

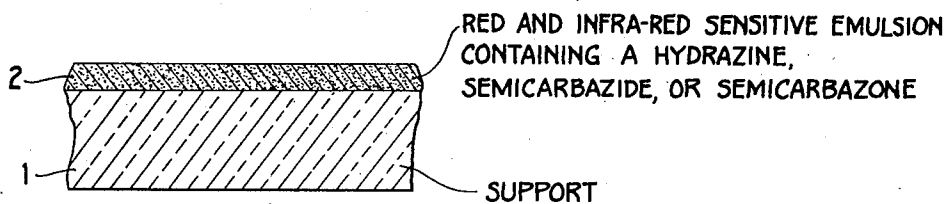
June 10, 1941.

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2,245,236

METHOD OF INCREASING INFRARED SENSITIVITY

Filed April 28, 1939



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UNITED STATES PATENT OFFICE

2,245,236

METHOD OF INCREASING INFRARED SENSITIVITY

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Application April 23, 1939, Serial No. 270,588

6 Claims. (Cl. 95—7)

This invention relates to photographic emulsions and more particularly to a method for increasing the red and infra-red sensitivity and the stability of emulsions.

It is known that reducing agents or halogen absorbers may be added to photographic print-out emulsions for the purpose of increasing the printing-out speed. Use of semi-carbazide salts for this purpose is described in Falleson and Staud U. S. Patent No. 2,126,316, August 9, 1933. Reducing agents of this type are of little value, however, in increasing the sensitivity of emulsions used for making developed images. For exposure within the ordinary range, that is, short of solarization, and for emulsions of sensitivity suitable for negatives, no improvement can be effected in this way if the emulsion has not been sensitized by sensitizing dyes and little or no improvement ordinarily can be brought about if the emulsion has been sensitized to the visible region of the spectrum.

We have found that sensitization to the red, deep red and infra-red regions of the spectrum can be improved by the addition of certain reducing agents to the emulsion prior to coating. A further improvement brought about in this way is an increase in the stability of the sensitizing. Emulsions sensitized to the infra-red commonly tend to lose a large proportion of this sensitivity within a few months after coating and we have found that this loss can be greatly diminished by adding certain reducing agents to the emulsion.

In the accompanying drawing, the single figure is a sectional view of a photographic element having a red and infra-red sensitive emulsion stabilized according to our invention.

It is an object of the present invention to provide a photographic emulsion having increased sensitivity to the red and infra-red region of the spectrum. A further object is to provide a red and infra-red sensitive emulsion having improved stability characteristics. A still further object is to provide a novel developing out red sensitive and infra-red sensitive photographic emulsion. Other objects will appear from the following description of our invention.

These objects are accomplished by adding to a silver halide photographic emulsion sensitized to the red and infra-red regions of the spectrum with optical sensitizing dyes, a reducing agent such as hydrazine, semi-carbazide, semi-carbazone or their salts.

According to our invention, a silver halide emulsion is sensitized with an optical sensitizing dye which extends the sensitivity into the red and

infra-red regions of the spectrum. To this emulsion is added a small amount of a suitable reducing agent and the emulsion is thereby increased in red and infra-red speed and this red and infra-red speed is found to be stable under adverse conditions, such as tropical incubation, for longer periods than the emulsion without the reducing agent.

Reducing agents which we have found suitable for use in this way are amino compounds such as hydrazine, semi-carbazide, and their salts such as hydrazine sulfate and semi-carbazide hydrochloride, and the reaction products of semi-carbazide with aldehydes or ketones, for example acetone semi-carbazone.

The photographic emulsions used according to our invention may be sensitized with various red and infra-red optical sensitizing dyes such as 4,4'-carbocyanines, thiadicarbocyanines, thia-2'-dicarbocyanines, dibenzothiadibocarbocyanines, thiatricarbocyanines, selenatricarbocyanines, 2,2'-dicarbocyanines, unsymmetrical di- and tri-carbocyanines, merodicarbocyanines, oxatricarbocyanines, and dibenzoxadibocarbocyanines. These sensitizing dyes, as well as others suitable for use according to our invention, extend the sensitivity range of the emulsion so that the maximum sensitivity in the red and infra-red region is for radiation of wave lengths greater than about 700 millimicrons.

The following examples, which are illustrative only, indicate methods of producing stable sensitized emulsions according to our invention.

Example 1

A gelatino silver halide emulsion was sensitized with an appropriate amount of 1,1'- β -hydroxyethyl-4,4'-carbocyanine. Part of this emulsion was kept as a control and to another portion before coating there was added 0.35 gram per liter of semicarbazide hydrochloride. After incubation for seven days at a temperature of 120° F. the control had lost over 50% of its speed and considerable contrast while the emulsion containing the semi-carbazide hydrochloride had gained slightly in speed and contrast without any more fog than the control.

Example 2

A gelatino silver halide emulsion was sensitized with an appropriate amount of 1,1'- β -hydroxy-2,2'-diethylthiatricarbocyanine. Part of this emulsion was kept as a control and to another part there was added 1.25 grams per liter of acetone semi-carbazone. After incubation of

both portions for seven days at 120° F., the sensitivity of the portion containing the acetone semi-carbazone was found to be more than double that of the control without an increase in fog.

Example 3

A gelatino silver halide emulsion was sensitized with 2,2'-diethylthiadicarbocyanine in appropriate concentration. Part of the emulsion was kept as a control and to another part there was added 0.05 gram per liter of hydrazine sulfate. After incubation for seven days at 120° F., the sensitivity of the portion containing the hydrazine sulfate was found to be more than double that of the control, without an increase in fog.

In preparing the emulsions according to our invention, both the optical sensitizing dyes and the reducing agents are added to the emulsion before coating rather than bathing the emulsion after coating. When silver halide emulsions are bathed after coating, some of the soluble bromides are removed from the emulsion and a change in the silver ion concentration results. There is, however, no change in the silver ion concentration when the sensitized dyes and reducing agents are added to the emulsion before coating.

The single figure of the accompanying drawing illustrates a photographic element made according to our invention. As shown therein, 1 is a support of glass, cellulosic compound such as cellulose acetate, a synthetic resin, or paper. On the support 1 there is coated a silver halide emulsion 2 sensitive to the red and infra-red regions of the spectrum and containing a hydrazine semicarbazide or semi-carbazone. It will be understood that the element may also have other layers such as subbing layers, anti-halation or backing layers, or overcoating layers.

The emulsions used according to our invention will usually be of the gelatino-silver halide type, although the halide may be dispersed in agents other than gelatin, such as cellulose mixed esters, synthetic resins, or collodion.

It is to be understood that the examples included in the above specification are illustrative

only and that our invention comprises all modifications and equivalents coming within the scope of the appended claims.

We claim:

1. The method of increasing the sensitivity and stability of a silver halide emulsion sensitized with a polymethine-cyanine dye containing at least seven carbon atoms between two cyanine nitrogen atoms and sensitizing to the red and infra-red regions of the spectrum, which comprises mixing therewith prior to coating an amino compound selected from the group consisting of hydrazines, semicarbazides, and semicarbazones.
2. The method of increasing the sensitivity and stability of a silver halide emulsion sensitized with a polymethine cyanine dye containing at least seven carbon atoms between two cyanine nitrogen atoms and sensitizing to the red and infra-red regions of the spectrum which comprises mixing therewith prior to coating a semicarbazide.
3. A method of increasing the sensitivity and stability of a silver halide emulsion sensitized with a 2,2'-dialkylthiadicarbocyanine to the red and infra-red regions of the spectrum, which comprises mixing a hydrazine therewith prior to coating.
4. A gelatino-silver halide emulsion sensitized to the red and infra-red regions of the spectrum with a polymethine cyanine dye containing at least seven carbon atoms between two cyanine nitrogen atoms, containing an amino compound selected from the group consisting of hydrazines, semicarbazides and semicarbazones.
5. A gelatino-silver halide emulsion sensitized to the red and infra-red regions of the spectrum with a polymethine cyanine dye containing at least seven carbon atoms between two cyanine nitrogen atoms, containing a semicarbazone.
6. A gelatino-silver halide emulsion sensitized with a 2,2'-dialkylthiadicarbocyanine and containing a hydrazine to increase the stability and the red and infra-red speed.

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Certificate of Correction

Patent No. 2,245,236.

June 10, 1941.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 51, Example 2, for "1,1'-hydroxy-" read *3,3'-dimethyl-*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of August, A. D. 1941.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.