United States Patent [19]

Ficken et al.

[11] **3,772,033**

[45] **Nov. 13, 1973**

[54] **SUPER-SENSITIZED PHOTHOGRAPHIC SILVER HALIDE MATERIAL**

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[22] Filed: **Nov. 30, 1971**

[21] Appl. No.: **203,367**

[30] **Foreign Application Priority Data**

Dec. 1, 1970 Great Britain 57,078/70

[52] **U.S. Cl.** **96/126,** 96/135

[51] **Int. Cl.** **G03c 1/14**

[58] **Field of Search** 96/126

[56] **References Cited**

UNITED STATES PATENTS

2,313,922	3/1943	Carroll et al.	96/126
2,316,268	4/1943	Mareis	96/126
2,533,426	12/1950	Carroll et al.	96/126
3,672,898	6/1972	Schwan et al.	96/126

Primary Examiner—J. Travis Brown

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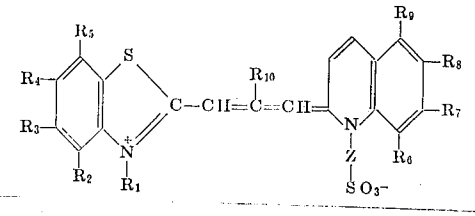
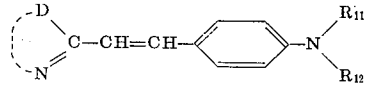
[57] **ABSTRACT**

A photographic silver halide emulsion comprising a super-sensitising combination consisting of a sensitising dye of the formula



(I)

where R_1 is a lower alkyl radical, R_2, R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are each selected from hydrogen and halogen atoms and lower alkyl or alkoxy radicals, R_{10} is a lower alkyl radical and Z is an alkylene radical, together with a styryl base of the formula:

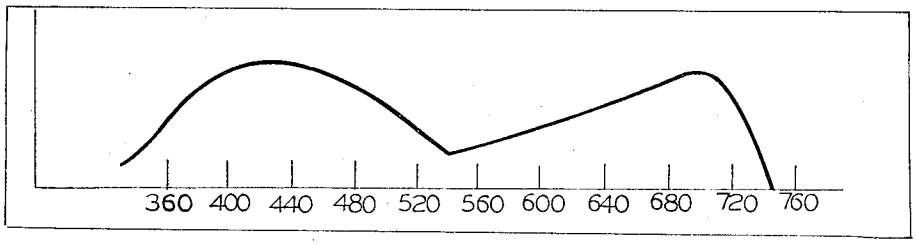


(II)

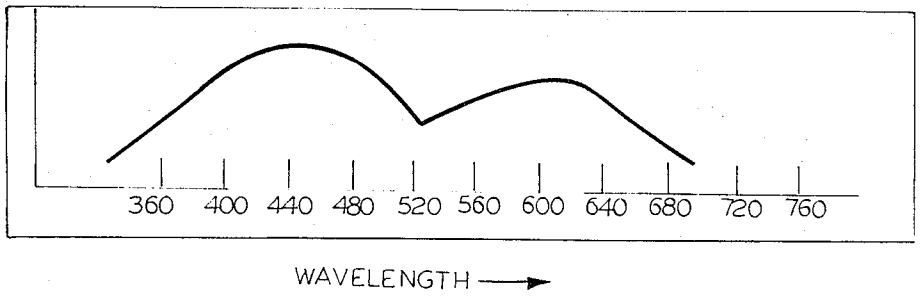
where D represents the atoms necessary to complete a heterocyclic ring and R_{11} and R_{12} are each lower alkyl radicals is described.

4 Claims, 1 Drawing Figure

DYE + STYRYL BASE



D + 5



j + 5

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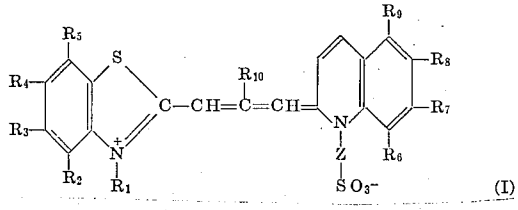
SUPER-SENSITIZED PHOTHOGRAPHIC SILVER HALIDE MATERIAL

This invention relates to photographic light-sensitive materials and more particularly to the manufacture of dye-sensitise photographic silver halide emulsions.

Photographic silver halide emulsions have a certain natural sensitivity to light but this is restricted to a short range of wavelengths in the ultraviolet and/or blue regions of the spectrum. The effect of incorporating a sensitising dye is to impart to the emulsion sensitivity to light of other wavelengths. It has been known for some years that by incorporating in the emulsion, together with the sensitising dye, a second substance which may or may not itself be a sensitising dye, there may sometimes be imparted to the emulsion an additional sensitivity beyond that which can be regarded as the sum effect of the separate substances. Combinations of sensitising dye and other substances which give this better result are known as supersensitising combinations. Examples of such supersensitising combinations e.g. of certain acid carbocyanine dyes and styryl bases are given in U.S. Pat. No. 2,533,426.

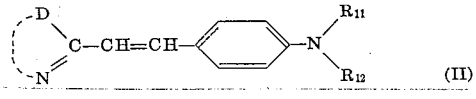
The present invention is based on the discovery of a supersensitising combination of certain acid carbocyanine dyes and certain styryl bases which yield, in some respects, superior results to the combinations described in U.S. Pat. No. 2,533,426.

According to the present invention there is provided a photographic silver halide emulsion which comprises a supersensitising combination which consists of a sensitising dye of the formula I:



(I)

wherein R_1 is a lower alkyl radical, R_2, R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are each selected from hydrogen and halogen atoms and lower alkyl or alkoxy radicals, R_{10} is a lower alkyl radical and Z is an alkylene radical, together with a styryl base of the formula II:



(II)

where D represents the atoms necessary to complete a heterocyclic ring and R_{11} and R_{12} are each lower alkyl radicals.

By lower alkyl or alkoxy radicals are meant radicals having one to four carbon atoms.

Preferably D represents the atoms necessary to complete a thiazole, benzothiazole, benzimidazole or benzoxazole ring system.

From 0.01 g to 0.5 g of the sensitising dye of formula I per 1.5 g moles of silver present in the emulsion can be conveniently used. Likewise from 0.005 g to 0.1 g of the styryl base of formula II per 1.5 g moles of silver present in the emulsion may be used.

By use of a combination of the dye and the styryl base as just set forth an enhanced sensitivity is obtained and is illustrated by the specific examples.

The following dyes and styryl bases were used in the Examples which follow:

Dyes

A. Anhydro-(1-3'sulphopropyl-2-quinoline)(3-ethyl-5-methoxy-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

B. Anhydro-(1,3'-sulphopropyl-2-quinoline)(5-bromo-3-ethyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

C. Anhydro-(6-chloro-1-3'sulphopropyl-2-quinoline)(5-bromo-3-ethyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

D. Anhydro-(6-bromo-1-3'-sulphopropyl-2-quinoline)(5-chloro-3-ethyl-2-benzothiazole) β-methyltrimethincyanine hydroxide.

E. Anhydro-(1-3'-sulphopropyl-2-quinoline)(3-methyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

F. Anhydro-(6-chloro-1-4'-sulphobutyl-2-quinoline)(5-bromo-3-ethyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

G. Anhydro-(6-fluoro-1-3'-sulphopropyl-2-quinoline)(5-chloro-3-ethyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

H. Anhydro-(6-chloro-1-3'-sulphopropyl-2-quinoline)(3-ethyl-5,6-dimethyl-2-benzothiazole) β-ethyltrimethincyanine hydroxide.

Styryl bases

1. 2-p-Dimethylaminostyrylbenzoxazole.
2. 2-p-Dimethylaminostyryl-4-methylthiazole.
3. 2-p-Diethylaminostyryl-4-methylthiazole.
4. 2-p-Dimethylaminostyrylbenzimidazole.
5. 2-p-Diethylaminostyrylbenzothiazole.
6. 2-p-Diethylaminostyrylbenzoxazole.

The following Examples will serve to illustrate the invention.

EXAMPLE 1

The above Dye A and the styryl bases, 1, 2 and 3 were added to high speed silver iodobromide emulsion containing 5.4 mol per cent of silver iodide, after digestion of the emulsion, the quantity shown for each compound being the amount per 1½ g mols of silver halide. The emulsion was divided into portions, each portion was coated onto a film strip. After exposure the strips were developed and the relative log speed of the emulsions were determined. The speeds are relative log speeds measured to light passing through a suitable filter, the term 'relative log speed' being directly related to the logarithm of the reciprocal of the exposure in metre-candle-seconds required to produce a density of 0.1 above fog. A higher figure indicates a higher speed. The filters used were minus blue, No. 110 and the tricolour red, No. 204 of the Ilford Colour Filters handbook.

Dye, mg.		Styryl base, mg.		Relative log speeds	
				Minus blue	red
A.	100		—	3.30	3.19
	—	1.	28	2.90	—
	100		28	3.65	3.53
A.	—		56	2.90	—
	100		56	3.80	3.69
A.	100		—	3.70	3.53
	—	2.	14	3.00	—
	100		14	3.73	3.60
A.	100		—	3.30	3.19
	—	3.	28	—	—

	100		28	3.40	3.25

EXAMPLE 2

The method of testing was as in Example 1, except that the dye and styryl base were added to the emulsion before digestion.

Dye, mg		Styryl base, mg		Relative log speeds Minus blue	red
B.	100		—	3.65	3.50
	—	1.	28	2.68	—
	100		28	3.93	3.80
B.	100		—	3.65	3.50
	—	3.	14	2.72	—
	100		14	3.70	3.60
C.	100		—	3.32	3.28
	—	1.	28	2.68	—
	100		28	3.74	3.67
C.	100			3.20	2.85
	—	4.	28	2.94	
	100		28	3.90	3.43
D.	200		—	3.79	3.67
	—	3.	28	2.80	—
	150		28	3.91	3.87
D.	100		—	3.78	3.70
	—	4.	28	3.08	—
	100		28	4.38	4.24
D.	200		—	3.79	3.67
	—	5.	14	2.84	—
	150		14	4.39	4.25
E.	150		—	4.21	4.14
	—	4.	28	3.00	—
	150		28	4.46	4.38
E.	150		—	4.21	4.14
	—	5.	14	2.86	—
	150		14	4.32	4.20
F.	150		—	3.36	3.30
	—	4.	28	3.00	—
	150		28	3.54	3.47
F.	150		—	3.36	3.30
	—	5.	14	2.86	—
	150		14	3.52	3.48
G.	100		—	4.22	3.83
	—	4.	28	—	—
	100		28	4.44	4.11
G.	150		—	4.24	3.90
	—	6.	14	2.74	—
	150		14	4.30	3.86
H.	100		—	4.06	4.01
	—	4.	28	3.08	—
	100		28	4.38	4.28

EXAMPLE 3

The method of testing of Example 1 was used, except that the dye was added before digestion of the emulsion and the styryl base after digestion.

Dye, mg		Styryl base, mg		Relative log speeds Minus blue	red
A.	100		—	3.70	3.53
	—	1.	21	3.05	—
	100		21	3.77	3.68
A.	100		—	3.70	3.53
	—	2.	14	3.00	—
	100		14	3.73	3.60

EXAMPLE 4

In this Example two supersensitising combinations of use in the present invention were compared with one of the dyes described in U.S. Pat. No. 2,533,426 used in combination with the same two styryl bases used in the above combinations.

The dyes used were dyes C and D as hereinbefore set forth and styryl bases 4 and 5 as hereinbefore set forth. The dye described in U.S. Pat. No. 2,533,426 was anhydro-(1-ethyl-2-quinoline) (5-chloro-3-2'-sulphoethyl-2-benzothiazole)trimethincyanine hydroxide. This is hereinafter designated dye *j*.

The emulsions containing the dye and styryl base combinations were prepared as in Example 2, i.e. both the dye and the styryl base were added to the emulsion before the digestion thereof.

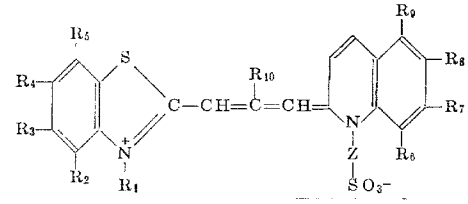
Dye mg.		Styryl base, mg.		Relative log speeds Minus blue	red
C.	100		—	3.99	3.95
	—	4.	28	3.01	—
	100		28	4.22	4.19
D.	130		—	4.06	3.98
	—	5.	13	3.27	—
	130		13	4.48	4.41
D.	100		—	4.10	4.11
	100	5.	13	4.61	4.44
j.	130		—	4.33	3.98
	—	4.	13	3.00	—
	130		13	4.44	4.10
i.	130		—	4.33	3.98
	—	5.	13	3.27	—
	130		13	4.52	4.12

These results show that an enhanced red speed of the emulsion is obtained using the supersensitising combinations used in the present invention compared with the supersensitising combination of a dye described in U. S. Pat. No. 2,533,426 and two styryl bases.

The supersensitising combinations used in the present invention sensitise the emulsion beyond 700 nm while the supersensitising combinations described in U. S. Pat. No. 2,533,426 do not extend the spectral sensitivity of the emulsions beyond about 670 nm. The comparative wedge spectrograms of two of the combinations compared above is shown in the accompanying diagram.

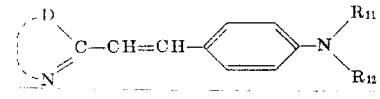
What we claim is:

1. A photographic silver halide emulsion which contains a super-sensitizing dye of the formula:



(I)

where R_1 is a lower alkyl radical, R_2, R_3Q R_4, R_5, R_6Q R_7, R_8 and R_9 are each selected from hydrogen and halogen atoms and lower alkyl or alkoxy radicals, R_{10} is a lower alkyl radical and Z is an alkylene radical, together with a styryl base of the formula:



(II)

where D represents the atoms necessary to complete a thiazole, benzothiazole, benzimidazole or benzoxazole ring system and R_{11} and R_{12} are each lower alkyl radicals.

2. A photographic silver halide emulsion according to claim 1 wherein from 0.01 to 0.5 g of the sensitising dye is present per 1.5 g moles of silver present in the emulsion.

3. A photographic silver halide emulsion according to claim 1 wherein from 0.005 to 0.1 g of the styryl base is present per 1.5 g moles of silver present in the emulsion.

4. A photographic silver halide emulsion according to claim 1 wherein from 0.01 to 0.5 g of the sensitizing dye and from 0.005 to 0.1 g of the styryl base each is present per 1.5 g moles of silver present in the emulsion.

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