# United States Patent

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[73] Assignee **Gevaert-AGFA**
**Mortsel, Belgium**
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[33] **Great Britain**
[31] **20,343/66**


[54] **SILVER HALIDE DIRECT POSITIVE EMULSIONS SPECTRALLY SENSITIZED WITH A COMBUSTION OF A DESENSITIZING DYE WITH A 2-PHENYLINDOLE METHINE DYE**
**6 Claims, No Drawings**


[52] **U.S. Cl.** ..... **96/104,** 96/101, 96/64
[51] **Int. Cl.** ..... **G03c 1/28**
[50] **Field of Search** ..... 96/101, 107, 104



[56] **References Cited**

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| 3,314,796 | 4/1967 | Gotze et al. | 96/101 |
| 3,364,026 | 1/1968 | Rees | 96/101 X |



*Primary Examiner*—Norman G. Torchin
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**ABSTRACT:** A direct-positive photographic silver halide emulsion for use in a solarization technique comprising a light-sensitive silver halide which has been fogged by light or chemical means and includes a spectrally sensitizing methine dye of the 2-phenylindole type in combination with a desensitizing nitrostyryl or nitrobenzylidene dye is described. In contrast to a direct-positive photographic silver halide emulsion containing only the 2-phenylindole type dye or nitrostyryl or nitrobenzylidene dye, the combination provides improved stability on storage, lower minimum densities, and increased total speed.

# SILVER HALIDE DIRECT POSITIVE EMULSIONS SPECTRALLY SENSITIZED WITH A COMBUSTION OF A DESENSITIZING DYE WITH A 2-PHENYLINDOLE METHINE DYE

This invention relates to light-sensitive direct-positive emulsions, more particularly to direct-positive emulsions, which possess an improved light-sensitivity in the visible spectrum.

It is known that positive photographic images can be obtained without previously forming a negative silver image, by applying e.g. the solarization effect and the Herschel effect.

Solarization is a reversal phenomenon, which is produced by overexposure of a silver halide emulsion layer. It is supposed that said overexposure results in the destruction of previously formed developing centers. The preparation of a solarized emulsion for the production of direct positives consists in producing a uniform latent image corresponding to the critical exposure. This can be realized by overall exposing the light-sensitive emulsion to actinic light or by appropriate overall chemically fogging it with reducing substances.

According to the Herschel effect a latent image can be reversed by a second exposure to red or infrared light. The sensitive layer is first fogged uniformly to its maximum density with blueviolet light and is imagewise exposed e.g. behind a positive transparency, with light of a wavelength greater than 600 nm., preferably at low intensity and for a long time. If the photographic material is treated with a so-called "desensitizing dye," the Herschel effect may be obtained with light of a shorter wavelength such as yellow light.

From the foregoing it is clear that the production of direct-positive images can proceed according to two different techniques, one of which being based on the solarization technique and the other on the Herschel effect. In both processes an increase in sensitivity was pursued.

In the direct-positive emulsions for use according to the solarization technique spectral sensitizers known for spectrally sensitizing silver halide emulsions of the negative type cannot be used since in said positive emulsions they show disadvantages as for example, discoloration of the white areas, a general flattening of the gradation curve and/or rise in density in the exposed parts immediately after exposure or on storage.

To remedy these defects, special types of spectrally sensitizing dyes have been proposed, an important class of which is formed by the methine dyes of the 2-phenyl-indole series. Dyes of that type are e.g. described in the United Kingdom Pat. Specifications Nos. 825,965 filed Mar. 19, 1957 and 970,601 filed Apr. 9, 1963 both by Agfa AG. Said dyes are but very weak spectrally sensitizing agents for common silver halide emulsions of the negative type.

The reversal speed of direct-positive images for use according to the Herschel effect, has been increased by a type of dyes which in silver halide emulsions of the negative type act as desensitizers and therefore are called desensitizing dyes (see e.g. C.E. Kenneth Mees, The Theory of the Photographic Process, Revised Edition (1954), the MacMillan Company New York p. 263). In that connection reference is particularly made to desensitizing dyes of the nitrostyryl and nitrobenzylidene type, representatives of which are e.g. described in the United Kingdom Pat. Specifications Nos. 667,206 filed June 28, 1949 by Kodak 698,576 filed Aug. 1, 1951 by Ilford and 834,839 filed May 27, 1957 by Ilford.

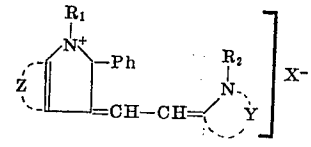
According to the present invention a direct-positive photographic silver halide emulsion for use in the solarization technique comprises light-sensitive silver halide, which has been fogged by light or chemical means and which includes a spectrally sensitizing methine dye of the 2-phenylindole type in combination with a desensitizing nitrostyryl or nitrobenzylidene dye.

The advantage resulting from that combination compared with the results obtained by the use of the 2-phenylindole dyes alone consists in an improved stability on storage, lower minimum densities i.e. brighter whites in the exposed areas of the developed material and especially an increased total speed.



In order to obtain a direct-positive silver image by means of a light-sensitive material according to the present invention it is only necessary to expose said material imagewise to white or blue light and to develop it in a silver halide developing solution.

Methine dyes of the 2-phenylindole class, which have proved to be very suitable for use according to the present invention can be represented by the following general formula:

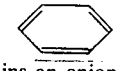



wherein represent:

$R_1$ and $R_2$ an alkyl group including substituted alkyl of the type generally known in cyanine dye chemistry such as methyl, ethyl, n-propyl, n-butyl, n-amyl, isopropyl, isobutyl, β-hydroxyethyl, β-acetoxyethyl, sulfoethyl, sulfopropyl, sulfobutyl, sulfatapropyl or sulfatobutyl, an unsaturated aliphatic group e.g. allyl, an aralkyl group e.g. benzyl, a substituted benzyl group such as carboxybenzyl, an aryl group e.g. phenyl, a substituted aryl group such as carboxyphenyl, a cycloalkyl group such as cyclohexyl and cyclopentyl or a substituted alkyl group such as the group –A–CO–O–B–$SO_2$OH wherein each of A and B represents a hydrocarbon group as described in the United Kingdom Pat Specification No. 886,271 filed June 20, 1957 by Gevaert PhotoProducten N.V., or the group –A–W—V–B, wherein A represents a methylene group, an ethylene group, a propylene group or a butylene group, B represents an alkyl group, an amino group, a substituted amino group and also a hydrogen atom if V is a single bond, and each of W and V represents a carbonyl group, a sulfonyl group or a single bond, but at least one of them representing a sulfonyl group, as described in the United Kingdom Pat. Specification No. 904,332 filed July 5, 1957 by Gevaert PhotoProducten N.V.;

Ph a phenyl group including substituted phenyl e.g. an alkyl-, aryl-, alkoxy- or halogen substituted phenyl group, said substituents preferably standing in the p-position,

Z the necessary atoms to form a fused benzene nucleus, which may be substituted e.g. by halogen, an alkyl, or an alkoxy group,

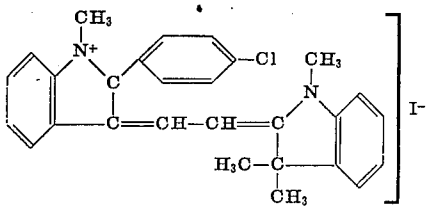
$X^1$ represents an anion e.g. $Cl^1$, $Br^1$, $I^1$, $C10_4{}^1$, $Ch_3SO_4{}^1$, and $H_3C$–  –$SO_3{}^1$, but $X^1$ is not present if $R_1$ itself contains an anionic group, and

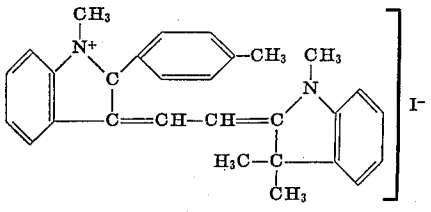
Y represents the necessary atoms to complete a heterocyclic nucleus of the types used in the production of cyanine dyes e.g. such as those of the thiazole series e.g. thiazole, 4-methylthiazole, 4-methyl-5-carbethoxythiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4-(p-tolyl)-thiazole, 4-(p-bromophenyl)-thiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4(2-thienyl)-thiazole, 4-(m-nitrophenyl)-thiazole, those of the benzothiazole series e.g. benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 6sulfobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, 4,5,6,7-tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, 5,6-dimethylbenzothiazole, those of the naphthothiazole series e.g. naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, 5methoxynaphtho[1,2-d]thiazole,

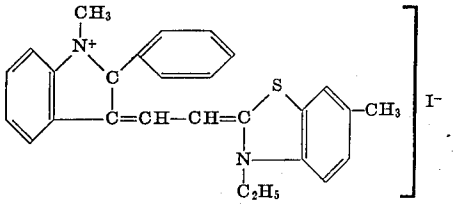
5ethoxynaphtho[d1,2-d]thiazole, 8methoxynaphtho[2,1-d]thiazole, 7methoxynaphtho[2,1-d]thiazole, those of the thionaptheno[ 7,6-d]-thiazole series e.g. 7-methoxythionaptheno[7,6-d]-thiazole, those of the thiadiazole series e.g. 4phenylthiadiazole, those of the oxazole series e.g. 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, those of the benzoxazole series e.g. benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, those of the naphthoxazole series, e.g. naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, those of the selenazole series e.g. 4-methylselenazole, 4-phenylselenazole, those of the benzoselenazole series e.g. benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 4,5,6,7-tetrahydrobenzoselenazole, those of the naphthoselenazole series e.g. naphtho[2,1-d] selenazole, naphtho[1,2-d]selenazole, those of the 2-quinoline series e.g. quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc., those of the pyrimidine series, those of the quinoxaline series, those of the quinazoline series, those of the 1-phthalazine series, those of the 2-pyridine series e.g. pyridine, 5-methylpyridine, 3-nitropyridine, those of the benzimidazole series e.g. benzimidazole, 5,6-dichlorobenzimidazole, 5-chlorobenzimidazole, 5,6-dibromobenzimidazole, 5chloro-6-amino-benzimidazole, 5-chloro-6bromobenzimidazole, 5-phenylbenzimidazole, 5-fluorobenzimidazole, 5,6-difluorobenzimidazole, 5-cyanobenzimidazole, 5,6-dicyanobenzimidazole 5-chloro-6-cyanobenzimidazole, 5-fluoro-6-cyanobenzimidazole, 5-acetylbenzimidazole, 5-chloro-6-fluorobenzimidazole, 5-carboxy-benzimidazole, 7-carboxybenzimidazole, 5-carbethoxybenzimidazole, 7-carbethboxybenzimidazole, 5-sulphamylbenzimidazole, or 5-N-ethylsulphamylbenzimidazole.

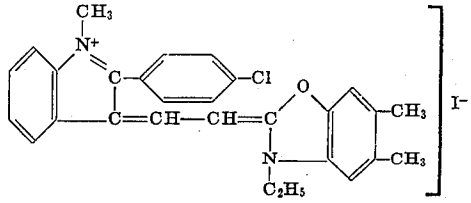
Examples of dyes corresponding to the said general formula are listed in the following table 1.

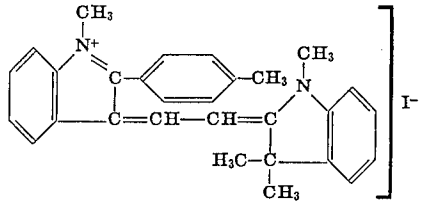
Table 1

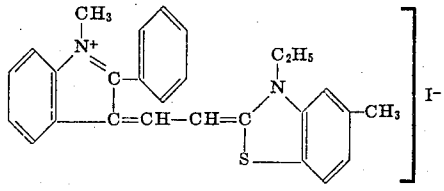
1 

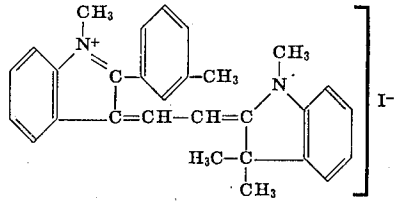
2 

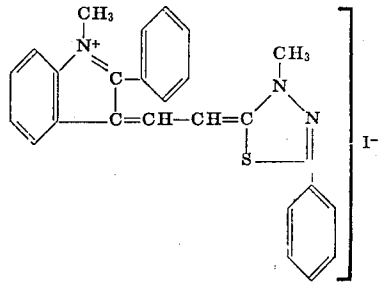
3 

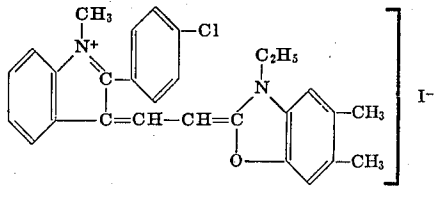
4 

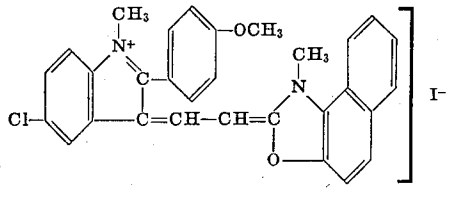
5 

6 

7 

8 

9 

10 

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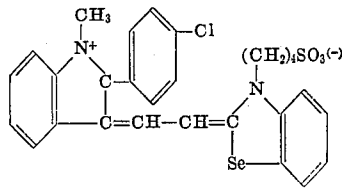
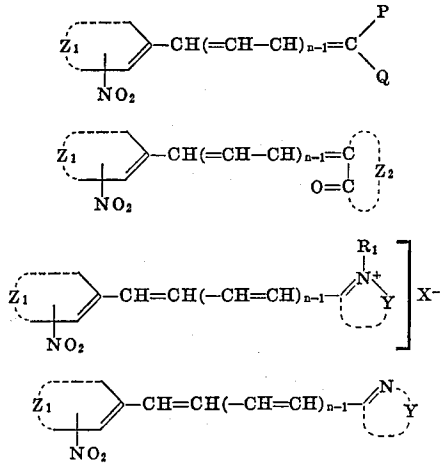


The dyestuffs according to the above general formula can be prepared according to the method described in the United Kingdom Pat. Specification No. 970,601 filed Apr. 9, 1963 by Agfa AG.

Suitable nitrobenzylidene and nitro-styryl dyes can be represented by the following general formulas:

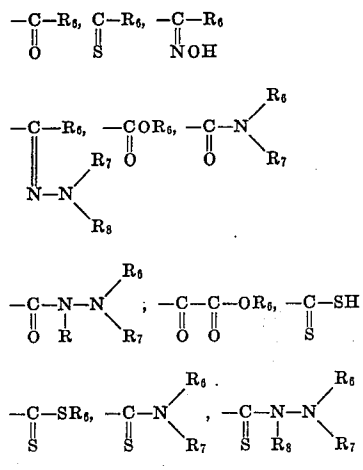


wherein one or more of the methine groups may be substituted e.g. with a cyano group,

$R_1$, $X^1$ and Y have the same significance as described above,

$Z_1$ represents the necessary atoms to close an aromatic nucleus e.g. a benzene nucleus, which may be further substituted e.g. with another nitro group,

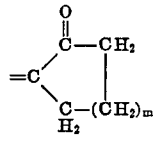
each of P and Q represents an organic group with electronegative character e.g.



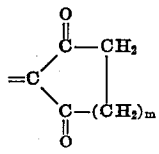
(wherein each of $R_6$, $R_7$ and $R_8$ represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, or a heterocyclic group, which groups may be substituted), $-NO_2$, $-CO$, an aromatic homocyclic monovalent group e.g. phenyl or naphthyl, which group may be substituted preferably with an electronegative group as hereinbefore described or a monovalent heterocyclic group with aromatic character e.g. a furyl, thienyl, pyrrolyl, indolyl, or –

group, wherein Z' represents the necessary atoms to close a heterocyclic nucleus with aromatic character, which groups may be substituted,

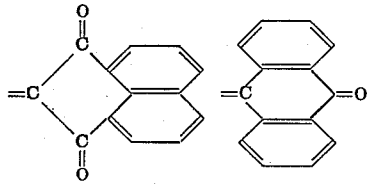
$Z_2$ represents the necessary atoms to close a cyclic ketomethylene nucleus such as one of those of the pyrazolone series e.g., 3-methyl-1-phenyl5-pyrazolone, 1-phenyl-5-pyrazolone, 1-(2-benzothiazolyl-3-methyl-5-pyrazolone, those of the isoxazolone series e.g., 3-phenyl-5-isoxazolone, or 3-methyl-5-isoxazonlone, those of the oxindole series e.g. 1-alkyl-2,3-dihydro-2-oxindoles, those of the 2,4,6-triketohexanhydropyrimidine series e.g. barbituric acid or 2-thiobarbituric acid as well as their derivatives such as those substituted in the 1-position by an alkyl group such as a methyl group, an ethyl group, an 1-n-propyl group, and a 1-n-heptyl group, or those substituted in the 1- and 3-position by an alkyl group, or those substituted in the 1- or 3-position by a $\beta$-methoxy-ethyl group, or those substituted in the 1- and 3-position by an aryl group such as a phenyl group, or those substituted in the 1- and 3-position by a substituted phenyl group such as a p-chlorophenyl group, or a p-ethoxycarbonylphenyl group, or those substituted only in the 1-position by a phenyl-, p-chlorophenyl-, or p-ethoxycarbonylphenyl group, further the mixed alkyl-alkyl-substituted derivatives such as 1-ethyl-3phenyl, and 1-n-heptyl-3-phenyl derivatives, those of the rhodanine series i.e., 2-thio-2,4-thiazolidinedione series, e.g. rhodanine, and aliphatically substituted rhodanines e.g., 3-ethyl-rhodanine, or 3-allyl-rhodanine, those of the imidazo[1,2-a]pyridone series, those of the 5,7-dioxo-6,7-dihydro-5-thiazole[3,2-a]pyrimidine series e.g. 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazole[3,2-a]pyrimidine series e.g. 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, those of the 2-thio-2,4-oxazolidinedione series i.e. those of the 2-thio-2,4-oxazoledione series e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, those of the thianaphthenone series e.g. 3-thianaphthenone, those of the 2-thio-2,5-thiazolidinedione series i.e. the 2-thio-2,5-thiazoledione series e.g. 3-ethyl-2-thio-2,5-thiazolidinedione series i.e. the 2-thio-2,5-thiazoledione series e.g. 3-ethyl- 2-thio-2,5-thiazolidinedione, of the 2,4-thiazolidinedione series e.g. 2,4thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3-$\alpha$-naphthyl-2,4-thiazolidinedione, those of the thiazolidone series e.g. 4-thiazolidone, 3-ethyl-4-thiazolidone, 3-phenyl-4thiazolidone, 3-$\alpha$-naphthyl-4-thiazolidone, those of the 4-thiazolone series e.g. 2-ethylmercapto-4-thiazolone, 2-alkylphenylamino-4-thiazolones, 2-diphenylamino-4-thiazolone, those of the 2-imino-2,4-oxazolinone i.e. pseudohydantoin series, those of the 2,4-imidazolinedione (hydantoin) series e.g. 2,4-imidazolinedione, 3-ethyl-2,4-imidazolinedione, 3-phenyl-2,4-imidazolinedione, 3-$\alpha$-naphthyl-2,4-imidazolinedione, 1,3-diethyl-2,4-imidazolinedione, 1-ethyl-3-phenyl-2,4-imidazolinedione, 1-ethyl-3-$\alpha$-naphthyl-2,4-imidazolinedione, 1,3-diphenyl-2,4-imidazolinedione, those of the 2-thio-2,4-imidazolinedione (i.e., 2-thiohydantoin) series e.g., 2-thio-2,4-imidazolinedione, 3-ethyl-2-thio-2,4-imidazolinedione, 3-phenyl-2-thio-2,4-imidazolinedione, 3-$\alpha$-naphthyl-2-thio-2,4-imidazolinedione, 1,3-diethyl-2-thio-2,4-imidazolinedione, 1-ethyl-3-phenyl- 2-thio-2,4-imidazolinedione, 1-ethyl-3-$\alpha$-naphthyl-2-thio-2,4-imidazolinedione, 1,3-diphenyl-2-thio-2,4-imidazolinedione, those of the 5-imidazolone series e.g., 2-n-propylmercapto-5-imidazolone, and those of the homocyclic ring systems represented by the following structural formulas:

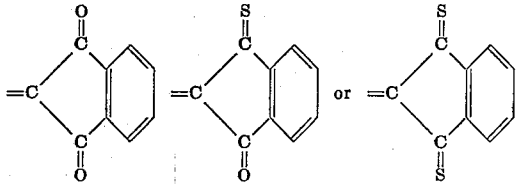


wherein $m$ represents 1, 2, or 3



wherein *m* represents 1, 2, or 3





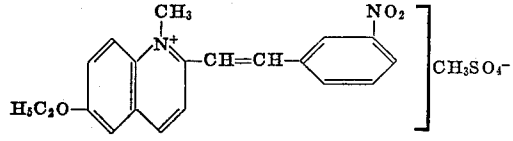
*n* represents a positive integer 1 or 2.

Desensitizing methine dyes containing an aromatic nitro group can be prepared by the condensation of a nitro-substituted aromatic compound containing an aldehyde group on the aromatic nucleus or such group linked thereto by a methine chain with a suitable heterocyclic compound having an active methyl or methylene group.

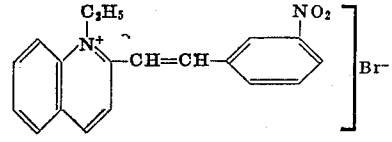
Particularly suitable desensitizing methine dyes according to said general formulas are listed in the following table 2.

TABLE 2

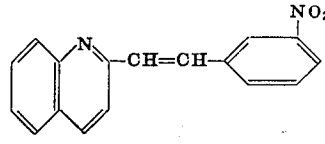
I



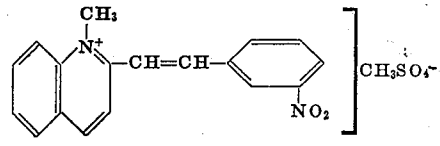
II



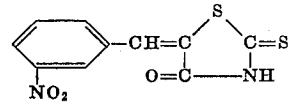
III



IV



V



Other suitable desensitizing methine dyes containing an aromatic nitro-substituted nucleus attached to the methine chain or group are described in the following United Kingdom Pat. Specifications Nos. 262,816 filed Dec. 13, 1926 by I.G. Farbenindustrie, 667,206 filed June 28, 1949 by Kodak, 698,575 filed Aug. 1, 1951, 698,576 filed Aug. 1, 1951, 834,839 filed May 27, 1957 all three by Ilford, German Pat. Specification No. 396,402 filed Jan. 2, 1922 by Farbenwerke Meister Lucius and Bruning and U.S. Pat. Specification No. 2,953,561 of Frederik C.-Schaefer-Darien and Grace A. Peters, issued Sept. 20, 1960 in which also the preparation of such dyes is described.

In the preparation of the emulsions, the dyes may be added to the emulsion in the form of a solution. Suitable solvents are e.g. alcohols such as methanol or ethanol. Preferably the desensitizing dye is used in a ratio of 0.15 to 3.5 moles per mole of the spectrally sensitizing dye, whereas the latter is normally added in an amount of 0.02 to 1 millimole per mole of silver halide.

In practice 10 to 500 mg., preferably 100 to 250 mg., of spectrally sensitizing due are used per mole of silver halide. It is, however, possible in view of particular requirements to use larger amounts.

The direct-positive emulsions can be prepared according to known methods. The silver halide composition is not critical, the silver halide may consist of silver chloride, silver bromide, silver iodide, or mixtures thereof. Preferred are emulsions that contain at least 50 percent by weight of silver bromide. The term "direct-positive emulsions" comprises fogged emulsions, which are developable without fogging exposure after the imagewise exposure.

The fogging of the emulsions can be accomplished by an overall exposure to light before the imagewise exposure or can be obtained by a chemical treatment.

Thus it is known e.g. to prefog the emulsion by means of a reducing agent such as hydrazine, hydroxylamine, formaldehyde, stannous chloride, and sodium thiosulphate. In a further fogging technique use is made of the fogging action of alkaline substances e.g. sodium hydroxide or potassium hydroxide, which substances preferably are applied during the precipitation of the silver halide and the first ripening.

The direct-positive emulsions may contain in addition to the light-sensitive silver halide salts minor amounts or traces of precious metal compounds such as gold, platina, palladium, iridium, ruthenium compounds, which compounds are known emulsion ingredients, as well as wetting agents, development accelerators, and optical brightening agents.

The advantageous effects resulting from the use of the combination of spectrally sensitizing compounds and desensitizing compounds according to the present invention will be evident on comparing the sensitivity results and minimum densities in the exposed areas of photographic materials described in the following example.

## EXAMPLE

To a washed silver iodobromide emulsion containing 60 g. of silver halide (95 moles percent of silver bromide and 5 moles percent of silver iodide) and which has been chemically fogged with sodium hydroxide (pH = 12) during the precipitation step and subsequent heat treatment (15 min. at 55° C. and 10 min. at 80° C.) the amounts of sensitizing compounds separately listed in the following table 3, were added respectively prior to the coating on a cellulose triacetate support.

The exposure of the coated emulsion layers resulting from said portions proceeded through a continuous grey wedge with constant 0.2. Two types of exposure were applied, one by means of a fluorescent light source "F 15 T 8 Daylight" contained in the "Blu-Ray" Radiograph Duplicating Printer marketed by Blu-Ray Reproduction Engineering Corporation, Essex, Connecticut U.S.A., the other by means of incandescent bulbs of a total energy of 375 Watt through a light-diffusing glass.

One group of the same emulsion strips was exposed and processed after normal storage at room temperature, whereas another group was exposed and processed under the same conditions after a preliminary treatment for 36 h. in an atmosphere of 34 percent of relative humidity at a temperature of 57° C.

The developer applied was a common developer on the basis of hydroquinone and N-methyl-p-aminophenol-hemisulphate.

The total speed is expressed in percent with respect to reference emulsions, the total speed of which is arbitrarily given the value 100. The total speed is denoted in the table by the letter S. The density in the exposed areas is a measure of the brightness of the whites and is denoted in the table by $D_1$(minimum density).

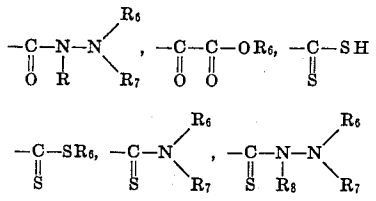
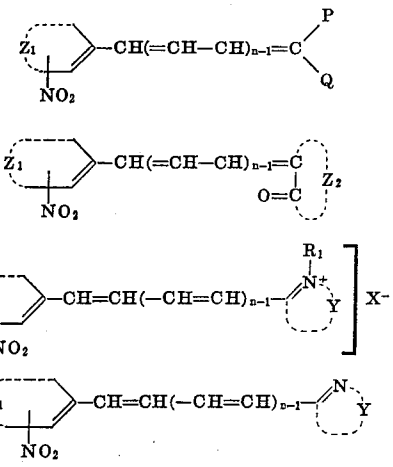


TABLE 3

| Test series | Number of the added dye mentioned in Table 1 or 2 | Amount in mg. per 60 g. of silver bromide | Fluorescent light source: Emulsion stored at room temperature $D_1$ | S | S | Exposure by means of: Incandescent bulbs: Emulsion stored at room temperature $D_1$ | S | S | Emulsion stored for 36 hours at 37% RH and 57° C. $D_1$ | S | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | 62 | 0.13 | 100 | | 0.05 | 100 | | 0.04 | 100 | |
| A | 1 | 62 | 0.08 | | 100 | 0.03 | | 100 | 0.04 | | 100 |
| | I+1 | 31+31 | 0.08 | 182 | 145 | 0.03 | 400 | 251 | 0.03 | 332 | 200 |
| | I | 62 | 0.09 | 100 | | 0.04 | 100 | | 0.03 | 100 | |
| B | 2 | 62 | 0.08 | | 100 | 0.03 | | 100 | 0.03 | | 100 |
| | I+2 | 31+31 | 0.06 | 138 | 138 | 0.01 | 316 | 240 | 0.01 | 288 | 263 |
| | I | 62 | 0.09 | 100 | | 0.04 | 100 | | 0.03 | 100 | |
| C | 3 | 62 | 0.09 | | 100 | 0.03 | | 100 | 0.03 | | 100 |
| | I+3 | 31+31 | 0.07 | 126 | 120 | 0.01 | 251 | 191 | 0.01 | 191 | 166 |
| | I | 62 | 0.11 | 100 | | 0.05 | 100 | | 0.03 | 100 | |
| D | 6 | 62 | 0.11 | | 100 | 0.04 | | 100 | 0.03 | | 100 |
| | I+6 | 31+31 | 0.09 | 100 | 110 | 0.03 | 209 | 151 | 0.03 | 174 | 126 |
| | II | 62 | 0.09 | 100 | | 0.05 | 100 | | 0.04 | 100 | |
| E | 1 | 62 | 0.08 | | 100 | 0.03 | | 100 | 0.04 | | 100 |
| | II+1 | 31+31 | 0.06 | 151 | 120 | 0.02 | 302 | 191 | 0.03 | 251 | 166 |
| | IV | 62 | 0.09 | 100 | | 0.06 | 100 | | 0.05 | 100 | |
| F | 1 | 62 | 0.06 | | 100 | 0.02 | | 100 | 0.02 | | 100 |
| | IV+1 | 31+31 | 0.06 | 126 | 145 | 0.01 | 257 | 151 | 0.02 | 251 | 151 |
| | III | 62 | 0.07 | 100 | | 0.05 | 100 | | 0.05 | 100 | |
| G | 1 | 62 | 0.06 | | 100 | 0.02 | | 100 | 0.02 | | 100 |
| | III+1 | 31+31 | 0.01 | 166 | 166 | 0.01 | 316 | 182 | 0.01 | 400 | 182 |

We claim:

1. A direct-positive photographic element comprising a fogged silver halide emulsion containing at least one nitrostyryl or nitrobenzylidene dye having a formula selected from the group

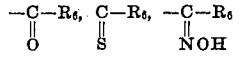


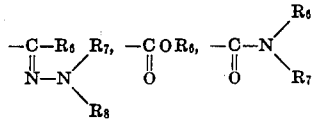
wherein

$R_1$ is an alkyl group,

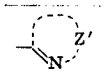
Y represents the necessary atoms to complete a heterocyclic nucleus of the type used in the production of cyanine dyes,

$Z_1$ represents the necessary atoms to close a benzene nucleus, each of P and Q is an organic group such as





wherein each of $R_6$, $R_7$, and $R_8$ represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, or a heterocyclic group, $-NO_2$, $-CN$, an aromatic homocyclic monovalent such as phenyl or naphthyl or a monovalent heterocyclic group with aromatic character such as furyl, thienyl, pyrrolyl, indolyl, or



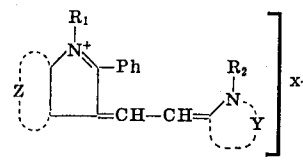
wherein Z' represents the necessary atoms to close a heterocyclic nucleus with aromatic character,

$Z_2$ represents the necessary atoms to close a cyclic ketomethylene nucleus,

$X^1$ is an anion, and

*n* is 1 or 2;

and a 2-phenyl-indole-methine dye having the formula



wherein

each of $R_1$ and $R_2$ is a lower alkyl group,

Ph is a phenyl group,

Z represents the necessary atoms to form a fused benzene nucleus,

Y represents the necessary atoms to complete a heterocyclic nucleus of the types used in the production of cyanine dyes, and

$X^1$ is an anion;

said nitrostyryl or nitrobenzylidene due and said 2-phenyl-indolemethine dye being present in said silver halide emulsion in amounts sufficient and in select ratios to provide a superadditively increased total speed for white light.

2. A process for the production of a direct-positive photographic material comprising adding to a direct-positive photo-

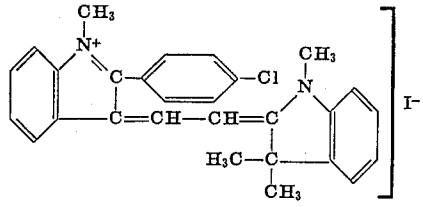
graphic silver halide emulsion a desensitizing methine dye containing an aromatic nitro-substituted nucleus attached to the methine chain or group and a methine dye of the 2-phenyl-indole class, and coating said emulsion as a layer.

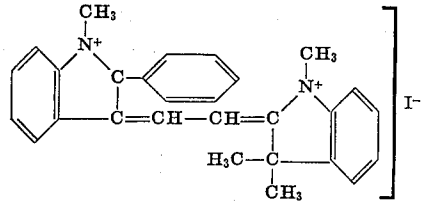
3. A process for the production of a direct-positive photographic material according to claim 9 wherein the methine dye of the 2-phenyl-indole class is a dye according to the general formula of claim 1.

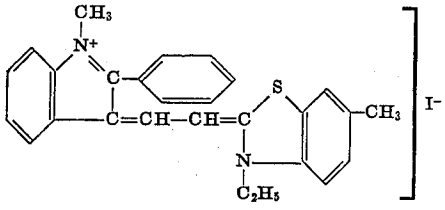
4. A direct-positive photographic element according to claim 1, comprising a fogged silver halide emulsion containing said 2-phenyl-indole-methine dye in an amount of 0.02 to 1 millimole per mole of silver halide and a nitrostyryl or nitrobenzylidene dye in a ratio of 0.15 to 3.5 moles per mole of the said methine dye.

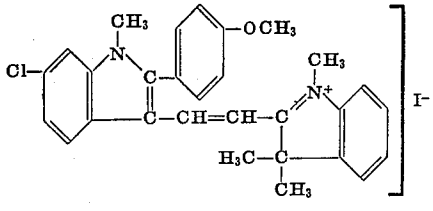
5. A direct-positive photographic element according to claim 4, wherein the said methine dye is used in a silver halide emulsion layer in an amount of 100 to 250 mg. per mole of silver halide.

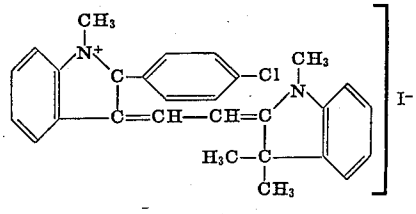
6. A direct-positive photographic element according to claim 1, comprising as fogged silver halide emulsion containing a methine due of one of the formulas selected from the group consisting of:

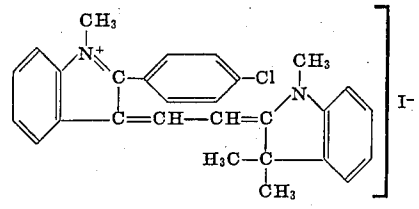


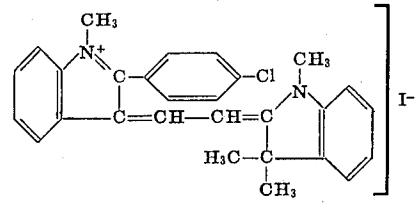




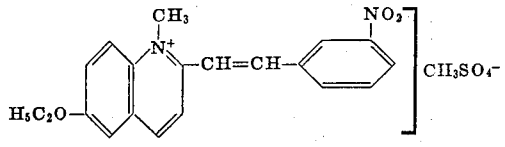


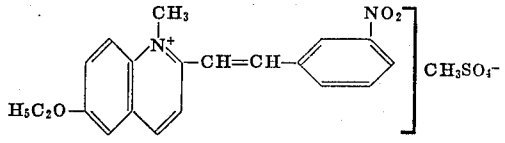


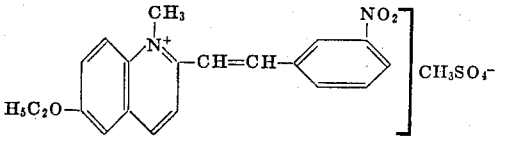


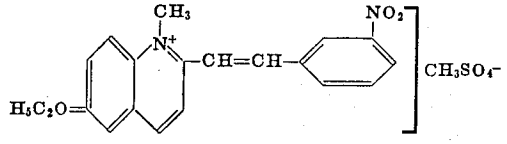


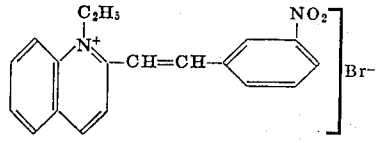
and a nitrostyryl dye of one of the formulas selected from the group consisting of:

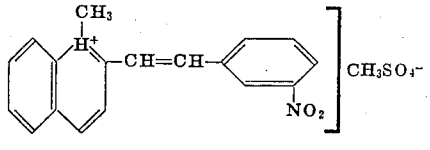


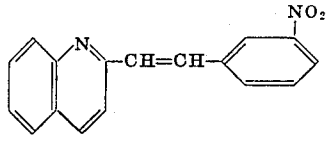












# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,615,610 Dated October 26, 1971

Inventor(s) Raymond Leopold FLORENS ET AL

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

Title page, [32] Priority, "May, 1966" should read -- May 9, 1966 --. Column 2, line 33, "-A-W-V-B" should read -- -A-W-NH-V-B --; Column 2, line 49, "$X^1$" should read -- $X^-$ --; Column 2, line 49, "$Cl^1$, $Br^1$, $I^1$, $C10_4{}^1$, $Ch_3SO_4{}^1$" should read -- $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, $CH_3SO_4^-$ --; Column 2, line 50, "$-SO_3{}^1$" should read -- $-SO_3^-$ --; Column 2, line 50, "$X^1$" should read -- $X^-$ --. Column 3, line 1, "5ethoxynaphth o [d1, 2-d]thiazole" should read -- 5-ethoxynaphtho[1, 2-d] thiazole --. Column 5, line 42, "$X^1$" should read -- $X^-$ --; Column 5, line 74, "-CO" should read -- -CN --. Column 6, line 29, "alkyl-alkyl-substituted" should read -- alkyl-aryl-substituted --; Column 6, lines 35 and 36, delete "5, 7-dioxo-3-phenyl-6, 7-dihydro-5-thiazole[3, 2-a] pyrimidine series e.g."; Column 6, lines 44-45, delete "series i.e. the 2-thio-2, 5-thiazoledione series e.g. 3-ethyl-2-thio-2, 5-thiazolidinedione"; Column 6, line 45, before "of" insert -- those --. Column 8, line 14, "due" should read -- dye --. Column 10, line 48, claim 1, "$X^1$" should read -- $X^-$ --; Column 10, line 68, claim 1, "$X^1$" should read -- $X^-$ --; Column 10, line 69, claim 1, "due" should read --dye--. Column 11, line 6, claim 3, "claim 9" should read -- claim 2 --; Column 11, line 21, claim 6, "due" should read -- dye --; Column 11, lines 33-41, claim 6, the formula should appear as follows:



USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.

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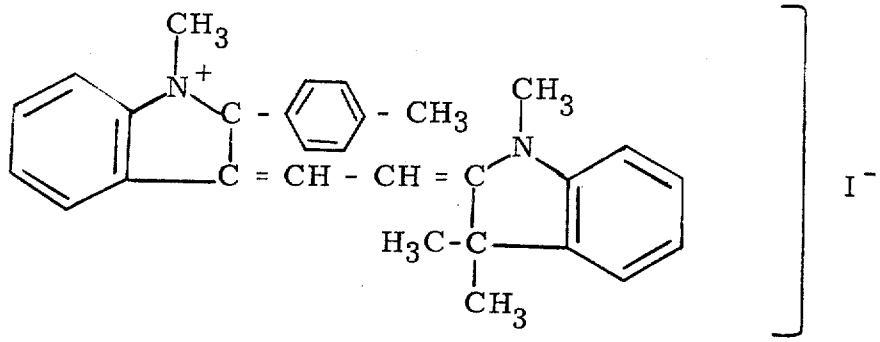
# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

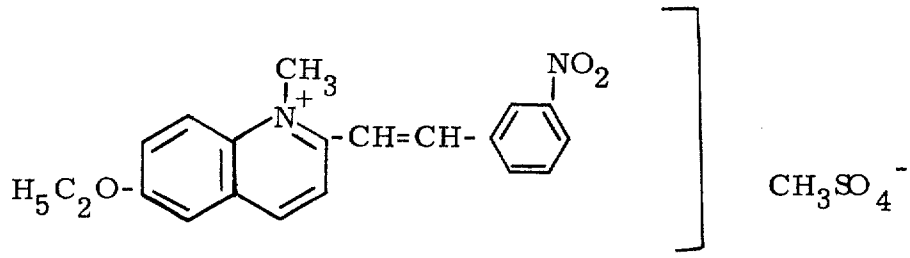
Patent No. 3,615,610 Dated October 26, 1971

Inventor(s) Raymond Leopold FLORENS ET AL Page 2

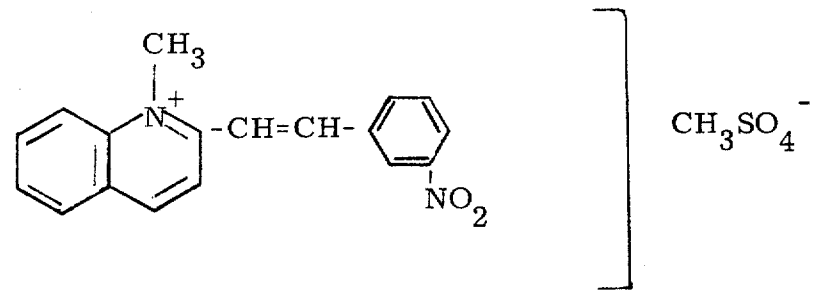
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:



Column 12, lines 43 - 48, claim 6, the formula should appear as follows:



Column 12, lines 58 - 63, claim 6, the formula should appear as follows:



Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents



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