ABSTRACT: A color photographic material having a silver halide emulsion layer containing a nonperformed development-inhibiting-releasing compound of the tetrazole class which is noncolor forming.
PHOTOGRAPHIC MATERIAL USING SPLITTABLE COUPLERS

The principle of adding to photographic layers substances that are split off in areas corresponding to the image in the course of development so that the properties of the original substance are altered and new substances with new properties occur in areas corresponding to the image has been known for a long time.

This group of substances includes, for example, the colored color couplers which contain at the coupling position a colored azo group which is split off at the exposed areas upon reaction with the oxidation product of the developer. The residue of the color coupler undergoing coupling to form a dye while the residue which contains the azo group is eliminated. The original dye remains in the unexposed areas. A new dye is formed in the exposed areas.

Furthermore, color couplers are already known which contain two-color coupler molecules connected together at the coupling points by thioether or dithioether bridges. These color couplers are diffusion resistant. During development, the thioether bridge is split by reaction with the oxidized developer. In this process, one part of the connected together molecules gives rise to a color coupler which is converted into a dye by coupling with the developer oxidation product, while a compound containing a mercapto group is formed from the other part of the molecules.

The above reaction principles were later used in color couplers which contain in their molecules a development inhibiting moiety capable of being split off by the oxidation product of a silver halide developer. Color couplers of this type are known as DIR couplers or development-inhibitor-releasing couplers. The development inhibitor acts only in the exposed areas, thereby causing a flattening of the gamma value and improvement in the grain size, and hence the sharpness. The utility of DIR couplers is, however, limited since they have to be incorporated in a diffusion-resistant manner and the color coupler residue of the whole molecule must be carefully selected and controlled to achieve the correct color balance in the photographic material. Owing to the specific absorption properties required in the resulting dye, the choice is restricted.

It is among the objects of the present invention to provide photographic materials which contain compounds that split off development inhibitors upon development in the exposed areas, but do not contain a color coupler moiety.

We now have found a photographic material with at least one light-sensitive silver halide emulsion layer which contains in that emulsion layer or an adjacent layer, a compound that reacts with oxidized developer to split off development inhibitors, the reaction products being colorless or are converted into colorless substances in the course of the photographic process so that they do not form part of the final photographic color image obtained.

Such compounds have the following formula:

\[
R - X - C - S - Y
\]

wherein

Y represents a group that when split off with the sulfur atom of the thioether bridge as a mercapto compound, e.g. a heterocyclic mercapto compound; has a development inhibiting effect, for example a tetrazole, especially that forms 1-phenyl-5-mercapto tetrazole, 1-nitrophenvyl-5-mercapto tetrazole or 1-naphthyl-5-mercapto tetrazole; a thiazole such as one that forms 2-mercapto benzthiazole, or a mercapto naphthiazole; or an oxadiazole; a pyrimidine; a series, from the mercapto thiadiazole such as one that forms a 2-mercapto thiadiazolotriazine; a triazine; a series, or from the mercapto triazole; a benzene such as one that forms thiophenole, 1-mercapto-2-benzoic acid, 1-mercapto-2-nitrobenzene or 1-mercapto-3-heptadecanlyaminobenzene; also a thiglycolic acid, cysteine or glutathione; R stands for (1) hydrogen or (2) alkyl with preferably up to 18 carbon atoms, (3) aralkyl such as benzyl or phenylethyl, (4) cycloalkyl such as cyclohexyl; (5) aryI, especially an aryl radical of the phenyl or naphthyl series; (6) a heterocyclic radical having five or six ring members which may contain one or more hetero atoms such as N, O, S or Se and benzene or naphthalene rings fused thereto, e.g. benzoxazole or benzothiazole; (7) the grouping —S—Y or (8) the grouping X.

X is one of the following groups which activates the carbon atom to which X, R and S—Y is attached, such as

\[
\begin{align*}
C - R, \quad C - CNI, \quad C - CNI C - CNI C - CNI C - CNI C - CNI C - CNI C - CNI C - CNI
\end{align*}
\]

...-SO\(_2\)R, -SO\(_2\)N(R)\(_2\), -CN, [-N(R)\(_2\)]\(^{2-}\), or the grouping S—Y.

R\(_1\) represents (1) a saturated or olefinically unsaturated aliphatic radical having up to 18 carbon atoms, preferably up to five carbon atoms, which may, if desired, be substituted, e.g., with hydroxyl, alkoxy or aryI, especially benzene, such as benzoI, phenylethyl, or styryl; (2) aryl, preferably phenyl or naphthyl, the phenyl rings of which may be substituted, for example, with alkyl having preferably up to 20 carbon atoms, alkoxy, halogen such as chlorine or bromine, nitrile et., or (3) a five- or six-membered heterocyclic radical which may contain one or more hetero atoms as ring members, such as N, O, S, or Se which may have benzene or naphthalene rings fused thereto; two of substituents R\(_1\), for example, in the grouping [-N(R)\(_2\)]\(^{2+}\) or -SO\(_2\)N(R)\(_2\), may represent together the ring members necessary for completing a saturated five- or six-membered nitrogen containing ring, such as piperidine, pyrrolidine, or morpholine.

Particular utility is exhibited by the following compounds:
(10)\[\text{Structural formula for compound 10}\]

(11)\[\text{Structural formula for compound 11}\]

(12)\[\text{Structural formula for compound 12}\]

(13)\[\text{Structural formula for compound 13}\]

(14)\[\text{Structural formula for compound 14}\]

(15)\[\text{Structural formula for compound 15}\]

(16)\[\text{Structural formula for compound 16}\]

(17)\[\text{Structural formula for compound 17}\]

(18)\[\text{Structural formula for compound 18}\]

(19)\[\text{Structural formula for compound 19}\]
The compounds of the present invention must not deleteriously affect the photographic properties of the silver halide emulsion. For example, they have to be stable during the preparation of the photographic layers. The development inhibiting moeity must not split off in the photographic layer before exposure, for instance by hydrolysis, since otherwise the sensitivity of the emulsion layer is considerably reduced. For this reason compounds which have a carboxyl or an esterified carboxylic group as activating group at the carbon atom to which —S—Y or R are linked, for example 1-phenyl-5-carboxymethylthiotetrazole, are of no practical use.

The stability of the compounds of the invention in the hydrophilic photographic layer is particularly important because the compounds are applied in a relatively high amount as compared with the usual quantities of stabilizers or antifoggants added to photographic layers.

The amount of the compound of the invention in the photographic layer can vary within wide limits depending on the velocity with which the development inhibiting moeity is split off, and depending on the efficacy of the development inhibitor which is split off. Generally amounts between 1–15 g. per kg. silver halide emulsions have proved sufficient. Optimum amounts can easily be determined by tests customarily employed in the art. Preferred are concentrations of 4–10 g. per kg. emulsion. It is self-explanatory that the concentration of the compounds further depends on the desired effect, in particular with respect to the desired reduction of the γ-value.

The compounds are prepared in well-known manner.

The preparation of a number of the compounds which may be used in accordance with the invention is described below:

**Compound 1**

20 g. of 2-chloroacetyl-β-cresol and 21.8 g. of 1-phenyl-5-mercapto-tetrazole sodium salt are heated under reflux in 250 cc. of acetone for 15 minutes. Sodium chloride which precipitates is removed by filtration under suction and the filtrate is concentrated by evaporation. The reaction product which crystallizes out is recrystallized from acetone. Yield: almost quantitative. m.p. 145°–146°C.

**Compounds 2 to 8** are prepared in a similar manner.

**Compound 2** can be prepared either from α-chloroacetophenone and the sodium salt of 1-phenyl-5-mercaptotetrazole or from acetoephene and the sulfenyl chloride of 1-phenyl-5-mercaptop-tetrazole.

**Compound 9**

p-Isododecyl-α-chloroacetophenone is prepared first. 105 g. of finely powdered aluminum chloride are added in the course of 30 minutes to a solution of 186 g. of isododecyl-benzene, 100 g. of chloroacetyl chloride and 300 cc. of carbon disulfide. The reaction mixture is heated for 2 hours on a water bath, carbon disulfide is distilled off, and 600 g. of ice, 300 ml. of water and 60 cc. of concentrated hydrochloric acid are added to the residue. The reaction product is taken up in ether and the extract is shaken with aqueous soda solution and then washed with water until neutral. After drying, the ether is distilled off and the residue is distilled under a high vacuum.

b.p. a.s.m., approximately from 170°C. upwards.

Yield: 160–200 g.

160 g. of p-isododecyl-α-chloroacetophenon and 100 g. of 1-phenyl-5-mercapto-tetrazole sodium are heated under reflux for 30 minutes in 500 ml. of absolute acetone. The sodium chloride that precipitates is suction-filtered and the filtrate is concentrated by evaporation until it is a viscous oil.

Yield: approximately 225 g.

To remove any traces of 1-phenyl-5-mercapto tetrazole present, the reaction product is dissolved in chloroform and the solution obtained is briefly heated with a little silver bromide. The product is then filtered and the filtrate again concentrated by evaporation.

**Compounds 10 to 12** are prepared in a similar manner.

**Compound 13**

To 150 ml. of pyridine, 43.6 g. (0.2 mol) of lauric acid chloride are slowly added dropwise at room temperature with stirring. The reaction mixture is then stirred for another 2 hours and heated for a further 1 hour at 50° to 60°C. and is finally poured onto a mixture of ice and concentrated hydrochloric acid. The precipitate is suction-filtered and recrystallized from methanol.

m.p. 104°–105°C.

A solution of 10.8 g. of 1-phenyl-5-tetrazolyl-sulfenyl chloride in absolute carbon tetrachloride is added to a solution of 15.8 g. of p-lauroyl-amino-acetophenone in absolute carbon tetrachloride. The mixture is left to stand overnight and the precipitate formed is separated by filtration under suction and recrystallized from methanol.

m.p. 138°–142°C.

**Method B**

The same compound may also be prepared satisfactorily from compound 13 and lauric acid chloride. Melting points and IR spectra are identical.

The photographic materials according to the invention are suitable both for use in the production of black-and-white photographs, and more particularly for the production of color photographs.

The additives which contain the residue that inhibits development may be added in various forms to the photographic material. They may be employed in a diffusion-fant or diffusible form in solution or in emulsion. The most advantageous method of usage depends in each case on the purpose for which the additive is to be used, and can easily be determined by simple tests.

Light-sensitive layers which may be used include any of the usual silver halide layers in which the light-sensitive silver halides are dispersed in the usual hydrophilic binders, preferably in gelatin.

The light-sensitive layers preferably contain the usual color couplers capable of reacting with the oxidation products of the developers to form dyes. The light-sensitive layers may be optically or chemically sensitized in the usual manner and contain the usual stabilizers and other additives.

Developer mixtures of the usual composition containing developer substances which have at least one primary aromatic amino group, preferably developers of the p-phenylenediamine series, e.g., N,N-diethyl-p-phenylenediamine; N-ethyl-N-α-sulfoethyl-p-phenylenediamine; 2-amino-5-diethylaminotoluene; p-amino-N-ethyl-N-β-hydroxyethylaniline, may be used for the development of the exposed silver halide emulsion layers according to the invention.

**Example I**

Layer I

1 g. of compound 1 is dissolved in 1 cc. of dibutyl phthalate and 6 cc. of ethyl acetate and emulsified in 40 cc. of 7.5 percent gelatine with the addition of 2 cc. of a 2 percent solution of dodecylbenzenesulfonate. The emulsion is mixed with 40 cc. of a light-sensitive silver iodobromide gelatine emulsion (5 mols percent AgI) and applied onto a support of cellulose acetate.

Layer thickness: 5/μ.

Layer II

For comparison, 1 cc. of dibutyl phthalate, 6 cc. of ethyl acetate and 40 cc. of 7.5 percent gelatine are emulsified and the emulsion is mixed with 40 cc. of the same light-sensitive silver halide emulsion and poured over a support as above.

The above two layers are processed as follows:

a. exposed in a sensitometer customarily employed in the art behind a step wedge and developed for 8 minutes at
20°C. in a color-forming developer solution of the following composition:

N,N-diethyl-p-phenylencadmiuminosulfate 2.5 g.
Anhydroous sodium sulfate 2.0 g.
Potassium bromide 1.0 g.
Anhydroous potassium carbonate 75.0 g.
p-Nitrosoazobenzene as magenta coupler 0.7 g.
Water up to 1 liter.

The samples are bleached in a 10 percent potassium ferricyanide solution after the usual intermediate rinsing, and then fixed in a sodium thiosulfate solution. A magenta dye image is obtained, the sensitivity of which is the same in both cases. The \( \gamma \)-value of layer II (without additive) amounts to 0.95; the \( \gamma \)-value of layer I (with additive) however, is reduced to 0.4.

b. Layers I and II are developed in a developer solution of the following composition:

- p-Methylaminophenol 0.7 g.
- Hydroquinone 2.5 g.
- anhydroous sodium sulfate 10.0 g.
- anhydroous potassium carbonate 25.0 g.
- potassium bromide 1.0 g.

and fixed in a 20 percent sodium thiosulfate solution. In this case, the development is not effected. Gamma and sensitivity are identical in the two layers.

Example 2

Layer I
6.5 g. of compound 9 are dissolved in 30 cc. of ethyl acetate and 7 g. of dibutylphthalate and emulsified in 150 cc. of gelatine. 130 cc. of the emulsion are mixed with 1 kg. of a light-sensitive silver bromide gelatine emulsion. 400 cc. of a 4 percent solution of a cyan coupler 1-hydroxy-2'(2'-hydroxy-N,N-dimethyl-N-octadecyl)-amino-5'-sulfo-1,2-naphthanilide are added to this mixture, and the mixture is applied onto a cellulose triacetate support.

Layer II
A comparison layer II is prepared under the same conditions with the color coupler only. The layer thickness is so adjusted that in black-white development according to example I(b), layer I is developed to a \( \gamma \)-value of 0.8 but layer II is only developed to a \( \gamma \)-value of 0.5.

The exposed material was developed in a color-forming developer solution of the following composition:

- 4-Amino-N,N-diethylaminomaleimide 2.5 g.
- anhydroous sodium sulfate 2.0 g.
- potassium bromide 1.0 g.
- anhydroous potassium carbonate 75.0 g.
- water up to 1 liter.

A cyan dye image is obtained. In spite of the different silver application, the same sensitivity and the same \( \gamma \) are obtained in both cases. The dye image of layer I shows a considerably finer grain.

Example 3

Layer I
10 g. of compound 71 are dissolved in 30 cc. of ethyl acetate and are emulsified in 160 cc. of a 10 percent aqueous gelatin solution. 70 cc. of the above emulsion and 19 g. of the magenta-forming colorless coupler I(2'-hexadecylthio)-phenyl-3-(2'-sulfo-benzoylamino)-pyrazolone-(5) are added to 1 kg. of a silver bromide gelatine emulsion which is sensitized to green light. The mixture is applied onto a cellulose triacetate support and dried.

Layer II
For a comparison test another layer is prepared under the same conditions but with the color coupler only.

Example 4

Layer I
10 g. of compound 9 were dissolved in 30 cc. ethyl acetate and emulsified in 160 ml. of a 10 percent aqueous gelatin solution. 180 cc. of the emulsion and 17 g. of the yellow-forming coupler 3-stearoyl-amino-benzyl(2-methoxy-5-sulfo)-acet-anilide are added to 1 kg. of an unsensitized silver bromide gelatine emulsion. The mixture is applied onto a cellulose triacetate support and dried.

Layer II
For a comparison test another layer is prepared under the same conditions but with the color coupler only.

Layer I and II are processed as described in example 2.

The yellow dye image obtained in layer I shows a reduced \( \gamma \)-value by about 40 percent as compared with the \( \gamma \)-value of the yellow image produced in layer II.

Example 5

This example shows the efficacy of the compounds of the invention with respect to the so-called interimage effect.

Photographic material I
70 cc. of the emulsion of compound 71 described in example 3 and 20 g. of the cyan forming coupler 1-hydroxy-2'-(N-methyl-N-octadeayl)-amino-5'-sulfo-1,2-naphthanilide are added to 1 kg. of a silver bromide emulsion containing 3.5 mol percent of silver iodide which is sensitized to red light. The above emulsion is applied onto a cellulose triacetate support.

Ointo the red-sensitive emulsion layer is applied a green-sensitive silver bromide gelatine emulsion which is described as layer III in example 3.

The green-sensitive emulsion layer is coated with a yellow filter layer and onto the yellow filter layer is applied a blue-sensitive silver bromide gelatine emulsion layer containing per kg. 18 g. of the yellow forming coupler 2-(4'-benzoylacetamino-phenyl)-1-octadecylbenzimidazole-5-sulfonic acid.

Photographic material II
For comparison purposes a photographic material is produced which is identical with the above material I with the exception that the red-sensitive layer contains the color coupler only and no compound of the invention.

Processing
The material is processed as described in example 2. Material II if exposed to green light as compared with day light shows a 10 percent reduced \( \gamma \)-value.

The magenta partial image produced with material I shows an increase in the \( \gamma \)-value if exposed to green light by 30 percent as compared with the magenta image obtained by exposure with day light.

Example 6

This example shows the improved reproduction in true colors with a photographic material containing compounds of the present invention.

Photographic material I
A cellulose triacetate support is coated with the following layers:

a. the red-sensitive layer II of example 5;

b. a green-sensitive silver bromide emulsion layer containing per kg. 15 g. of the magenta forming coupler 1-(3'-
sulfo-4′-phenoxy-phenyl)-3-stearoylamino-pyrazolone-(5) and 80 cc. of an emulsion of compound No. 69(10 g. of compound No. 69, dissolved in 30 cc. ethyl acetate emulsified in 160 ml. of a 10 percent aqueous gelatine solution);

c. a yellow filter layer;
d. the blue-sensitive layer II of example 4.

Photographic material II:
The material is identical with material I, with the exception that the green-sensitive silver halide emulsion layer contains the magenta-forming coupler only.

The above materials are exposed and processed as described in example 2.

The red-sensitive layers of the above materials were sensitized in such a manner that they respond also in minor degree to green light. The color reproduction is far better with photographic material I as compared with material II. The sensitivity difference between the green-sensitive and the red-sensitive layer is increased by 2–3° DIN in photographic material I which results in a far better color separation.

This effect is shown in FIG. 1. The axis of ordinates is the density plotted against log 1/f as the axis of abscissa. Curve 1 represents the characteristic curve of the magenta image of materials I and II. Curve 2 represents the characteristic curve of the cyan image of material II, while curve 3 represents the characteristic curve of the cyan image of material I.

Example 7

This example shows the action of a compound of the invention if added to the developed solution.

1. Color forming development

A photographic material containing a silver bromide gelatine emulsion layer, is exposed in a sensitometer customarily employed in the art through a grey step wedge. Four samples of the exposed material are developed in color-forming developers of composition A–D shown in the following table. The development time is 8 minutes. The development temperature is 20° C. After the development they are bleached and fixed in usual manner.

<table>
<thead>
<tr>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
</tr>
<tr>
<td>N,N-diethyl p-phenylenediamine H2SO4</td>
</tr>
<tr>
<td>sodium sulfite</td>
</tr>
<tr>
<td>potassium bromide</td>
</tr>
<tr>
<td>potassium carbonate</td>
</tr>
<tr>
<td>hydroxyamine HCl</td>
</tr>
<tr>
<td>magenta-forming coupler</td>
</tr>
<tr>
<td>compound No. 32</td>
</tr>
<tr>
<td>water up to</td>
</tr>
</tbody>
</table>

FIG. 2 shows the characteristic curves of the magenta image obtained by development with the above color-forming developers. The γ-reducing effect of compound No. 32 is readily apparent, the effect being greater the higher the concentration of compound No. 32. The sensitivity of the layers remains constant.

2. Black-and-White Development

In order to show that the compounds of the invention are only effective with color-forming developers, the above material is exposed in the same manner and four samples are developed for 5 minutes at 20° C. with the black-and-white developers of the following table.

<table>
<thead>
<tr>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
</tr>
<tr>
<td>p-methylaminophenol</td>
</tr>
<tr>
<td>hydroquinone</td>
</tr>
</tbody>
</table>

The silver images obtained have identical γ-values, the sensitivity is not reduced. The fog is negligibly increased.

We claim:

1. A light-sensitive color photographic material capable of development inhibition in areas subjected to light exposure without adding color to the image comprising at least one support light-sensitive silver halide emulsion layer which contains a nonpreformed development-inhibitor-releasing compound having the formula

R X—C—S—Y

wherein

Y represents a group that has a development-inhibiting effect if the sulfur atom of the thioether bridge is split off to release a heterocyclic mercapto compound, an aryl mercapto compound, a compound from the thioglycolic acid series, cysteine or glutathione;

R stands for hydrogen, alkyl, aralkyl, cycloalkyl, aryl, a heterocyclic radical having five or six ring members, or the grouping —S—Y;

X stands for

—C—R1, —CONH2, —CONHR1, —CON(R)2, —SO2H, —SO2R1, —SO2OH, —SO3H, —SO2OH, —SO3H, —SO3H, —SO3H, —SO3H, or the group —S—Y.

R1 represents a saturated or olefinically unsaturated aliphatic radical having up to 18 carbon atoms; aryl or a five- or six-membered heterocyclic radical; two of substituents R1 may represent together the ring members necessary for completing a saturated five- or six-membered nitrogen containing ring; the nonpreformed development-inhibitor-releasing compound being such that reaction with the oxidation product of a primary aromatic amino silver halide developer forms a colorless development inhibitor and a substantially colorless compound.

2. The composition of claim 1, wherein the development-inhibiting compound is contained in the silver halide emulsion layer in an amount of 1–5 g. per kg. of silver halide emulsion.

3. The composition of claim 2, wherein cyclic ring from the tetrazole series, the triazole series, the oxadiazole series, the pyrimidine series, the thiazole series, the triazine series or triazole series or phenyl which may be substituted with carbocyclic, nitro- or an acylated amino group.

4. The composition of claim 2, wherein the development-inhibitor-releasing compound forms the development inhibitor 1-phenyl-5-mercapto tetrazole.

5. The composition of claim 2, wherein the development-inhibitor-releasing compound is
6. The composition of claim 2, wherein the development-inhibitor-releasing compound is

7. The composition of claim 2, wherein the development-inhibitor-releasing compound is

8. The composition of claim 2, wherein the development-inhibitor-releasing compound is

9. The composition of claim 2, wherein the development-inhibitor-releasing compound is
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the drawing, "Ulrich HeB" should be -- Ulrich Hess -- .
On the front page, under [72] Inventors, "Ulrich HeB" should be -- Ulrich Hess -- .
Also on the front page, under the Abstract, line 2, "nonperformed" should be -- nonpreformed -- .

Signed and sealed this 27th day of June 1972.

EDWARD M. PLETCHER, JR.  ROBERT GOTTSCALK
Attesting Officer  Commissioner of Patents
CERTIFICATE OF CORRECTION

Patent No. 3,632,345 Dated January 4, 1972
Inventor(s) Paul Marx 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 1, line 18, delete the hyphen between "two" and "color".
Column 2, line 15, delete "series, from the mercapto".
Column 2, line 17, delete "series, or from the mercapto".
Column 21, formula 85, change the tetravalent "0" to -- C -- .
Column 27, line 31, change "developed" to -- developer -- .
Column 28, claim 2, line 52, change "1-5 g" to -- 1-15 g -- .

Signed and sealed this 21st day of November 1972.

(S Seal)
Attest:
EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents