spectrum and containing developers that form purple dyestuffs, the improvement according to which the emulsion contains a coupler component of the following formula:



In this formula

R_1 is H or an alkyl-, alkoxy-, alkylthio-, phenoxy-, halogen, carboxy-, sulfo acid-, alkylsulfonyl-, carbalkoxy-, carbamido-, sulfofluorido-, cyano-, nitro group;

R_2 is alkyl, aryl, O-alkyl, O-aryl, NH-alkyl, NH-aryl, wherein R_2 has a diffusion-preventing group in the form of one of several straight, branched or cyclic hydrocarbon radicals with collectively at least 8 carbon atoms;

R_3 is H or halogen-, alkyl-, alkoxy-, alkylthio group;

R_4 is H, Cl, SO_3H , phenylazo;

n is 1 or 2.

2. In a photographic silver halide emulsion as defined in claim 1, a mixture of mono- and disulfo- acids of the coupler component.

* * * * *