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
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 accessible 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 a physiologically 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 large 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 the so-called organic radicals which contain a free carboxylic acid group, such as alkylcarboxylic acids, are used. Such dyestuffs may be represented by the following formula:

\[
\text{Formula: } X-C=\overset{\text{CH}_2}\text{COOH}, \quad \text{CH}_2-\text{CH}_2-\text{COOH}
\]

These organic radicals which contain a free carboxylic acid group such as alkylcarboxylic acids are used for sensitization. They are added at a rate of 0.1 to 30 mg. per litre of emulsion, depending on the increase in sensitivity which is desired. They 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 sensitizers 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:

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{N} & \quad \text{Se} \\
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\end{align*}
\]

shows a sensitisation maximum at about 454 nm 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. dimethylsulphate on the water bath for 5 minutes and treated with a solution of 1 g. N-ethyl-seleno-rhodanine 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 propa- nol or benzene with the addition of animal charcoal.

**Example 2**

The pale yellow dyestuff of the following constitution:

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\text{N} & \quad \text{Se} \\
\text{N} & \quad \text{C} \\
\end{align*}
\]

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 nm.

The dyestuff is prepared as follows:

2-piperidine is dissolved in chloroform and treated with excess phosphorussulphide at a temperature of 30–40°. The resultant 2-thiopyrrolidone has the boiling point 184–185° at 13–14 mm. Hg. The thiopyrrolidone is re-acted in an alcoholic sodium alcoholate solution with methylidione to form 2-methyl-mercapto-3,4,4,6-tetrahydro-dihydropyridine, which latter is a liquid of the boiling point 71–79° at 13 mm. Hg. 1.3 g. 2-methylmercaptotetrahydro-dihydropyridine and 1 ml. of dimethylsulphate 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:

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{O} & \quad \text{C} \\
\text{N} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\end{align*}
\]

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

The dyestuff is prepared as follows:

5.2 g. of N-phenyl-2-thiopyrrolidone (–2) is added to a solution of N-phenyl-2-thiopyrrolidone by melting with excess phosphorus pentasulphide at 130° C. and reacting the thus obtained thiopyrrolidone with methyl-iodide 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:

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{N} & \quad \text{Se} \\
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\end{align*}
\]

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 nm.

The dyestuff is prepared as follows:

2-thiolactam as obtained from caprolactam by sulfurization with P2S5 is methylated with dimethyl-sulphate in dilute 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 dimethylsulphate 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 dyestuff 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 methylisobutylate.

**Example 5**

The dyestuff is prepared as follows:

5-spirocyclohexyl-pyrorrolidone (–2) is melted with excess phosphorus pentasulphide at 130° C. 2-mercaptoethyl-5-spirocyclohexyl-1-pyrorrolidone 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 pyrrolline and 1 cc. of dimethylsulphate are heated at 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 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.
The increase is 7 to 8 times. The sensitization maximum is in the region of 456 μm.

The dyestuff is prepared as follows:
3-cyclohexyl-pyrrolidone-(2) are converted, as described in the foregoing example, in 2-mercaptomethyl-3-cyclohexyl-1-pyrrole. The pyrrole is a liquid of the boiling point 151° C. at 21 mm. Hg. 2 g. of pyrrole 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-selenohydantone 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 456 μm.

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 selenohydantone. 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.

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 μm.

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. ethylrhodamine 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. ethylrhodamine and 172 g. butrolactone 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° on ¾ 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:

\[
\begin{align*}
\text{H}_2 & \text{H} \\
\text{O} & \text{O} \\
\text{C} = \text{S} & \\
\text{CH}_3 & \\
\end{align*}
\]

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-thiopyrroolidone(-2) and 4 cc. of dimethylsulfate are reacted by heating in the steam bath. After cooling 2 cc. of N-ethyl-oxazoloidone(-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:

\[
\begin{align*}
\text{H}_2 & \\
\text{O} & \\
\text{C} = \text{S} & \\
\text{CH}_3 & \\
\end{align*}
\]

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-thiopyrroolidone(-2) and 9 cc. of dimethylsulfate are reacted by heating to about 90°C. The mixture is slowly cooled and 2 g. of ethyleneinodane 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 neurocyanin of one of the formulæ selected from the group consisting of

\[\text{I) } \begin{align*} & \\
& \end{align*}\]

\[\text{II) } \begin{align*} & \\
& \end{align*}\]

\[\text{III) } \begin{align*} & \\
& \end{align*}\]

and

\[\text{IV) } \begin{align*} & \\
& \end{align*}\]

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, oxoninophthene, indandione, and pyrazoline-5 rings; \(B\) stands for a saturated bivalent aliphatic hydrocarbon radical having a chain length of 5 to 5 carbon atoms completing the ring with the \(N-C\) chain; and \(R\) stands for an alkyne 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 neurocyanin having the formulæ

\[\text{V) } \begin{align*} & \\
& \end{align*}\]

\[\text{VI) } \begin{align*} & \\
& \end{align*}\]

\[\text{VII) } \begin{align*} & \\
& \end{align*}\]

in which \(R_2\) 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, oxoninophthene, indandione, and pyrazoline-5 rings; \(B\) stands for a saturated bivalent aliphatic hydrocarbon radical having a chain length of 5 to 5 carbon atoms completing the ring with the \(N-C\) chain; and \(R\) stands for an alkyne group.
to complete a ring selected from the group consisting of thiodydantoin, 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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