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O. RIESTER

2,278,947

PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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FIG. 1.

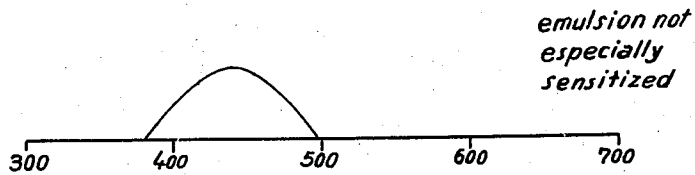
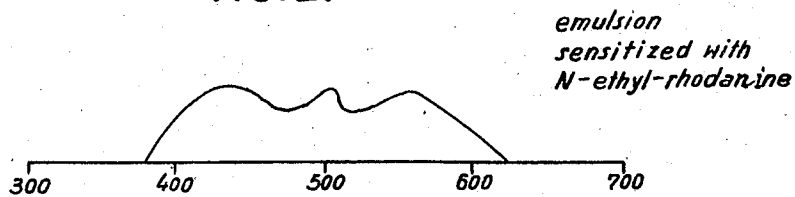


FIG. 2.



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UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC SILVER HALIDE EMULSION

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In Germany November 13, 1939

4 Claims. (Cl. 95-7)

My present invention relates to photographic silver halide emulsions and more particularly to silver halide emulsions which contain compounds capable of sensitizing said emulsions.

Since Vogel has recognized that it is possible to render a silver halide emulsion sensitive to light beyond the range of the characteristic sensitiveness of silver halide by means of an addition of a sensitizing dyestuff, a great number of dyestuffs have been proposed for sensitizing a silver halide emulsion more or less intensively in all spectral regions. It has hitherto commonly been believed necessary that the sensitizers are dyestuffs. There is a direct relation between the absorption range and the sensitization range of the dyestuffs or between the absorption maximum and the sensitization maximum. The known rule expresses that the sensitization maximum is 20-40 $m\mu$, in special cases to 80-90 $m\mu$ distant from the absorption maximum of the dyestuff.

Besides these optical sensitizers there are chemical sensitizers the effect of which is of another kind. The chemical sensitizers only increase the natural sensitiveness of the silver halide emulsion without changing the spectral sensitiveness range.

It is one object of my invention to provide a photographic silver halide emulsion containing a compound with a rhodanine ring as a sensitizer.

Another object is the provision of a photographic emulsion containing a colorless compound with a rhodanine ring as a sensitizer.

A further object is to provide a photographic emulsion containing a colorless compound with a rhodanine ring, said compound having not the constitution of a dyestuff.

A still further object is to provide a photographic emulsion containing a colorless compound with at least one rhodanine ring as a sensitizer.

Yet another object is the provision of a photographic emulsion containing a colorless compound with a rhodanine ring, at least one sulfur atom of said ring being substituted by a selenium atom.

Other objects of my invention will appear from the disclosure following hereinafter.

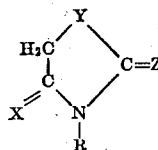
Reference is made to the accompanying drawing in which

Figure 1 shows the spectral region of a silver halide emulsion not especially sensitized and

Figure 2 shows the spectral region of a silver halide emulsion sensitized by N-ethyl-rhodanine.

The silver halide emulsions are optically sensitized in the spectral green by the compounds defined in the statement of invention. The com-

pounds of this kind have the following general formula:



in which

X is oxygen, sulfur or selenium,
Y and Z are sulfur or selenium,
R is a non-substituted or substituted alkyl, alkylene, cyclo-alkyl, aralkyl, aryl, amino group or an N-alkylene-rhodanine ring.

Whereas all known optical sensitizers are undistillable, high-melting substances, many compounds are among the sensitizers defined above which may be distilled in vacuum, under atmospheric pressure or with steam or are even liquid at room temperature as for example N-ethyl-rhodanine. The class of these compounds has further the great advantage that by using them undyed photographic images are obtained in contrast with the hitherto known sensitizing dyestuffs. The colorless sensitizers have a sensitization maximum and an absorption maximum which are about 100-200 $m\mu$ distant from each other.

The colorless rhodanine compounds may be added to the emulsion at any stage of the making of the photographic emulsion or incorporated in the finished emulsion in a bath procedure. The quantities which are necessary for the sensitization generally amount to about 1-100 milligrams and more per 1 kilogram of emulsion. The addition quantities, however, may also be, if necessary with regard to the purpose of application, greater or smaller than those aforementioned.

The following examples serve to illustrate the invention but they are not intended to limit it thereto. The rhodanine compounds are generally prepared according to known processes.

Example I

A silver halide emulsion sensitized with N-ethyl-rhodanine shows sensitization maxima at 500 and 550 $m\mu$.

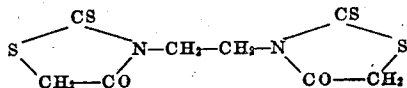
Example II

A silver halide emulsion sensitized with N-allyl-rhodanine shows sensitization maxima at 500 and 555 $m\mu$.

Example III

A silver halide emulsion sensitized with N-ethylene-rhodanine, prepared for instance as

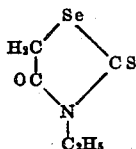
described in "Monatshefte für Chemie," volume 33, page 941, and having the following constitution



shows sensitization maxima at 510 and 560 mμ.

Example IV

A silver halide emulsion sensitized with N-ethyl-seleno-azolonthion made as described in Belgian Patent No. 437,921 and having the formula

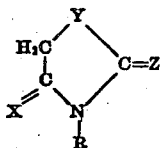


shows a sensitization maximum at 525 mμ.

Further examples for compounds of this class are N-phenylrhodanine, N-hydroxy-propylrhodanine, N-amino-rhodanine, N-phenyl-ethylrhodanine, N-cyclohexyl-rhodanine, and N-methyl-seleno-azolonthion the sensitization maxima of which are in the green.

I claim:

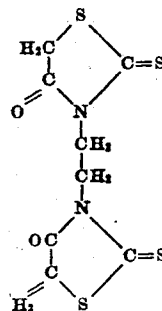
1. A photographic silver halide emulsion containing as a sensitizer a compound having the following general formula:



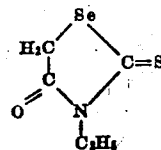
wherein X is a member selected from the class consisting of oxygen, sulfur, and selenium; Y and Z are members selected from the class consisting of sulfur and selenium; R is a member selected from the class consisting of alkyl, alkylene, cyclo-alkyl, aralkyl, aryl, amino-group, and N-alkylene-rhodanine.

2. A photographic silver halide emulsion containing N-ethyl-rhodanine.

3. A photographic silver halide emulsion containing a compound of the following constitution:



4. A photographic silver halide emulsion containing a compound of the following constitution:



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