April 11, 1939. J. D. KENDALL 2,153,928

SENSITIZED PHOTOGRAPHIC EMULSIONS

Filed May 1, 1936

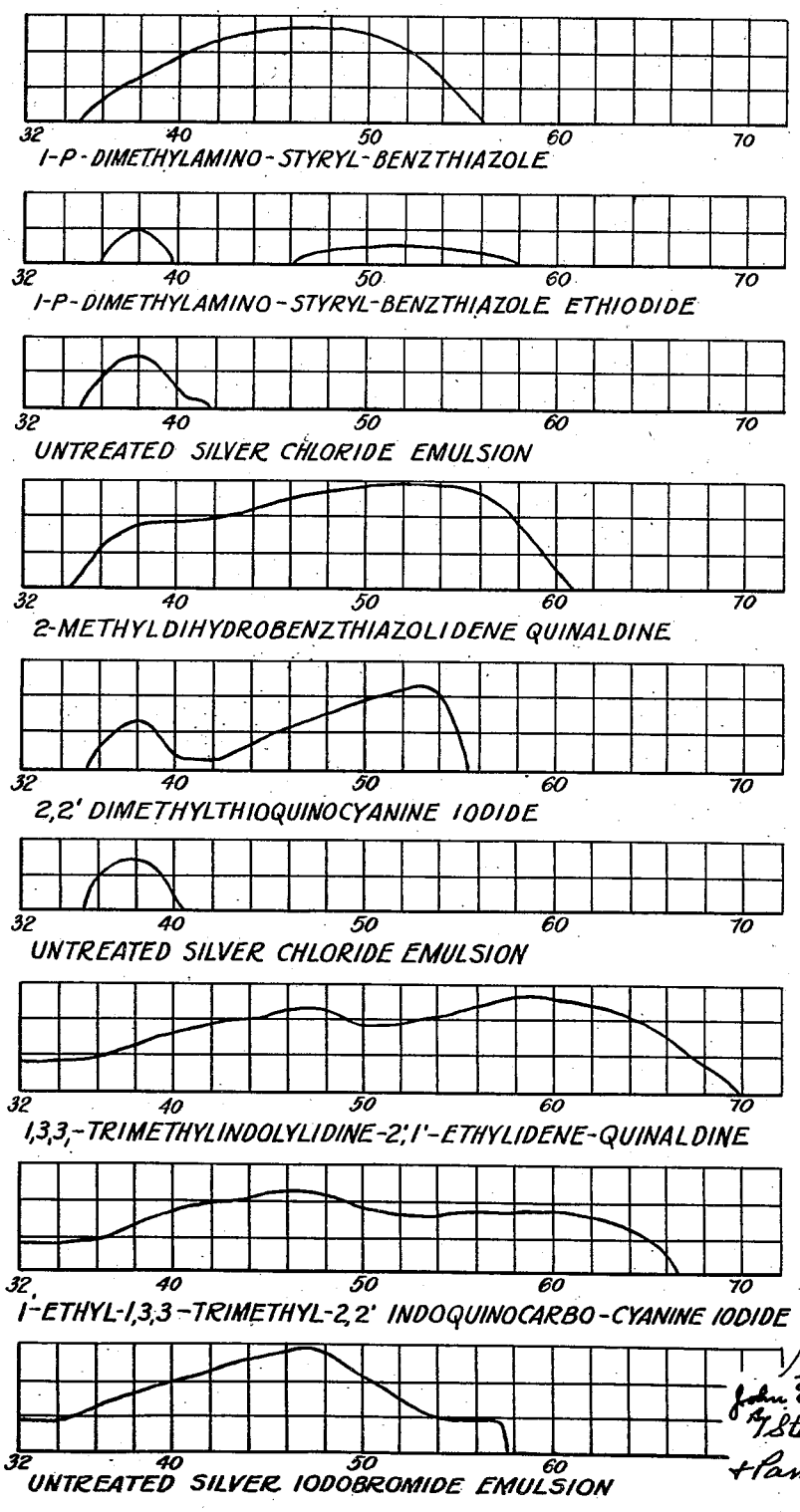


Fig. I

Fig. II

Fig. III

Inventor:
John David Kendall,
By Stebbins, Blenko
& Pamely, Attys.

Patented Apr. 11, 1939 2,153,928

UNITED STATES PATENT OFFICE

2,153,928

SENSITIZED PHOTOGRAPHIC EMULSIONS

John David Kendall, Ilford, England, assignor to Ilford Limited, Ilford, Essex, England, a British company

Application May 1, 1936, Serial No. 77,441
In Great Britain May 8, 1935

12 Claims. (Cl. 95—7)

This invention consists in improvements in or relating to sensitizing photographic silver halid emulsions.

The colour senstive range of photographic silver halide emulsions has been extended by incorporating in the emulsion many different compounds, including dyestuffs of the cyanine and of the pinaflavol classes. The cyanine dyestuffs consist of a heterocyclic nitrogen nucleus containing a quinquivalent nitrogen atom, such as that in a quaternary salt, which is linked to a heterocyclic nitrogen nucleus containing a trivalent nitrogen atom by a methine or polymethine chain. The pinaflavol dyestuffs consist of a heterocyclic nucleus containing a quinquivalent nitrogen atom which is linked to a trivalent nitrogen atom by a conjugate chain of carbon atoms part of which is included in a homocyclic ring. Both these types of compound have been employed extensively for sensitizing photographic silver halide emulsions, and in both classes an essential feature is the presence of a quaternary nitrogen atom linked by a completely conjugate chain to a trivalent nitrogen atom. It has generally been supposed that it is the presence of this system which imparts the sensitizing action to the compounds and that compounds which do not contain the system would not possess sensitizing properties.

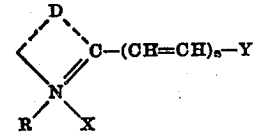
I have now found that the above-mentioned system is not essential for a compound to have sensitizing properties, and that compounds containing no quinquivalent nitrogen atom, but containing two trivalent nitrogen atoms linked together by a completely conjugate chain of an odd number of carbon atoms possess strong sensitizing properties.

According to the present invention therefore a method of sensitizing photographic silver halide emulsions comprises incorporating in the emulsion an organic nitrogen compound containing no quinquivalent nitrogen atom but containing two trivalent nitrogen atoms linked together by a completely conjugate chain of an odd number of carbon atoms linked by alternate double and single bonds.

Although a completely conjugate chain of carbon atoms is referred to above, it is to be understood that compounds containing a single methine group connecting two trivalent atoms, and linked to one by a single bond and to the other by a double bond, act as sensitizers and are included within the method of the present invention. It is found, however, that compounds which are visibly coloured, i. e., which absorb light falling within the visible spectrum or in the near ultra violet, e. g. about 3500 Å are more effective as sensitizers than the uncoloured or faintly coloured compounds which absorb the radiations in the shorter ultra violet wave lengths. The colour of the compounds which are to be employed in accordance with the present invention is dependent to a certain extent on the number of carbon atoms in the chain linking the two ternary nitrogen atoms and it appears that the longer the chain the more the absorption and sensitizing range is displaced towards the red or longer wave lengths so that generally speaking compounds containing a number of carbon atoms in the chain are preferred. It is also found that the nature of the systems or nuclei containing the nitrogen atoms seems to influence the colour sensitizing effect of the compound, for example the inclusion of one or both of the nitrogen atoms in heterocyclic nuclei tends to displace the absorption band towards the red or longer wave lengths and to give a more extended colour sensitivity effect.

Investigations have shown that the best sensitizing effects are obtained when compounds are used in which two nitrogen atoms are contained in different heterocyclic nuclei and are linked by a completely conjugate chain of at least three carbon atoms, for example the bases corresponding to the cyanine and carbocyanine dyes and other dyes of the same or analogous series.

The cyanine bases may be obtained, for example by condensing a heterocyclic nitrogen base having a reactive methyl group in the α or γ position to the nitrogen atom with a quaternary salt of a heterocyclic nitrogen compound having a reactive thioether or selenoether grouping (including the reactive grouping of an alkyl salt of an N-alkyl thione or selenone) or an amino-vinyl or substituted amino-vinyl grouping (including an arylamino, acylamino, or acylarylamino-vinyl grouping) in the α or γ position to the nitrogen atom, or with a condensation product having the general formula:



where D=the residue of the heterocyclic system, R=an alkyl, aryl or aralkyl group, X=an acidic group, Y=arylamino group and n=a positive integer, such as is obtained by condensing a compound of the general formula

$$Z=(CH)_{2n-1}—Y$$

(where Z=a substituted amino group, and Y and n as above) with a quarternary salt of a heterocyclic nitrogen base having a reactive methyl group in the α or γ position to the nitrogen atom.

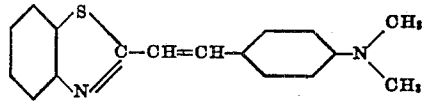
Generally speaking the carbon atoms forming the completely conjugate chain may be linked to hydrogen atoms or to other neutral monova-

lent atoms or groups e. g., alkyl, aryl or aralkyl groups or halogen atoms and they may form parts of cyclic nuclei, and provided there is an odd number of carbon atoms in the chain, that is 1, 3, 5, 7, etc. in all cases the compounds possess the desired sensitizing action.

In carrying out the present invention in practice one of more of the compounds to be used in accordance with the present invention may be incorporated in the photographic silver halide emulsion before it is coated on a support, or alternatively the support (e. g. a film or a plate) coated with the emulsion may be bathed in a solution of one or more of the compounds. The actual quantity of the compound incorporated in the emulsion will vary to a certain extent with the individual compounds, and with the ultimate effect which it is desired to obtain. As an indication of the order of the quantities employed 100 cc. of a one in one thousand solution of the dye may be incorporated in six and a half litres of emulsion equivalent to about two hundred and fifty grammes of silver nitrate, or the coated support may be bathed in a one in one thousand solution of the compound. The strength of the solution may vary according to the dye used and may be as low as one in ten thonsand.

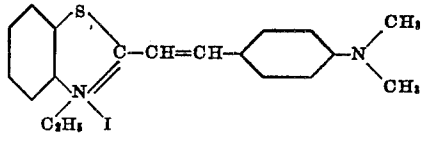
The difference between the effects produced on photographic emulsions by the cyanine and pinaflavol bases employed according to the present invention and the effects produced by the corresponding salts (e. g. cyanine and pinaflavol dyes) are shown in the following examples and illustrated in the accompanying drawing:

(*A*) *1-p-dimethylamino-styryl-benzthiazole*



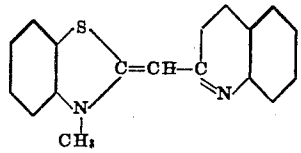
extends the sensitivity of photographic silver chloride emulsion to about λ 5600 Å. with a maximum effect at about λ 4800 Å.

The corresponding quaternary salt 1-p-dimethylaminostyryl benzthiazole ethiodide



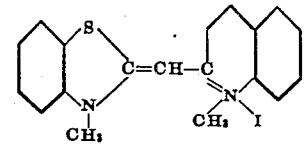
has very little sensitising action on silver chloride photographic emulsion. The sensitising curves of these two compounds are shown in the accompanying drawing in Figure I, the top curve of which shows the spectrogram of a silver chloride emulsion treated with the base and Figure I the middle curve of which shows the spectrogram of the same emulsion treated with the salt. Figure I the bottom curve shows the spectrogram of the untreated emulsion.

(*B*) *2-methyldihydrobenzthiazolylidene quinaldine*



is a powerful sensitiser and sensitises a silver chloride emulsion to about λ 5900 Å. with a maximum at about λ 5200 Å.

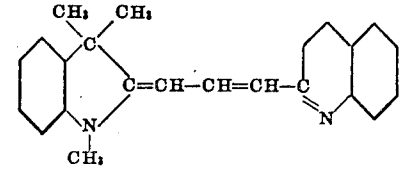
The corresponding salt 2.2'-dimethylthioquinocyanine iodide



is a moderate sensitiser and extends the sensitivity of the same silver chloride emulsion as used above over a band from about λ4200 Å. to λ 5500 Å. with a strong maximum at about λ 5350 Å.

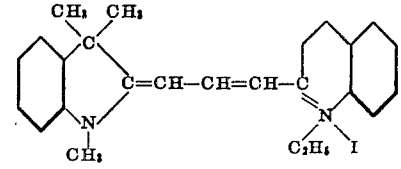
The sensitising effects of these compounds are shown in Figure II, the top curve of which shows the spectrogram of a silver chloride emulsion treated with the base and the middle curve of which shows the spectrogram of the same emulsion treated with the salt. The bottom curve shows the spectrogram of the untreated emulsion.

(*C*) *1:3:3-trimethylindolylidine-2':1':-ethylidene quinaldine*



is a powerful sensitiser and extends the sensitivity of the normal silver iodo bromide emulsion to about λ 7000 Å. with a maximum at about λ 6200 Å.

1'-ethyl-1:3:3-trimethyl-2:2'- indoquinocarbocyanine iodide

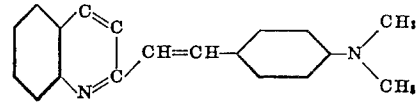


is a moderate sensitiser and extends the sensitivity of the same silver iodo-bromide emulsion to about λ 6700 Å. with an indeterminate maximum at about λ 6200 Å.

Their sensitising effects are shown in Figure III the top curve of which shows the spectrogram of a silver iodobromide emulsion treated with the base, the middle curve of which shows the spectrogram of the same emulsion treated with the salt, and which shows the spectrogram of the untreated emulsion.

Other examples of pinaflavol and cyanine bases which may be used in accordance with the present invention are as follows:

(1) *2-paradimethylamin- -tyryl-quinoline*



extends the sensitivity of a silver chloride photographic emulsion to about λ 5800 Å. with a maximum effect at about λ 4800 Å.

(2) *4-p-dimethylaminostyrylquinoline* is a powerful sensitiser and extends the sensitivity of a silver chloride emulsion to approximately λ 5600 Å. with a maximum to about λ 5000 Å.

(3) *1-p-dimethylaminostyryl-4-dimethylaminobenzthiazole* is a powerful sensitiser and increases the sensitivity of a silver chloride emulsion to approximately λ 5600 Å.

(4) *1-p-dimethylaminostyryl-3:4-benzthiazole* is a powerful sensitiser and extends the sensitivity of a silver chloride emulsion to λ 5400 Å. with a maximum at about λ 4600 Å.

(5) *N-methyldihydrobenzthiazolylidene quinaldine* is a powerful sensitiser and extends the sensitivity of a silver chloride emulsion to about λ 5600 Å. with maximum at about λ 4700 Å. and λ 5150 Å.

(6) *N-methyldihydrobenzthiazolylidene quinaldine* is a powerful sensitiser and extends the sensitivity of a silver bromide emulsion to about λ 5600 Å. with maxima at about λ 4800 Å. and λ 5100 Å.

(7) *N-ethyldihydrobenzthiazolylidene quinaldine* is a powerful sensitiser and extends the sensitivity of a silver bromide emulsion to about λ 5700 Å. and λ 5800 Å. with a maximum of about λ 5100 Å.

(8) *1-methyldihydroquinolylidene-(2:2')-quinaldine* is a sensitiser and extends the sensitivity of a silver chloride emulsion to about λ 5800 Å. with maxima at about λ 5200 Å. and λ 5500 Å.

(9) *N-methyldihydrobenzoxazolylidene quinaldine* is a sensitiser and increases the sensitivity of a silver chloride emulsion to about λ 5000 Å. with two maxima at about λ 4400 Å. and λ 4800 Å.

(10) *N-methyldihydrobenzthiazolylidene lepidine* is a sensitiser and sensitises silver chloride emulsion over a band from about λ 4300 Å. to λ 5400 Å. with a maximum at about λ 5200 Å.

(11) *N-methyldihydrobenzthiazolylidene-4'-methylquinaldine* is a powerful sensitiser and extends the sensitivity of a silver chloride emulsion to about λ 5500 Å. with maxima at about λ 4700 Å. and λ 5100 Å.

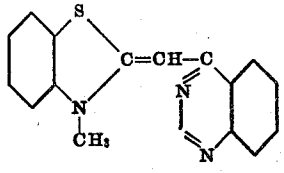
(12) *N-methyl-4-5-dimethoxydihydrobenzthiazolylidene quinaldine* is a sensitiser and extends the sensitivity of silver chloride emulsions to about λ 5800 Å. with maxima at λ 5000 Å. and λ 5500 Å.

(13) *N-methyl-4:5-dimethoxydihydrobenzselenazolylidene quinaldine* is a sensitiser and extends the sensitivity of a silver chloride emulsion to about λ 5400 Å. with an indeterminate maximum at about λ 4750 Å.

(14) *N-methyl-5:6-benzdihydrobenzthiazolylidene quinaldine* is a powerful sensitiser and extends the sensitivity of a silver chloride emulsion to about λ 5600 Å. with maxima at about λ 4700 Å. and λ 5200 Å.

(15) *N-methyldihydrobenzthiazolylidene-4'-methylthiolquinaldine* is a powerful sensitiser and increases the sensitivity of a silver chloride emulsion to λ 5600 Å. with an indeterminate maximum at about λ 5150 Å.

(16) *N-methyldihydrobenzthiazolylidene-1:4'-methylquinazoline*



is a sensitiser and extends the sensitivity of a photographic silver chloride emulsion to λ 5500 Å. with two indeterminate maxima at λ 4500 Å. and λ 4800 Å.

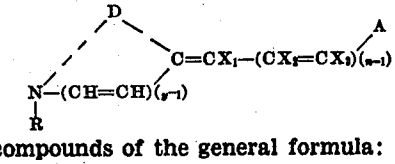
I claim:

1. A sensitized photographic silver halide emulsion in which is incorporated p-dimethylamino styryl benzthiazole.

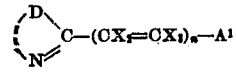
2. A sensitized photographic silver halide emulsion in which is incorporated 2-methyl-dihydrobenzthiazolylidene quinaldine.

3. A sensitized photographic silver halide emulsion in which is incorporated 1:3:3-trimethyl indolyidine-2':1'-ethylidene quinaldine.

4. A photographic silver halide emulsion containing in sensitizing amounts a compound selected from the group consisting of compounds of the general formula:

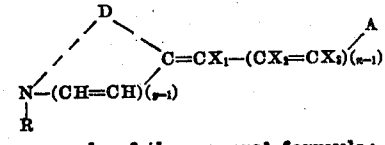


and compounds of the general formula:

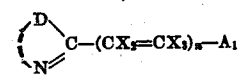


wherein D represents the atoms necessary to complete a heterocyclic nitrogen molecule; R represents a hydrocarbon radical; A is a radical selected from the group consisting of heterocyclic nitrogen bases linked to the open chain in a position of the group consisting of α and γ to the ring nitrogen atom; A' is an aminoaryl radical, *n* is a positive integer and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl and halogen groups, and Y is a positive integer less than 3; having a conjugated chain with an odd number of carbon atoms between the two nitrogen atoms.

5. A photographic silver halide emulsion containing in sensitizing amounts a compound selected from the group consisting of compounds of the general formula:

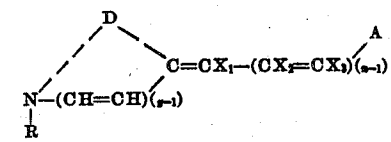


and compounds of the general formula:

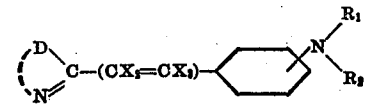


wherein D represents the atoms necessary to complete a heterocyclic nitrogen nucleus of the type contained in cyanine dyes; R represents a hydrocarbon radical; A is a radical selected from the group consisting of heterocyclic nitrogen bases linked to the open chain in a position of the group consisting of α and γ to the nitrogen atom; A' is an aminoaryl radical; *n* is a positive integer less than 3 and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl, and halogen groups, having a conjugated chain with an odd number of carbon atoms between the two nitrogen atoms.

6. A photographic silver halide emulsion containing in sensitizing amounts a compound selected from the group consisting of compounds of the general formula:

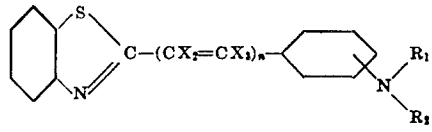


and compounds of the general formula:



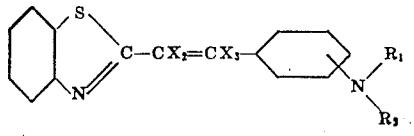
wherein D represents the atoms necessary to complete a heterocyclic nitrogen nucleus of the type contained in cyanine dyes; the R's represent alkyl radicals; A is a radical selected from the group consisting of heterocyclic nitrogen bases linked to the open chain in a position of the group consisting of α and γ to the nitrogen atom; n is a positive integer less than 3 and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl and halogen groups; having a conjugate chain with an odd number of carbon atoms between the two nitrogen atoms.

7. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula



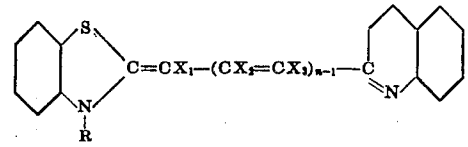
wherein the R's are hydrocarbon groups; n is a positive integer; and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl, and halogen groups, and having a conjugated chain with an odd number of carbon atoms between the two nitrogen atoms.

8. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula:



wherein the R's are alkyl groups; and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl, and halogen groups, and having a conjugated chain with an odd number of carbon atoms between the two nitrogen atoms.

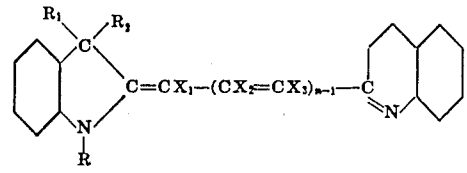
9. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula:



wherein the R's are hydrocarbon groups; n is a positive integer less than 3; and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl, and halogen groups.

10. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula set forth in claim 9, wherein the hydrocarbon radicals are alkyl groups.

11. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula



wherein the R's are hydrocarbon groups; n is a positive integer less than 3; and the X's are members of the group consisting of hydrogen, alkyl, aryl, aralkyl, and halogen groups.

12. A photographic silver halide emulsion containing in sensitizing amounts a compound of the formula set forth in claim 11, wherein the hydrocarbon radicals are alkyl groups.

JOHN DAVID KENDALL.