

[54] **SILVER HALIDE PHOTOGRAPHIC EMULSION FOR RECORDING ELECTRON BEAM**

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Related U.S. Application Data

[62] Division of Ser. No. 181,136, Sept. 16, 1971, abandoned.

[30] **Foreign Application Priority Data**

Sept. 16, 1970 Japan..... 45-81112

[52] U.S. Cl. 346/1; 96/129; 250/475

[51] Int. Cl.² G01D 9/00

[58] Field of Search 96/129; 250/475; 346/1

[56] **References Cited**

UNITED STATES PATENTS

3,303,341	2/1967	Fram et al.	96/82
3,632,348	1/1972	James	96/137
3,706,566	12/1972	Shiba et al.	96/129

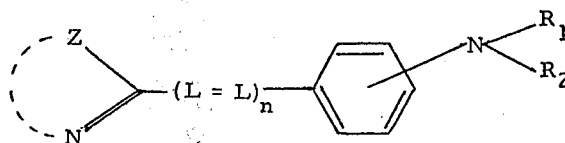
OTHER PUBLICATIONS

Herz, The Photographic Action of Ionizing Radiations, pp. 59-61, Wiley-Interscience, New York, 1969.

Primary Examiner—J. Travis Brown
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

The invention relates to a photographic emulsion for recording an electron beam which comprises fine grains of silver halide having adsorbed thereon at least one aminostyryl base represented by the following general formula:



wherein Z is an atomic group required for forming a heterocyclic ring, R₁ and R₂ are lower alkyl group, L is a methine group, and n is 1 or 2.

6 Claims, No Drawings

SILVER HALIDE PHOTOGRAPHIC EMULSION FOR RECORDING ELECTRON BEAM

This is a division of application Ser. No. 181,136, filed Sept. 16, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a silver halide photographic emulsion and particularly to a silver halide photographic emulsion having fine particles the sensitivity of which, with respect to an electron beam, in the case of irradiation with an electron beam, is remarkably elevated by sensitizing the emulsion with an aminostyryl base which is known as a sensitizing dye.

2. Description of the Prior Art

In the art of producing silver halide photographic emulsions, it is well-known to add a certain kind of sensitizing dye to a silver halide emulsion to thereby expand its light-sensitive wavelength region.

Furthermore, it has been found that when spectral sensitization is applied to a silver halide emulsion of fine particles by employing a certain sensitizing dye, its region of light-sensitive wavelength is not only expanded, but also the light sensitivity in the region of intrinsic absorption wavelength of the silver halide is remarkably elevated (U.S. Pat. No. 3,706,570).

In light-sensitive materials for high density recording, particularly light-sensitive materials for recording an electron beam, it is required to obtain an image of a high image quality and accordingly, first of all, it is required that the particle size of the silver halide be as small as possible in order to obtain an image of a high resolving power. However, the reduction of the particle size of the silver halide generally effects the reduction of sensitivity to the electron beam.

Next, it is important that the surface charge of a light-sensitive element at the time of irradiating the electron beam be made to decrease in order to represent a clear image. For this reason, a light-sensitive element having a high sensitivity to electron beams is required so that the intensity of the electron beam to be irradiated can be decreased.

For the above-mentioned reasons, for the production of light-sensitive elements for recording electron beams, a silver halide emulsion having a high electron beam sensitivity and as small a particle size of the silver halide as is possible is required, and accordingly, a sensitizing technique with respect to electron beams becomes a serious problem.

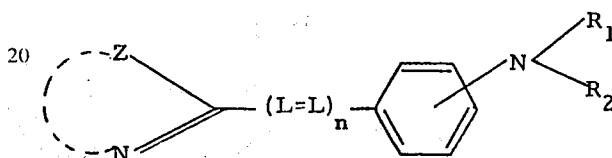
SUMMARY OF THE INVENTION

An object of the present invention, therefore, is to provide a silver halide photographic emulsion having a high electron beam sensitivity and which gives a high image quality.

The present inventors have found a method for elevating remarkably the electron beam sensitivity of the silver halide emulsion by adding an aminostyryl base to the photographic emulsion containing fine particles of silver halide crystal.

The above described object is attained by incorporating at least one aminostyryl base represented by the following general formula into the photographic emulsion containing fine grains of silver halide.

General Formula



wherein Z is an atomic group required for forming a heterocyclic ring (which may be substituted); R_1 and R_2 are lower alkyls (for example, methyl, ethyl, or the like); L is methine (the hydrogen atom of the methine may be substituted with nitrile or the like), and n is 1 or 2.

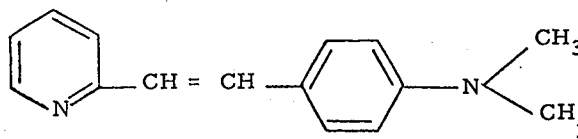
DESCRIPTION OF THE PREFERRED EMBODIMENTS

As the above described heterocyclic ring, there are, for example, pyridines, oxazoles, benzoxazoles, naphthoxazoles, benzimidazoles, naphthoimidazoles, thiazoles, benzthiazoles, naphthothiazoles, selenazoles, benzselenazoles, naphthoselenazoles, and the like.

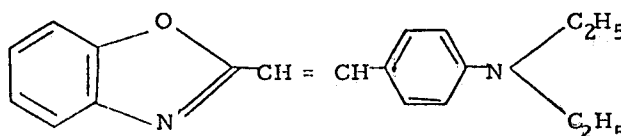
The aminostyryl bases employed for this invention can be easily synthesized by those skilled in the art by referring to the specifications of, e.g., U.S. Pat. No. 2,169,434 and U.S. Pat. No. 2,345,094, and a publication entitled "The Cyanine Dyes and Related Compounds" authored by Frances M. Hamer and published by John Wiley and Sons Ltd. (1964).

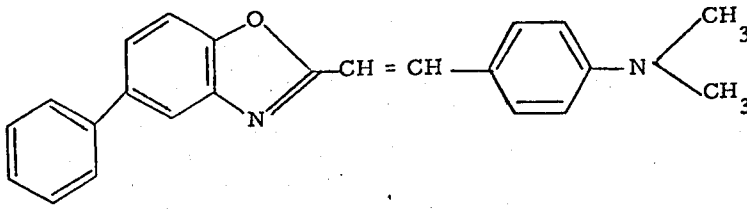
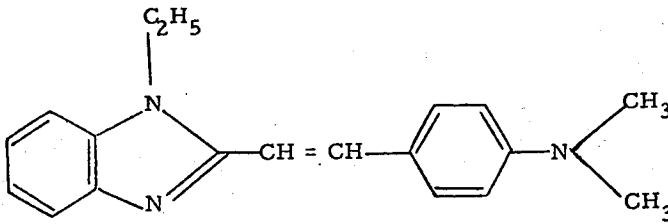
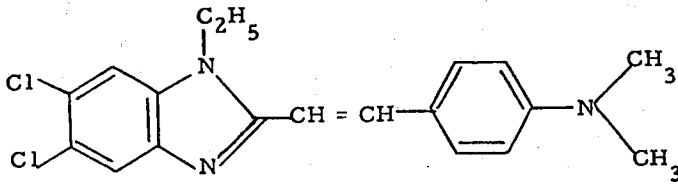
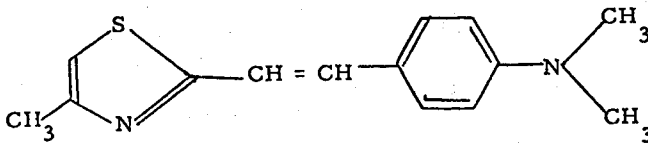
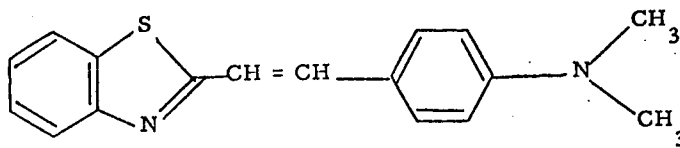
In the following, typical aminostyryl bases which may be employed in the present invention will be illustrated, but it is to be noted that the aminostyryl bases are not limited to them.

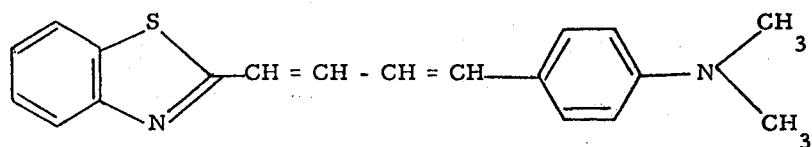
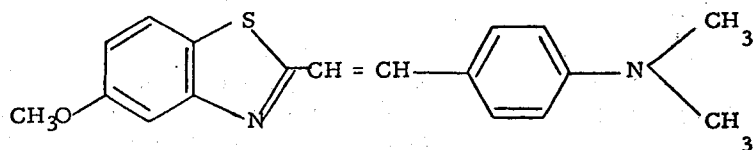
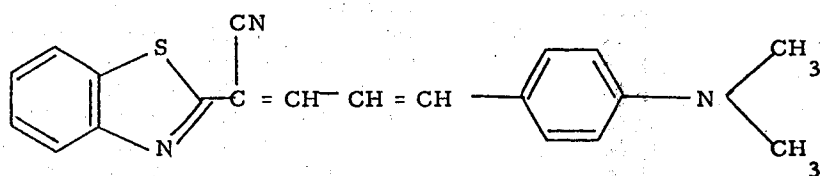
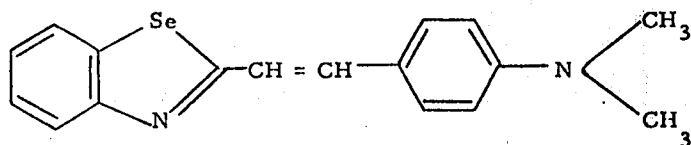
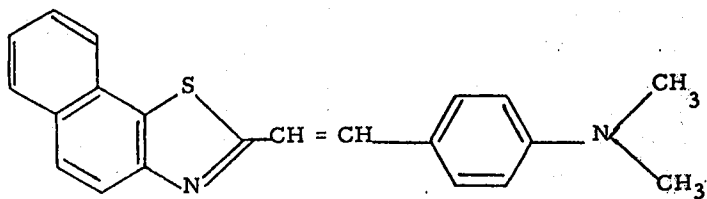
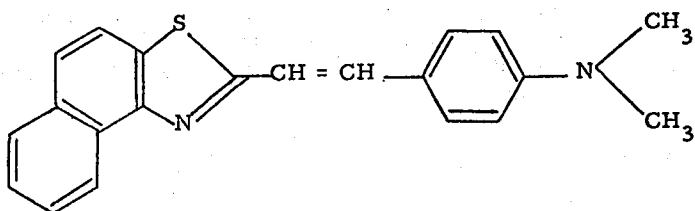
Dye 1



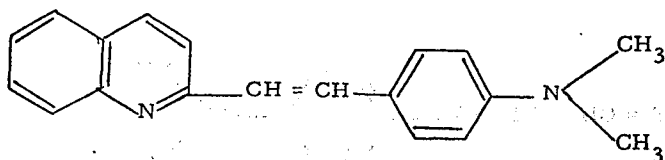
Dye 2



Dye 3Dye 4Dye 5Dye 6Dye 7

Dye 8Dye 9Dye 10Dye 11Dye 12Dye 13

Dye 14



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The silver halide emulsion employed for the present invention contains gelatin or other synthetic polymers as a binder and a silver halide such as silver chloride, silver bromide, silver chlorobromide, silver iodobromide, and silver chloriodobromide (particularly, silver bromide or silver iodobromide emulsions), said silver halide preferably having a mean grain size, by number or by weight, of no more than 0.2 μ , particularly no more than 0.1 μ .

In order to prepare this silver halide photographic emulsion in accordance with the present invention, the dye of the present invention may be added to a silver halide emulsion prepared by an ordinary process and on the other hand, a silver halide photographic emulsion having similar advantageous effects as mentioned above can also be obtained by adding the dye to the emulsion in the production process, physical ripening process, or chemical ripening process of the silver halide crystal. The silver halide emulsion of the present invention may be sensitized with a sulfur compound and gold complex salt or not sensitized therewith, or the emulsion may be spectrally sensitized with a sensitizing dye such as a cyanine and a merocyanine. Furthermore, in accordance with a common method, the silver halide photographic emulsion of the present invention may be used in combination with chemical sensitizing agents, stabilizing agents, antifogging agents, matting agents, antistatic agents, hardening agents, surface active agents, plasticizers, or development accelerators etc. and, if required, color formers, fluorescent brightening agents, or color toning agents, etc.

It is usual that the aminostyryl base employed in the present invention is used in the form of a suitable solution which is prepared by dissolving the aminostyryl base into a suitable solvent such as methanol, ethanol, or the like, and the quantity to be added thereof can be varied within a wide range of 5 mg - 500 mg per 1 Kg of the emulsion in accordance with desired effects or advantages.

The present invention will be more specifically described by the following illustrative examples.

EXAMPLES

A silver bromide emulsion having a mean grain size, by number, of 0.08 μ was prepared by a concurrent mixing method, and sulfur sensitization and gold sensitization were applied thereto. Then, the sensitized emulsion was divided into two parts, and the aminostyryl

base of the present invention was added to one emulsion and was not added to the other. Each of the resulting emulsions was applied onto a film base of cellulose triacetate to prepare specimens, respectively.

These specimens were subjected to irradiation in a stepwise manner by the use of an electron beam irradiating apparatus under conditions such that the acceleration voltage was 20 KV and the beam current density was within a range of from 10^{-10} to 10^{-8} coulomb/cm², respectively. Then, the irradiated specimens were subjected to development by the use of D-76 developer at a temperature of 20°C for 4 minutes, and each characteristic curve of the specimens was obtained.

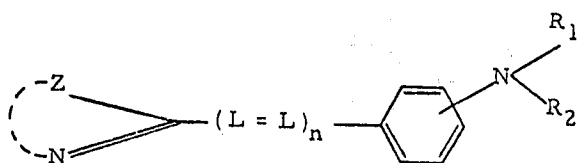
Assuming that the sensitivity of the emulsion without the aminostyryl base is 1 at the point where the optical density is fog +0.5, the common logarithms of the sensitivity of the emulsions to which each suitable quantity of the aminostyryl base was added, that is $\Delta \log E$, are shown in the following Table 1 as the sensitizing factors of these compounds, respectively.

Table 1

Ex. No.	Dye No.	Results of Electron Beam Sensitometry		
		Quantity Added gr. mol/Kg Emulsion	Sensitization Factor ($\Delta \log E$) at Fog + 0.5	Fog
	Without Addition	0	0	0.03
1	1	4×10^{-4}	0.48	0.05
2	2	4×10^{-4}	0.40	0.04
3	3	4×10^{-4}	0.38	0.04
4	4	4×10^{-4}	0.46	0.03
5	5	4×10^{-4}	0.43	0.03
6	6	4×10^{-4}	0.30	0.03
7	7	4×10^{-4}	0.36	0.03
8	8	4×10^{-4}	0.40	0.04
9	9	4×10^{-4}	0.34	0.03
10	10	4×10^{-4}	0.35	0.04
11	11	4×10^{-4}	0.36	0.03
12	12	4×10^{-4}	0.30	0.04
13	13	4×10^{-4}	0.30	0.04
14	14	4×10^{-4}	0.30	0.06

What is claimed is:

1. An electron beam recording process comprising irradiating, with an electron beam, an electron beam recording material comprising a silver halide emulsion whose silver halide grains have a mean grain size no more than 0.2 micron and have adsorbed thereon at least one aminostyryl base represented by the following formula:



wherein Z is an atomic group required for forming a pyridine, oxazole, benzoxazole, naphthoxazole, benzimidazole, naphthiomidazole, thiazole, benzthiazole, naphthothiazole, selenazole, benzselenazole, or naphthoselenazole ring, R_1 and R_2 are lower alkyl groups, L

is a methine group, and n is 1 or 2, and developing the irradiated material to form an image.

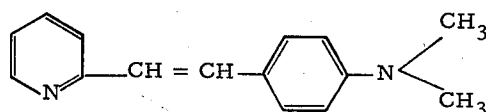
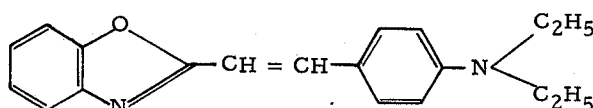
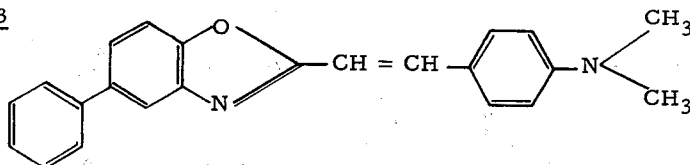
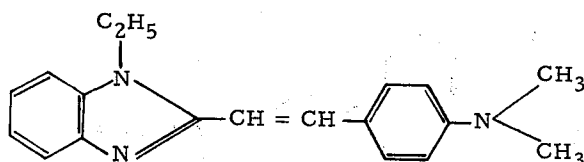
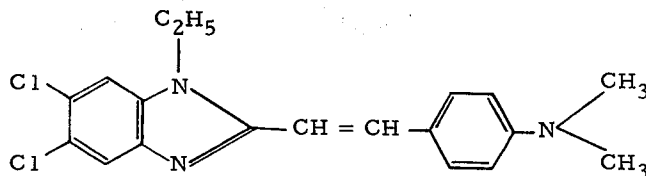
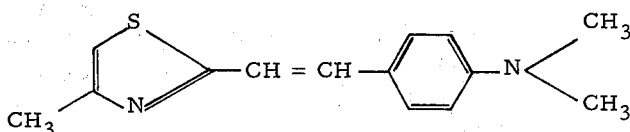
2. The process according to claim 1, wherein said silver halide has a mean grain size of not more than 0.1 μ .

3. The process according to claim 1, wherein the silver halide is silver bromide or silver iodobromide.

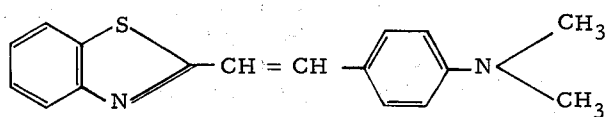
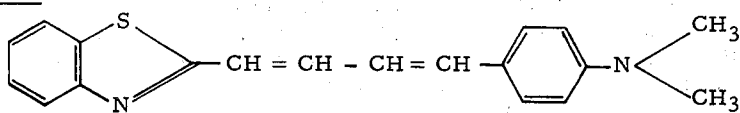
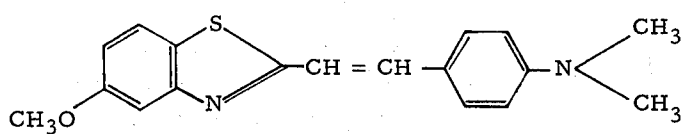
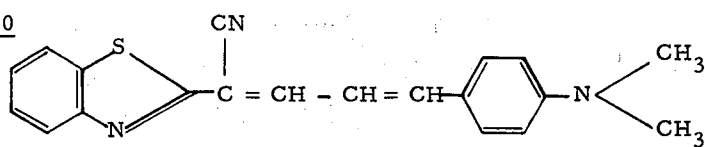
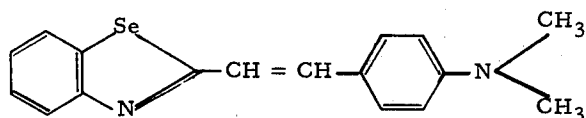
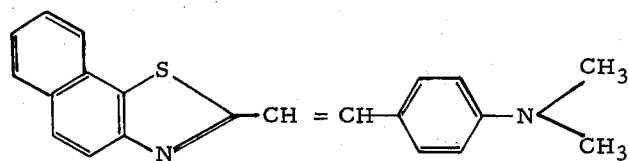
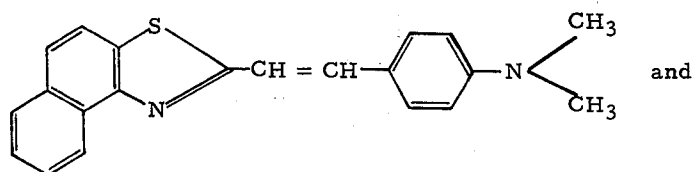
4. The process according to claim 1, wherein the quantity of the aminostyryl base is within the range of 5 mg to 500 mg per 1 Kg of the emulsion.

5. The process according to claim 1, wherein said aminostyryl base is selected from the group consisting of:

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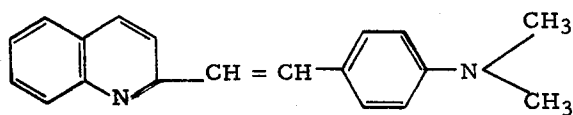
Dye 1Dye 2Dye 3Dye 4Dye 5Dye 6

11

Dye 7Dye 8Dye 9Dye 10Dye 11Dye 12Dye 13

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Dye 14

6. The process according to claim 1, wherein the irradiating is conducted under ambient temperature conditions.

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