April 11, 1939. J. D. KENDALL 2,153,929

MODIFYING THE SENSITIVITY OF PHOTOGRAPHIC EMULSIONS

Filed May 25, 1936

Fig. 1. N-ethyldihydroquinoline-2-thione

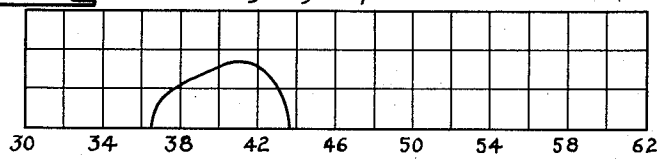


Fig. 2. N-methyldihydroquinoline-4-thione

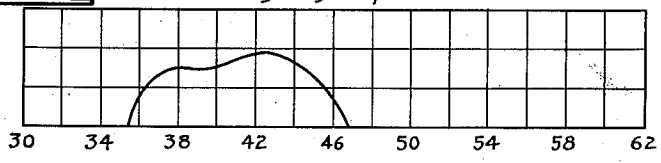


Fig. 3. N-ethyldihydropyridine-2-thione

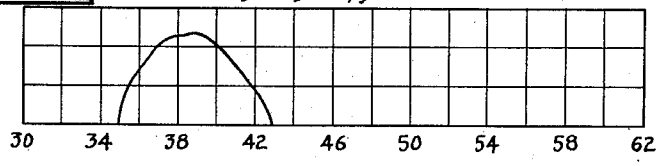
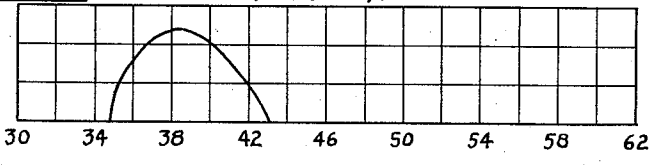


Fig. 4. N-methyldihydropyridine-2-thione



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2,153,929

MODIFYING THE SENSITIVITY OF PHOTOGRAPHIC EMULSIONS

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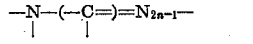
Application May 25, 1936, Serial No. 81,782
In Great Britain May 30, 1935

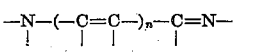
15 Claims. (Cl. 95—7)

This invention consists in an improved method of modifying the sensitivity of silver halide photographic emulsions.

In the specification of my copending British patent application No. 13601/35 I have described a method of modifying the sensitivity of photographic silver halide emulsions by treating them with a compound containing a system

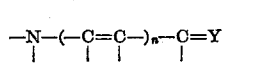


in which n is a positive integer, which system may also be represented as



in which n is 0 or a positive integer.

According to the present invention a method of modifying the sensitivity of a photographic silver halide emulsion comprises treating the emulsion with a compound which contains the system



(where Y represents S or Se, and n is 0 or a positive integer) and in which the nitrogen atom of the above system forms part of a heterocyclic ring.

The present invention also includes a photographic silver halide emulsion in which one or more of the above mentioned compounds is incorporated.

Examples of compounds which may be used according to the present invention are the α and γ thiones and selenones of any of the heterocyclic nitrogen compounds commonly used for the preparation of cyanine dyes, for example unsubstituted and substituted thiazoles, thiazolines, oxazoles, oxazolines, selenazoles, selenazolines, quinolines, indolenines, pyridines, their analogues and homologues including those of the benzene and naphthalene series, and also diazoles such as pyrimidine, described in British Patent No. 425,609.

A convenient method of preparing the thiones and selenones of compounds containing a five-membered heterocyclic nitrogen ring is as follows: The corresponding mercaptan (or selenomercaptan) is alkylated, for example with methyl sulphate in caustic soda solution, to form the thioether (or selenoether) which is then heated at about 130–150° C. for several hours with a molecular proportion of an alkyl sulphate or para-toluenesulphonate to form a quaternary salt; the reaction mixture is then boiled with a small quantity of pyridine for about an hour or until complete solution effected; on dilution the thione (or selenone) is precipitated and may be purified by crystallisation from an alcohol or benzene or by distillation at low pressures. In many cases the yields obtained are almost theoretical when calculated on the quantity of thioether (or selenoether) employed.

Many of the compounds which may be employed in accordance with the present invention are coloured and absorb portions of the visible spectrum, in which case they act as so-called optical or colour sensitisers, that is they increase the range of colour sensitivity of certain photographic silver halide emulsions. Other compounds possessing the necessary characteristics are colourless and do not absorb light of the visible spectrum, but nevertheless they act as sensitisers and increase the speed of the emulsion without apparently adding any additional colour sensitivity to the emulsion.

In treating the emulsion the substances may be added at any convenient stage during the preparation of the emulsion before coating it on a support, or the finished coated material may be bathed in a solution of the substance.

The amount of substance added and the strength of the solution for bathing may vary over quite wide limits according to the substances and types of emulsions used. In general an addition of the order of 80 ccs. of a $\frac{1}{1000}$ solution of the substance per unit of 6½ litres of emulsion equivalent to 250 gms. of silver nitrate will give useful results, but the amount added may be as little as 40 ccs. or as much as 400 ccs. or even more.

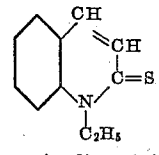
In general a $\frac{1}{1000}$ solution is used for bathing but this may also be varied in strength over quite wide limits.

The above methods of treating the emulsions follow the usual known practice and in carrying out the present invention it is found that these methods are applicable to the cases where compounds are employed which are coloured or absorb portions of the visible spectrum and increase the range of colour sensitivity of the emulsion. In the case of the compounds which are not coloured and do not absorb portions of the visible spectrum, however, it is found advantageous to incorporate them in the emulsion at an earlier stage during its production, that is they should be added either to the silver nitrate solution or to the alkali halide solution employed in the preparation of the emulsion.

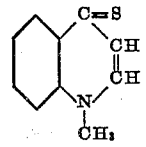
The following are typical examples of compounds which may be used in accordance with the

present invention and which have colour sensitising properties.

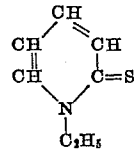
N-ethyl-dihydroquinoline-2-thione extends the sensitivity of a silver chloride gelatin emulsion to about λ 4400 Å. with a maximum at about λ 4100 Å.



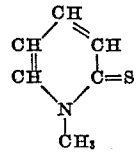
N-methyl-dihydroquinoline-4-thione extends the sensitivity of a silver chloride emulsion to about λ 4600 Å. with a maximum at about λ 4300 Å.



N-ethyl-dihydropyridine-2-thione extends the sensitivity of a silver chloride emulsion to about λ 4300 Å. with a maximum effect at about λ 3900 Å.



N-methyl-dihydropyridine-2-thione extends the sensitivity of a silver chloride emulsion to about λ 4300 Å. with a maximum effect at about λ 3900 Å.



The sensitivity curves of the above-described emulsions are shown in the accompanying drawing in which

Fig. 1 is a spectrogram of a silver chloride emulsion containing N-ethyldihydroquinoline-2-thione.

Fig. 2 is a spectrogram of a similar emulsion containing N-methyldihydroquinoline-4-thione.

Fig. 3 is a spectrogram of a similar emulsion containing N-ethyldihydropyridine-2-thione.

Fig. 4 is a spectrogram of a similar emulsion containing N-methyldihydripyridine-2-thione.

The following examples are given in order to illustrate the use in accordance with the present invention of compounds which increase the speed of photographic silver halide emulsions without having any apparent effect on the colour sensitising properties.

Example I

A normal unwashed silver chloride emulsion containing a small proportion, less than 1% together, of silver bromide and silver iodide, was prepared by adding a solution of silver nitrate to a solution of alkali halide in gelatin and ripening the mixture by maintaining it at 115° F. for fifty minutes. The emulsion was then made up to bulk by the addition of gelatin solution, finished in the normal manner, and then coated on paper and tested in the standard manner described below.

Identically similar batches of emulsion were also prepared in a similar manner but with the addition of varying quantities of a $\frac{1}{1000}$ solution of N-ethyl-dihydrobenzoxazole-1-thione in 50% aqueous methylated spirit; the quantities were the equivalent of multiples of 100 ccs. of solution per 4½ litres of emulsion containing 54.5 gms. of silver and were added to the gelatin solution of the alkali halides before the addition of the silver nitrate solution.

The emulsions were then tested as described below, the results being given in the following table:

Quantity of solution added	Relative exposure time	Fog
Cubic centimeters		
None	850	0.00
100	470	.00
200	270	.00
400	180	.01

Another series of experiments was carried out in which the solution of the compound was added to the silver nitrate solution before the silver nitrate was added to the alkali halide; the figures for this series of experiments are given in the following table, from which it will be seen that the variation in procedure does not make any material alteration in the result:

Quantity of solution added	Relative exposure time	Fog
Cubic centimeters		
None	850	0.00
100	470	.00
200	220	.00
400	160	.01

In the above experiments the data relating to emulsion speeds was derived from the characteristic curve of the emulsion obtained in following manner: A strip of paper coated with the emulsion was exposed under a normal step-wedge of known characteristics at a known distance from a calibrated light source in the form of a half-watt lamp of known intensity. The strip was then processed under standard conditions, i. e. developed for one minute at 65° F. in a standard metol hydroquinone developer as normally used for gaslight papers, fixed, and then washed, to produce an image comprising a series of patches varying in density inversely in accordance with the densities of the corresponding patches of the step-wedge. These patches of graded density were then examined in a standard reflection densitometer and their densities so determined were plotted against the logarithms of the exposures employed to produce them so giving the characteristic curve.

The logarithms of the corresponding exposures can be easily obtained from the known intensity of the light source, the distance at which the exposure was made and the transmission densities of the respective strips of the neutral step-wedge employed.

From this characteristic curve the relative exposure time is obtained by interpolation and is expressed as the number of candle meter seconds

exposure required to produce a density of 1.0 as measured in the densitometer.

This figure, of course, is inversely proportional to the working speed of the emulsion, but expresses this speed in its most useful form for this type of material.

The figure for the fog is obtained as the density measured in the same densitometer produced on development, under the same conditions, of a portion of the strip which has not received any exposure to light.

Similar series of experiments were carried out using N-ethyl-dihydrobenzthiazole-1-thione in place of N-ethyl-dihydrobenzoxazole - 1 - thione with similar results, except that the speed increase was not quite so large.

Similar results were also obtained by using N-methyl-dihydrobenzthiazole-1-thione, N-methyl-dihydrobenzoxazole- 1 -thione, N - methyl - 5:6 - benzdihydrobenzthiazole-1-thione and N-methyl-4:5-dimethyldihydrobenzoxazole- 1 - thione, with the the exception that the increase in speed was not quite so great.

Example II

The experiments described below illustrate the effect of the addition of compounds such as described in Example I to an emulsion of low initial sensitivity prepared from inert gelatin.

In this case a normal iodobromide emulsion was made up by adding a solution of silver nitrate to a solution of ammonium bromide, potassium iodide and a gelatin known to yield emulsions of a slow type; the mixture was ripened by maintaining it at a temperature of 120° F. for twenty minutes. Further quantities of silver nitrate and gelatin of the same kind were then added and the emulsion was set, shredded, washed, and then digested by maintaining at a temperature of 125° F. for fifty minutes.

The emulsion was then cooled and coated upon glass plates.

A similar batch of emulsion was prepared with the addition of a quantity of a dilute solution of N - ethyl - dihydrobenzoxazole - 1 - thione. The quantity was equivalent to 80 ccs. of solution per unit of 6½ litres of emulsion equivalent to 250 gms. of silver nitrate, the solution being added partly to the gelatin solution of the alkali halides and partly to the bulk gelatin added after the ripening stage, the quantities added to each being proportional to the quantity of gelatin added at each stage, the emulsion being further treated as above (i. e. washed, digested, etc.).

Strips of these plates were then exposed under a neutral step-wedge at a known distance from a light source of known characteristics and then developed for eight minutes at 65° F. in a normal metol-hydroquinone developer as commonly employed for this type of emulsion, fixed, washed and dried and tested as follows: The characteristic curves were obtained by measuring the densities of the graded patches of the test image in a standard transmission densitometer and by plotting them against the logarithms of the exposures producing them, which are obtained directly from the known characteristics, that is the intensity of the light source, the distance at which the exposure was made and the known transmission density of the corresponding patches of the step-wedge.

From these curves two speed figures were obtained, one C as the reciprocal of the anti-logarithm of the exposure at which the curve showed a density of 0.1 above the minimum fog density, and T. S. as the reciprocal of the anti-logarithm of the exposure of the point on the curve at which a tangent to the curve makes an angle $\tan-\theta=0.2$ with the abscissa.

As before the fog values were obtained as the density measured in the same densitometer of a portion of the plate unexposed to light and developed, fixed and washed and dried under the same conditions.

The following results were obtained:

Quantity of solution added	Fog	Speed C	Speed TS
Cubic centimeters			
None	.04	50	74
80	.06	52	85

A further experiment was carried out in a similar manner using a different gelatin and adding the compound to the first addition of silver nitrate solution, and otherwise proceeding as before.

Results obtained from this experiment were as follows:

Quantity of solution added	Fog	Speed C	Speed TS
Cubic centimeters			
None	.04	30	45
80	.09	81	150

Both results show an increase in speed on the addition of the 80 ccs. of solution with a slight increase in fog.

Similar series of experiments were carried out with emulsions containing varying quantities of N-ethyl-dihydro-benzoxazole-1-thione and digested for varying times. The results showed that with increasing quantities of the compound added the same emulsion speeds were obtained in shorter digestion times.

I claim:

1. A photographic silver halide emulsion of modified sensitivity in which is incorporated in sensitizing amounts N-ethyl-dihydrobenzoxazole-1-thione.

2. A photographic silver halide emulsion of modified sensitivity in which is incorporated in sensitizing amounts N-ethyl-dihydrobenzthiazole-1-thione.

3. A photographic silver halide emulsion of modified sensitivity in which is incorporated in sensitizing amounts N-ethyl-dihydroquinoline-2-thione.

4. A photographic silver halide emulsion containing in sensitizing amounts a mononuclear heterocyclic mono-nitrogen compound selected from the group consisting of α thiones and selenones of the N-hydrocarbon substituted thiazoles, benzthiazoles, naphthathiazoles, thiazolines, oxazoles, benzoxazoles, naphthaoxazoles, oxazolines, selenazoles, benzselenazoles, naphthaselenazoles, selenazolines, indolenines, pyridines, quinolines, and γ thions and selenones of N-hydrocarbon substituted pyridines, quinolines and naphthaquinolines.

5. A photographic silver halide emulsion containing in sensitizing amounts a mono-nuclear heterocyclic mono-nitrogen compound selected from the group consisting of α thiones and selenones of the N-alkyl substituted thiazoles, benzthiazoles, naphthathiazoles, thiazolines, oxazoles,

benzoxazoles, naphthaoxazoles, oxazolines, selenazoles, benzselenazoles, naphthaselenazoles, selenazolines, indolenines, pyridines, quinolines, and γ thiones and selenones of N-alkyl substituted pyridines, quinolines and naphthaquinolines.

6. A photographic silver halide emulsion containing in sensitizing amounts a mono-nuclear heterocyclic mono-nitrogen compound selected from the group consisting of α thiones and selenones of the N-hydrocarbon substituted oxazoles selected from the group consisting of oxazoles, benzoxazoles and naphthaoxazoles.

7. A photographic silver halide emulsion containing in sensitizing amounts of a mono-nuclear heterocyclic mono-nitrogen compound selected from the group consisting of α thiones and selenones of the N-alkyl substituted oxazoles selected from the group consisting of oxazoles, benzoxazoles and naphthaoxazoles.

8. A photographic silver halide emulsion containing in sensitizing amounts a mono-nuclear heterocyclic mono-nitrogen compound selected from the group consisting of α thiones and selenones of the N-lower alkyl substituted oxazoles selected from the group consisting of oxazoles, benzoxazoles and naphthaoxazoles.

9. A photographic silver halide emulsion containing in sensitizing amounts a mononuclear heterocyclic mononitrogen compound selected from the group consisting of the α thiones and selenones of the N-hydrocarbon substituted thiazoles taken from the group consisting of thiazoles, benzthiazoles and naphthathiazoles.

10. A photographic silver halide emulsion containing in sensitizing amounts a mononuclear heterocyclic mono-nitrogen compound selected from the group consisting of the α thiones and selenones of the N-alkyl substituted thiazoles taken from the group consisting of thiazoles, benzthiazoles and naphthathiazoles.

11. A photographic silver halide emulsion containing in sensitizing amounts a mononuclear heterocyclic mononitrogen compound selected from the group consisting of the α thiones and selenones of the N-lower alkyl substituted thiazoles taken from the group consisting of thiazoles, benzthiazoles and naphthathiazoles.

12. A photographic silver halide emulsion containing in sensitizing amounts a mono-nuclear heterocyclic nitrogen compound selected from the group consisting of α thiones and selenones of N-hydrocarbon substituted compounds selected from the group consisting of pyridine, quinolines and naphthaquinoline.

13. A photographic silver halide emulsion in sensitizing amounts, a mono-nuclear heterocyclic nitrogen compound selected from the group consisting of α thiones of N-hydrocarbon substituted compounds selected from the group consisting of pyridine, quinoline and naphthaquinoline.

14. A photographic silver halide emulsion in sensitizing amounts, a mono-nuclear heterocyclic nitrogen compound selected from the group consisting of α thiones and selenones of N-alkyl substituted compounds selected from the group consisting of pyridine, quinoline and naphthaquinoline.

15. A photographic silver halide emulsion in sensitizing amounts, a mono-nuclear heterocyclic nitrogen compound selected from the group consisting of α thiones and selenones of N-lower alkyl substituted compounds selected from the group consisting of pyridine, quinoline and naphthaquinoline.

JOHN DAVID KENDALL.

CERTIFICATE OF CORRECTION.

Patent No. 2,153,929. April 11, 1939.

JOHN DAVID KENDALL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 22, for "the the" read the; same page, second column, line 67, claim 4, for "thions" read thiones; page 4, first column, line 15, claim 7, strike out the word "of"; 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 6th day of June, A. D. 1939.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.