July 12, 1960 O. RIESTER 2,944,896

PROCESS FOR SENSITIZING SILVER HALIDE EMULSIONS

Filed May 16, 1956

Fig. 1.

Sensitization with dye of Example 1.

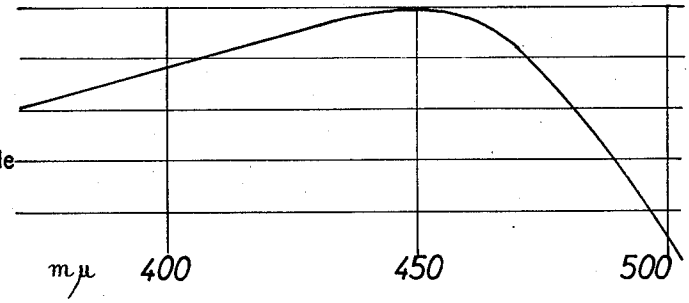


Fig. 2.

Sensitization with dye of Example 2

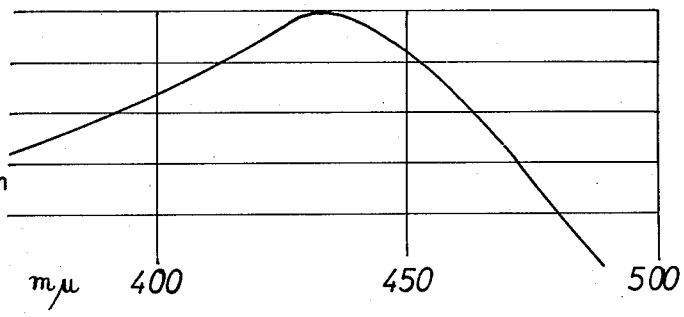


Fig. 3.

Sensitization with dye of Example 4

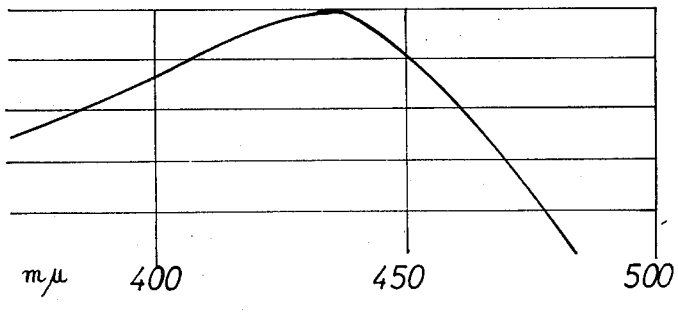
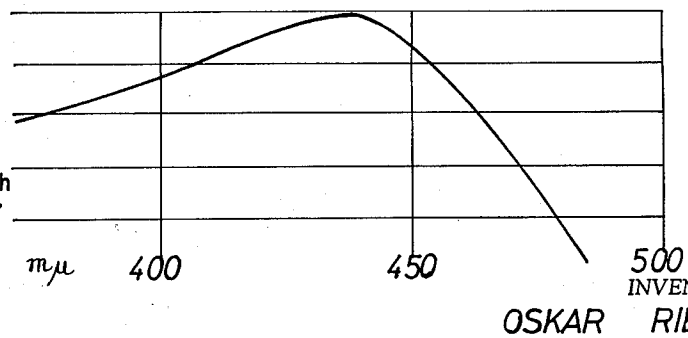


Fig. 4.

Sensitization with dye of Example 7



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United States Patent Office

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PROCESS FOR SENSITIZING SILVER HALIDE EMULSIONS

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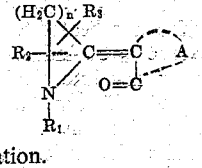
8 Claims. (Cl. 96—63)

It is known that silver halide emulsions show an inherent sensitivity in the violet zone of the spectrum. Particularly with silver chloride emulsions, only a small part of the sensitivity is in the range of visible light, while the main sensitivity is in the ultra-violet. When used practically, however, the effect of the glass intercalated between the light source and the emulsion layer is to cut off by far the greatest part of this sensitivity. The main effect of this is seen when the exposure is made with artificial light, because the short-wave spectral zone thereof is very slight. Therefore, with the photographic copying process, only a small part of the effective light is utilized.

It is known that a new sensitivity range can be added to the photographic emulsion for visible light by introducing dyestuffs and thus a better light yield, i.e. a higher total sensitivity, is obtained.

However, a serious disadvantage which is thereby produced is that only a smaller part of the visible light spectrum is available for the processing in the dark-room, since it is in fact necessary to exclude those rays for which the photographic layer has additionally been made sensitive. Consequently, for the lighting in the dark-room, it is necessary to use a light which physiologically appears darker, but this makes it substantially more difficult to judge the image appearing during development; this is particularly undesirable when the image involved is a positive image, for example a paper image. Actually, these images are in practice best produced with the psysiologically very bright yellow light, for example, of the Agfa dark-room filter 112, with which it is possible to estimate very satisfactorily the condition of the image formed as regards the correct gradation and density. It would of course be possible to use a pure silver chloride emulsion, which can then be readily processed with bright yellow light. In such cases, however, comparatively long exposure times are obtained, especially with hard layers. If this silver chloride emulsion is sensitized, there is obtained an increase in the sensitivity and thus the desired reduction of the copying time. Simultaneously, however, the sensitivity to the yellow dark-room light is increased in an undesirable manner, so that exposures take place which have the effect of varying the gradation or even of fogging.

It has now been found that an increase in the sensitivity of the silver halide emulsions can be achieved without deleteriously affecting dark-room safety if neutrocyanines of the following general formula:



are used for sensitization.

In this formula: R_1 stands for alkyl, such as methyl, ethyl, propyl, butyl, amyl, alkyl, dodecyl, isopropyl, isobutyl, isoamyl, cycloalkyl, such as cyclohexyl, aryl such as phenyl, chlorphenyl, naphthyl, furyl, aralkyl such as benzyl, phenyläthyl, organic radicals which contain a free carboxylic acid group, such as alkylenecarboxy-groups as for instance

$$—CH_2COOH, —CH_2—CH_2—COOH$$

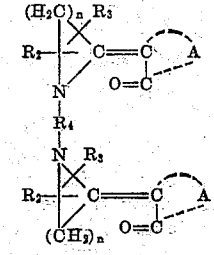
group, organic radicals which contain an esterified acid groups such as $—CH_2COOH$, $—CH_2CH_2COOH$ groups which are esterified with aliphatic and cycloaliphatic alcohols such as methyl-, ethyl, cyclohexylalcohol, organic radicals which contain a sulfonic acid group such as alkylensulfonic and groups as for instance propylene-ω sulfonic acid, butylene-ω sulfonic acid groups, and

R_2 and R_3 stand for alkyl, cycloalkyl, aralkyl, aryl or a heterocyclic radical without nitrogen, such as furyl or thienyl, any such radical being substituted in place of an appropriate number of hydrogen atoms of the CH_2 groups in the left hand ring, or alternatively the left hand ring may be unsubstituted, R_2 and R_3 being the same or different, while R_1 and R_3 or R_2 and R_3 may be joined to form a ring;

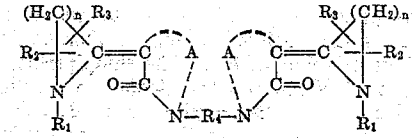
n=a whole number from 3 to 12;

A=atomic groups necessary for closing a five and six-membered ring. Ring systems of this type are for example: thiohydantoin, rhodanine, isorhodanine, selenorhodanine, oxythionaphthane, indandione, pyrazolone (—5).

The entire dyestuff molecule can also be multiplied, for example, by the ring nitrogen atoms being combined with one another by a divalent organic radical, such as for example an alkylene group. Such dyestuffs may be represented by the following formulae:



and



In these formulae n, R_1, R_2, R_3 and A have the same significance as in the first formula, whereas R_4 stands for a bivalent organic radical such as an alkylene group.

These neutrocyanines are produced according to the process of German Patent 927,043.

Particularly with such photographic emulsions as consist predominantly of silver chloride, the dyestuffs yield increases in sensitivity up to 10 times the inherent sensitivity and nevertheless permit a perfect processing with bright yellow light. Substantial advantage of these sensitisers consists in that completely uncoloured layers are left after the processing when they are used, whereas otherwise with good sensitisers, a so-called residual colouring frequently remains in the gelatine or in the baryta layer, this being evident by a yellowish toning similar to a yellow fogging.

An additional advantage is their stability with respect to the conventional emulsion additives, such as stabilisers, wetting agents, fluorescing substances, etc.

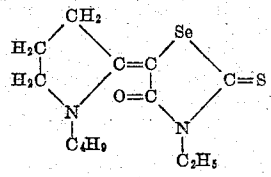
The sensitisers are added in amounts of for example 3 to 100 mg. per litre of emulsion, depending on the increase in sensitivity which is desired. It can be added at

any desired time, for example, as a casting additive to the finished emulsion or already in the final digestion, or the sensitisers are used in the so-called bath process.

The effectiveness of these sensitizers is more clearly shown in the following examples and in the accompanying drawings where the individual figures show the effect produced by some of these examples.

Example 1

The yellow dyestuff of the following constitution:



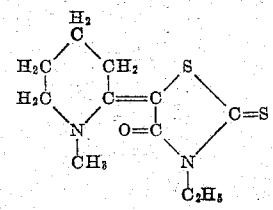
shows a sensitisation maximum at about 454 mμ and a tenfold increase in the sensitivity of a silver chloride emulsion containing approximately 2% of silver iodide.

The dyestuff is prepared as follows:

2.5 ml. of N-butyl-thiopyrrolidone(−2) are heated with 2 ml. dimethylsulfate on the water bath for 5 minutes and treated with a solution of 1 g. N-ethyl-selenorhodanine in 10 cc. of pyridine. Two drops of piperidine are added and the mixture is heated to 110° for one hour. The dyestuff formed is re-crystallized from propanol or benzene with the addition of animal charcoal.

Example 2

The pale yellow dyestuff of the following constitution:



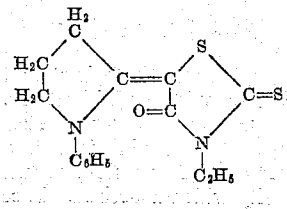
yields an increase of about 7 times in the sensitivity with a silver chloride emulsion of average contrast. Sensitization maximum is in the region of 434 mμ.

The dyestuff is prepared as follows:

2-piperidone is dissolved in chloroform and treated with excess phosphorpentasulfide at a temperature of 30–40°. The resultant 2-thiopiperidone has the boiling point 184–185° at 13–14 mm. Hg. The thiopiperidone is reacted in an alcoholic sodium alcoholate solution with methyliodide to form 2-methyl-mercapto-3,4,4,6-tetrahydropyridine, which latter is a liquid of the boiling point 71–79° at 13 mm. Hg. 1.3 g. 2-methylmercaptotetrahydropyridine and 1 ml. of dimethylsulfate are heated with one another, the mixture substantially rises in temperature and reacts vigorously. It is heated to 90° C. for a further 5 minutes, the reaction product is cooled, 2.1 g. N-ethylrhodanine and 60 cc. of absolute alcohol are added. Thereupon 2 cc. of triethylamine are added and the mixture is refluxed on the water bath for 30 minutes. The dyestuff crystallizes out while boiling. It is re-crystallized from a solution of pyridine and alcohol.

Example 3

The dyestuff of the following constitution:



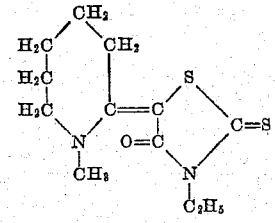
yields an increase by about 5 to 6 times and the sensitization maximum is in the region of 442 mμ.

The dyestuff is prepared as follows:

3.2 g. of N-phenyl-2-thiopyrrolidone-methiodide (which is obtainable from N-phenyl-2-pyrrolidone by melting with excess phosphorus pentasulfide at 130° C. and reacting the thus obtained thiopyrrolidone with methyliodide) and 1.6 g. N-ethylrhodanine are mixed and treated with 20 cc. of absolute alcohol and 2 cc. of triethylamine. The mixture is refluxed on a water bath for 30 minutes. The dyestuff re-crystallizes upon cooling. It is re-crystallized from 50 cc. of methanol.

Example 4

The dyestuff of the following constitution:

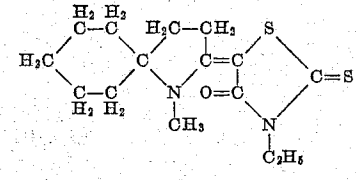


yields an increase of about 6 times in the initial sensitivity of a contrasty silver chloride emulsion with the addition of 30 mg. to 1 kg. of emulsion. The sensitization maximum is in the region of 434 mμ.

The dyestuff is prepared as follows:

The thiolactam as obtained from caprolactam by sulfurization with P_2S_5 is methylated with dimethyl-sulfate in diluted caustic soda solution and distilled in vacuum after separation by means of ether. 1.4 g. of this product is mixed with 1 cc. of dimethylsulfate and the mixture is heated on an oil bath for 5 minutes at 90° C. The reaction mixture is cooled in ice water, 1.6 g. N-ethylrhodanine are added and treated with 20 cc. of absolute alcohol and 2 cc. of triethylamine. The mixture is heated to boiling on the water bath for 30 minutes. The hot yellow dystuff solution is mixed with 20 cc. of water, the mixture is cooled in ice water. A yellow, crystallized dyestuff is obtained. It is dried in the exsiccator over sulfuric acid and re-crystallizes from methylisoheptane.

Example 5

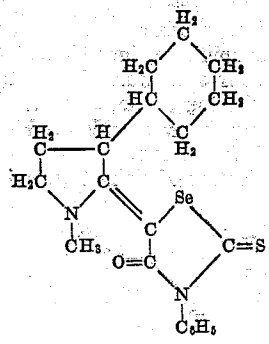


The increase is sixfold. The sensitization maximum is in the region of 436 mμ.

The dyestuff is prepared as follows:

5-spirocyclohexyl-pyrrolidone-(2) is melted with excess phophorus pentasulfide at 130° C. 2-mercaptomethyl-5-spiorcyclohexyl-1-pyrroline is thus obtained. This substance is a liquid of the boiling point 127–128° at 19.5 mm. Hg. 1.8 g. of the thus obtained pyrroline and 1 cc. of dimethylsulfate are heated to 100° for 10 minutes. The reaction mixture is cooled and 1.6 g. of N-ethylrhodanine, 20 cc. of absolute alcohol and 2 cc. of triethylamine are added. The mixture is refluxed to boiling for 30 minutes. The dyestuff becomes crystalline while boiling. It is cooled in ice water and filtered with suction. The dyestuff is re-crystallized for several times from 200 cc. of alcohol.

Example 6



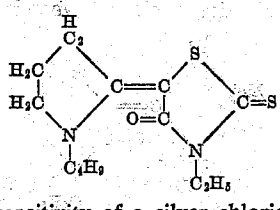
The increase is 7 to 8 times. The sensitization maximum is in the region of 456 mμ.

The dyestuff is prepared as follows:

3-cyclohexyl-pyrrolidone-(2) are converted, as described in the foregoing example, in 2-mercaptomethyl-3-cyclohexyl-1-pyrroline. The pyrroline is a liquid of the boiling point 151° C. at 21 mm. Hg. 2 g. of pyrroline thus obtained and 1 cc. of dimethylsulfate are heated in the oil bath for 10 minutes to 100° C. The reaction mixture is cooled, 2.6 g. of N-phenyl-selenorhodanine 10 cc. of pyridine and 1.5 cc. of triethylamine are added. The mixture is heated to 100° C. in the oil bath for 1 hour. It is then treated while hot with 5 cc. of alcohol and 20 cc. of water. Upon cooling for a long period the dyestuff becomes crystalline. The dyestuff is filtered with suction and re-crystallized for several times from 50 cc. of alcohol.

Example 7

The dyestuff



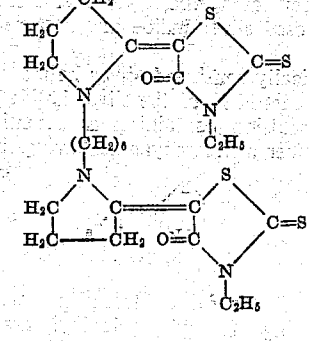
increases the sensitivity of a silver chloride emulsion to 6 to 7 times; the sensitization maximum is in the region of 436 mμ.

The dyestuff is prepared as follows:

The dyestuff is prepared in accordance with the procedure described in Example 1 using 1 g. of N-ethylrhodanine instead of the selenorhodanine. The methanolic solution of the dyestuff absorbs the ultraviolet spectral region.

Example 8

The dyestuff of the following constitution:



is dissolved in methyl pyrrolidone in the ratio of 1:1000 and added to a silver chloride emulsion prior to casing.

The increase in sensitivity is 6 to 7 times; the sensitization maximum is in the region of 439 mμ.

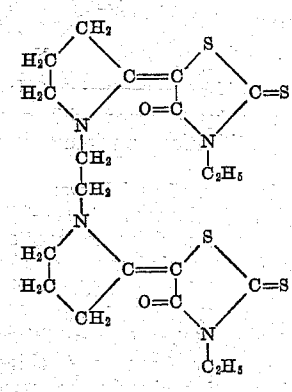
The dyestuff is prepared as follows:

5.6 g. of N,N'-hexamethylene-bis-(thiopyrrolidone-2) and 5 cc. of dimethylsulfate are heated at 100° C. for 10 minutes. After cooling 8 g. of N-ethylrhodanine in 20 cc. of pyridine are added and the mixture is heated on the steam bath for 15 minutes. Upon addition of 150 ml. of ice water the dyestuff precipitates as a semi-solid mass and is re-crystallized after isolation from 250 ml. of methanol-chloroform (1:2). The absorption of the methanolic solution is in the ultraviolet spectrum.

The hexamethylene-bis-(pyrrolidone-2) is prepared by heating 116 g. of hexamethylenediamine with 175 g. of butyrolactone in the autoclave at 260–280° C. for 3 hours and subsequent distillation (B.P. 226–228° C. at 3 mm. Hg). 100 g. of this pyrrolidone are stirred with 86 g. phosphorus pentasulfide in 350 cc. of xylene and 5 g. of magnesia at 120–140° for 30 minutes. Thereupon it is decomposed with ca. 200 cc. of water and 100 cc. of 50% sodium hydroxide solution, the oil is separated, dried with potash and distilled. The N,N'-hexamethylene-bis-(thiopyrrolidone) distilled over at 280–295° under 2 mm. Hg.

Example 9

A dyestuff of the constitution:



dissolved in acetone-methyl pyrrolidone (1:1) yields an increase up to 9 times with a very contrasty silver chloride emulsion; the sensitization maximum is in the region of 442 mμ.

The dyestuff is prepared as follows:

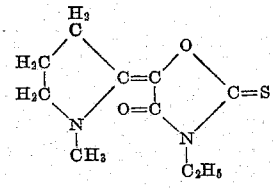
4.6 g. of N,N'-ethylene-bis-(thiopyrrolidone-2) are slowly heated with 5 cc. of dimethylsulfate, the inside temperature rising to 103° C. The reaction mixture is heated on the steam bath for 10 minutes. Then a solution of 8 g. ethylrhodanine in 10 cc. of pyridine is added, heated on the steam bath for 15 minutes, 2.8 cc. of triethylamine are added and the mixture is reacted on the steam bath for a further 50 minutes. After precipitating with 150 cc. of ice-water the mixture is left standing on the ice for 2 hours and the precipitated crystals are then filtered with suction. The crystals are re-crystallized from chloroform. The methanolic solution absorbs in the ultraviolet region of the spectrum.

The N,N'-ethylene-bis-pyrrolidone is prepared by heating 60 g. ethylenediamine and 172 g. butyrolactone at 260–270° C. in the autoclave. It is purified by distillation at 193–195° C. at 5 mm. Hg. M.P. 110° C.

66 g. of the pyrrolidone are stirred with 57 g. phosphorus pentasulfide and 5 g. magnesia in 230 cc. of xylene at 120–140° for ½ hour. After decomposing with aqueous sodium hydroxide solution and shaking with benzene crystals of N,N'-ethylene-bis-(thiopyrrolidone-2) are obtained by evaporating the benzenic solution after standing for some time. M.P. 143° C.

Example 10

A dyestuff of the constitution:



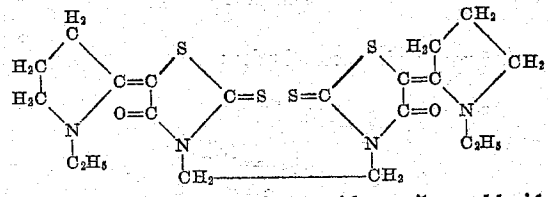
yields an increase in sensitivity up to 3 to 4 times in a silver chloride emulsion; the sensitization maximum is in the region of 430 mμ.

The dyestuff is prepared as follows:

4.4 cc. of N-methyl-thiopyrrolidone(—2) and 4 cc. of dimethylsulfate are reacted by heating in the steam bath. After cooling 2 cc. of N-ethyl-oxazolidone-(2)thione-(5) in 10 cc. of pyridine and thereafter 1 cc. of triethylamine are added. The mixture is left standing at 40° C. for 5 hours and the dyestuff formed is precipitated with 200 cc. ice water. The dyestuff is filtered with suction and re-crystallized from methanol after. The solution in methanol absorbs the ultraviolet.

Example 11

A dyestuff of the constitution:



yields an increase by 9 times with a silver chloride emulsion; the sensitization maximum is in the region of 440 mμ.

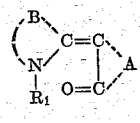
The dyestuff is prepared as follows:

10 cc. of N-ethyl-thiopyrrolidone(—2) and 9 cc. of dimethylsulfate are reacted by heating to about 90° C. The mixture is slowly cooled and 2 g. of ethylenerhodanine in 20 cc. of pyridine are added and the mixture is heated to about 40° C. for 12 hours. The formed dyestuff is thereafter precipitated by addition of water and re-crystallized from methanol and chloroform (1:1). The methanolic solution absorbs the spectral violet and ultraviolet.

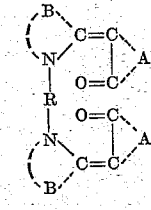
I claim:

1. An optically sensitized silver halide emulsion layer in which at least 98% of the silver halide is silver chloride, said emulsion containing as essentially the only optical sensitizer a neutrocyanine of one of the formulae selected from the group consisting of

(I)

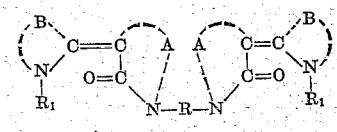


II



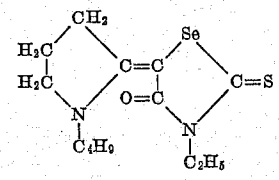
and

III

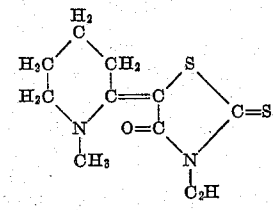


in which R_1 stands for a substituent selected from the group consisting of alkyl, cycloalkyl, aralkyl, and aryl radicals; A represents the non-metallic atoms necessary to complete a ring selected from the group consisting of thiohydantoin, rhodanine, isorhodanine, selenorhodanine, oxythionaphthene, indandione, and pyrazolone-5 rings; B stands for a saturated bivalent aliphatic hydrocarbon radical having a chain length of 3 to 5 carbon atoms completing the ring with the N–C chain; and R stands for an alkylene group.

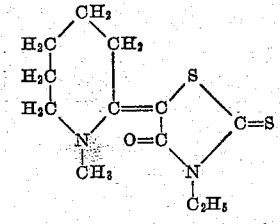
2. The combination of claim 1 wherein the sensitizer is



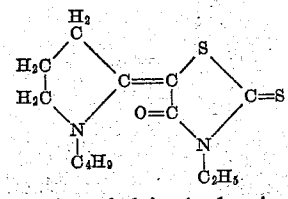
3. The combination of claim 1 wherein the sensitizer is



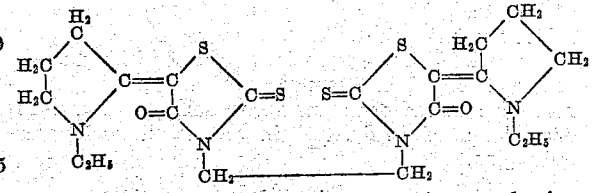
4. The combination of claim 1 wherein the sensitizer is



5. The combination of claim 1 wherein the sensitizer is

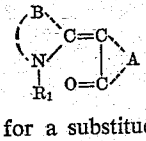


6. The combination of claim 1 wherein the sensitizer is



7. A method for making photographic reproductions, said method including the steps of providing a support that carries the optically sensitized silver halide emulsion of claim 2, exposing the emulsion to the desired optical image, and developing the exposed emulsion in a developer for exposed silver halide and in a relatively bright yellow light.

8. An optically sensitized silver halide emulsion layer in which at least 98% of the silver halide is silver chloride, said emulsion containing as essentially the only optical sensitizer a neutrocyanine having the formula



in which R_1 stands for a substituent selected from the group consisting of alkyl, cycloalkyl, aralkyl, and aryl radicals; A represents the non-metallic atoms necessary

to complete a ring selected from the group consisting of thiohydantoin, rhodanine, isorhodanine, selenorhodanine, oxythionaphthene, indandione, and pyrazolone-5 rings; and B stands for a saturated bivalent aliphatic hydrocarbon radical having a chain length of 3 to 5 carbon atoms completing the ring with the N–C chain.

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