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3,788,859 FINE GRAIN SILVER HALIDE PHOTOGRAPHIC EMULSION CONTAINING HEMICYANINE SENSITIZING DYE

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U.S. Cl. 96—139

8 Claims

ABSTRACT OF THE DISCLOSURE

A hemicyanine dye is used to spectrally sensitize silver halide photographic emulsions to produce emulsions having high photosensitivity in the region of wavelengths of absorption intrinsic to silver halide and in the region of wavelengths of the dye.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a spectrally sensitized silver halide photographic emulsion, in particular, to a silver halide photographic emulsion of fine grains having remarkably high photosensitivity in the region of wavelengths of absorption intrinsic to silver halide, not only in the region of the absorption wavelengths of a sensitizing dye, by spectrally sensitizing with hemicyanine dye.

(2) Prior art

It is well known in the art of producing silver halide photographic emulsions that the region of photosensitive wavelength of silver halide emulsions can be extended by adding a certain kind of sensitizing dye to the silver halide emulsion. Generally, however, when the silver halide emulsion containing silver halide crystals, whose size is that used in the production of normal silver halide photographic sensitive material, is spectrally sensitized, the photosensitivity in the region of wavelengths of absorption intrinsic to silver halide is lowered. This well known phenomenon is called desensitization. Therefore, sensitizing dyes having small desensitizing actions of this kind are desired in the selection of sensitizing dyes used in the production of silver halide photographic sensitive materials. On the other hand, it is preferable to make the grain size of silver halide crystals contained in the silver halide emulsion as small as possible in order to improve the image quality such as resolving power, state of grains therein, etc., obtained from the silver halide photographic sensitive material. However, this lowers the sensitivity of the photographic material in general.

Accordingly, in the field of correlated arts, the art to make the grain size of silver halide crystals as small as possible and to prepare a silver halide emulsion having sufficient sensitivity has resulted in chemical sensitization such as sulfur sensitization or reduction sensitization and the like, becoming a necessity.

"Capri-blue effect" is known as another phenomenon of a rise in photosensitivity by sensitizing dyes in the region of absorption intrinsic to silver halide. However, the Capri-blue effect is the phenomenon which appears at the short time expose with high illuminance when desensitizing or sensitizing dyes are added to the silver halide emulsion which have not been sensitized with sulfur or have not undergone reduction sensitization.

(3) Objects of the invention

An object of the present invention is to obtain a silver halide photographic emulsion whose photosensitivity in

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the region of wavelengths of absorption intrinsic to silver halide is remarkably raised in addition to the region of wavelengths of sensitivity thereof being extended.

Other objects will be apparent to those skilled in the art as the description of this invention proceeds.

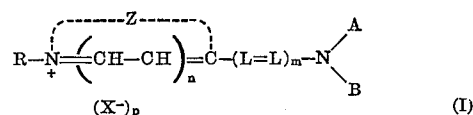
BRIEF SUMMARY OF THE INVENTION

The effect found by this invention is quite different from the aforesaid Capri-blue in that the photosensitivity of the silver halide in the region of wavelengths of absorption intrinsic to silver halide is remarkably raised by adding a hemicyanine dye to the emulsion containing silver halide crystals of certain size even when this emulsion is sensitized by the sulfur sensitization, reduction sensitization or gold sensitization, and that this effect is especially great in long time exposure.

We have found that when silver halide emulsion containing silver halide crystals at least 95% by number of which is no more than 0.2 micron in diameter or silver halide emulsion containing silver halide crystals whose mean particle diameter by number is no more than 0.18 micron is spectrally sensitized in the usual way using hemicyanine dye, the photosensitivity of the silver halide in the region of wavelengths of absorption intrinsic to silver halide can be remarkably raised in addition to the region of wavelengths of sensitivity of the dye used being extended.

DETAILED DESCRIPTION OF THE INVENTION

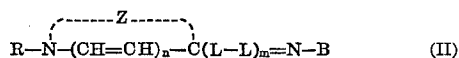
The above-mentioned objects are accomplished by adding at least one of the hemicyanine dyes having the following general Formula I or II to a silver halide emulsion containing silver halide crystals 95% by number of which is no more than 0.2 micron in diameter or to a silver halide emulsion containing silver halide crystals whose mean particle diameter by number is no more than 0.18 microns:



wherein Z represents a group of atoms necessary to complete a five- or six-membered heterocyclic nucleus, such as oxazoline, thiazoline, oxazole, thiazole, selenazole, benzoxazole, benzothiazole, benzoselenazole, naphthoxazole, naphthothiazole, indoline, imidazol, benzimidazole, naphthimidazole, pyridine, quinoline nucleus, etc., which may be substituted, R represents lower alkyl group such as methyl, ethyl, n-propyl, hydroxyalkyl (e.g. beta-hydroxyethyl, beta-methoxyethyl), acetoxyalkyl (such as beta-acetoxyethyl), an alkyl group containing a carboxy group (such as beta-carboxyethyl, gamma-carboxypropyl, delta-carboxybutyl, omega-carboxypentyl, p-carboxyphenylethyl), an alkyl group containing a sulfo group (such as beta-sulfoethyl, gamma-sulfoethyl, gamma-sulfobutyl, delta-sulfobutyl, p-sulfophenylethyl), vinylmethyl, an aralkyl (such as benzyl and phenylethyl), and the like, A represents a hydrogen atom or, when taken together with B, represents a group of atoms necessary to complete a ring, preferably containing at least one heterocyclic atom connected through a polymethylene chain, such as morpholine, pyrrolidine, piperazine, and piperadine, B represents an aryl group (such as phenyl, tolyl, etc.) or, when taken together with A, represents a group of atoms necessary to complete a ring, L represents a methine chain or L and R may be connected with each other through a polymethylene chain, X represents anion such as usually

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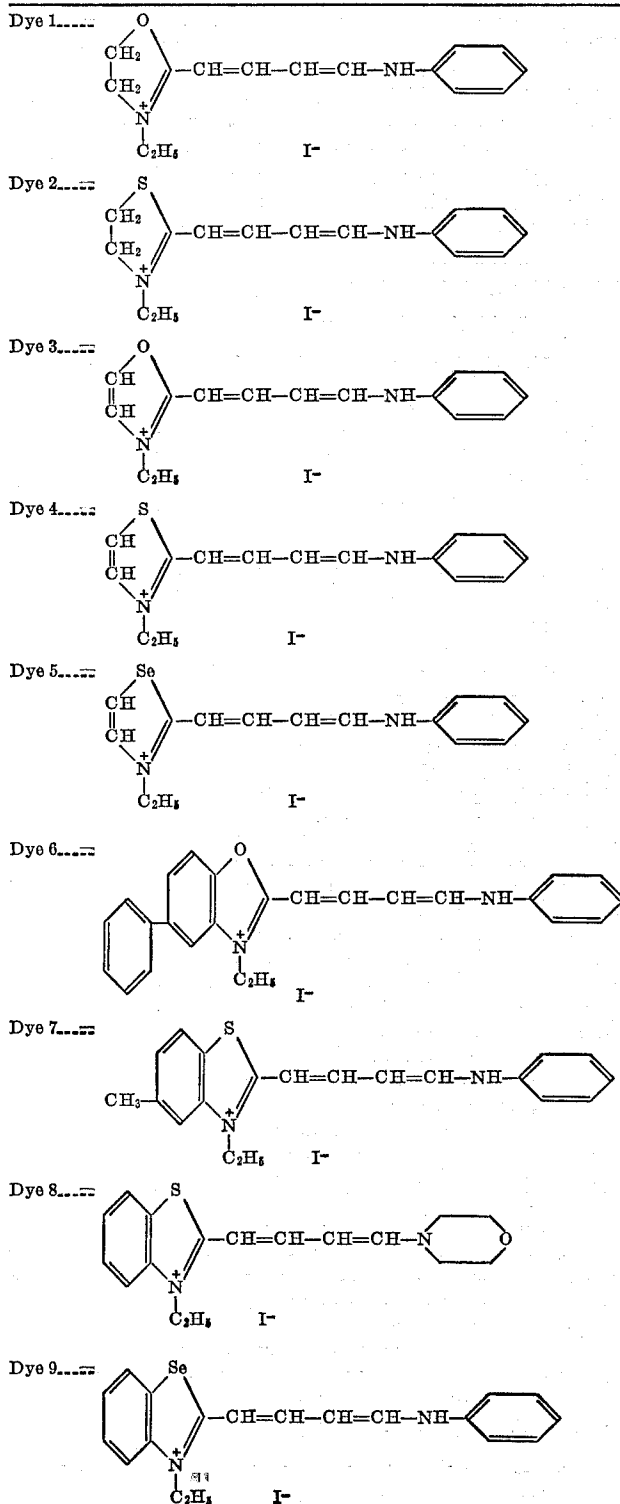
used in the field of the sensitizing dyes (e.g. chloride, bromide, perchlorate, etc., m represents 1, 2 or 3, n represents 0 or 1, p represents 0 or 1, and $p=0$ if an intra-molecular salt thereof is formed.



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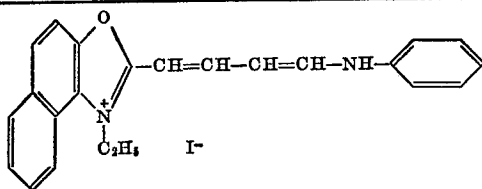
wherein Z, R, L, m and n are the same meanings as those in the general Formula I, B represents an aryl group, such as phenyl, tolyl group, etc.

Representative hemicyanine dyes used in this invention are illustrated as follows, but are not limited only to them.

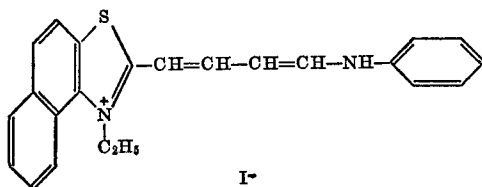


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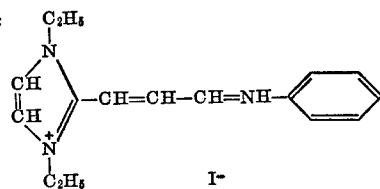
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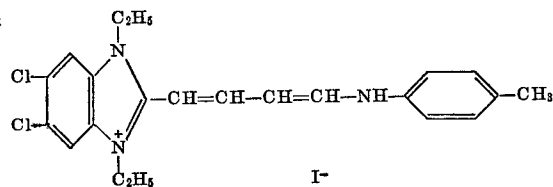
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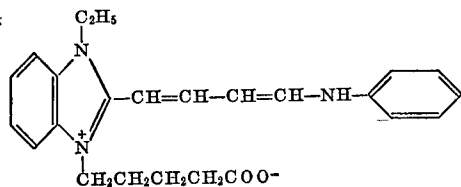
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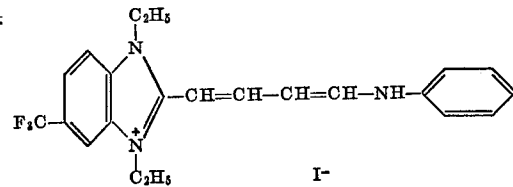
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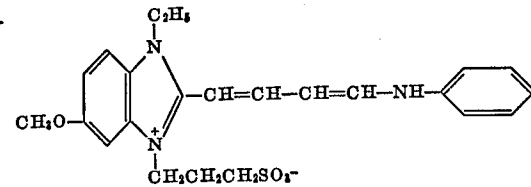
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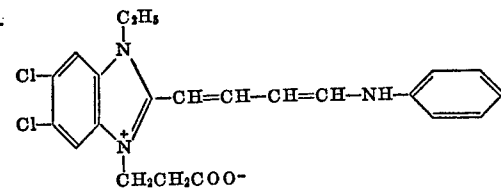
Dye 15....



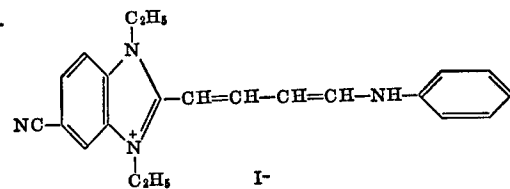
Dye 16....



Dye 17....

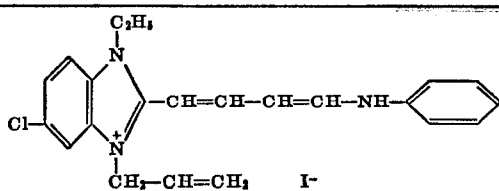


Dye 18....

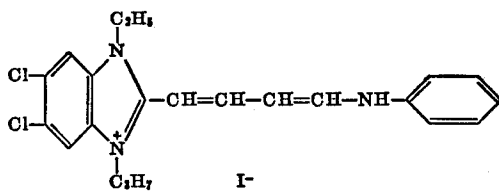


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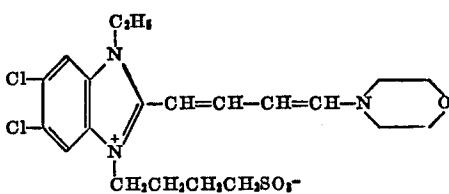
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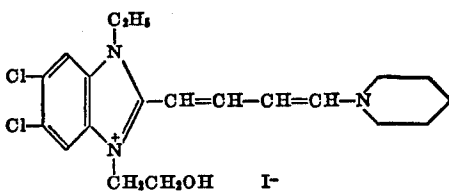
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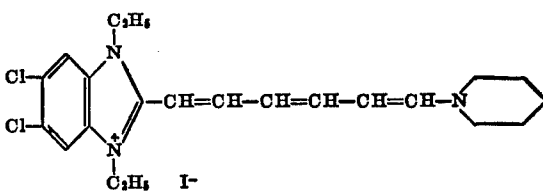
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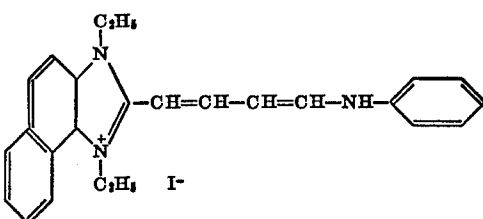
Dye 22....



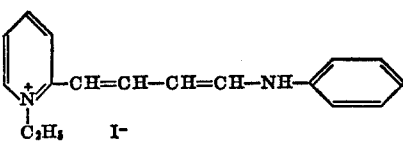
Dye 23....



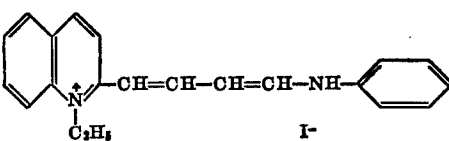
Dye 24....



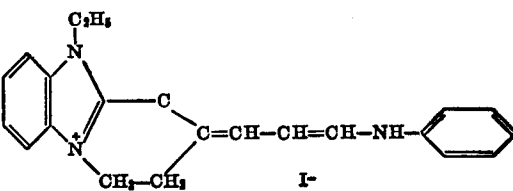
Dye 25....



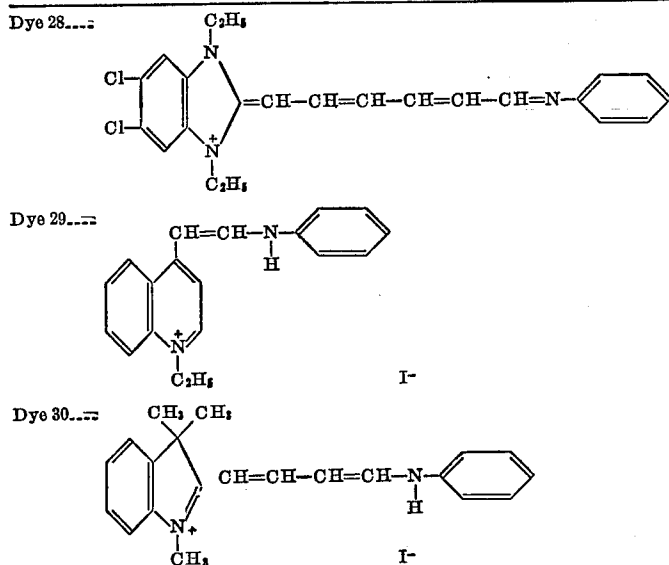
Dye 26....



Dye 27....



TABLE—Continued



The sensitizing dyes used in this invention represented by the general Formula I or II can be readily prepared according to the procedure described for example, in the specification of the British Pat. No. 355,693, or U.S. Pat. Nos. 2,298,732 and 2,369,509.

The hemicyanine dyes used in this invention are capable of not only extending the wavelength region of sensitivity of the photographic emulsion, but at the same time, raising the photosensitivity of silver halide in the region of wavelengths of absorption intrinsic to silver halide, when used in combination with a photographic emulsion containing silver halide crystals at least 95% by number of which is no more than 0.2 micron in diameter or with a photographic emulsion containing silver halide crystals whose mean particle diameter by number is no more than 0.18 micron.

This is especially effective for a gelatin-silver halide emulsion, but it is also effective for a silver halide emulsion containing a hydrophilic colloid other than gelatin, such as agar-agar, collodion, water-soluble cellulose derivative or synthetic or natural hydrophilic resins such as polyvinylalcohol, etc.

Silver halide photographic emulsions used in this invention may be any of silver chloride, silver bromochloride, silver bromide, and silver bromide emulsion, but especially excellent effect is obtained in the case of silver bromide or silver bromide emulsions.

The sensitizing effect of the hemicyanine dyes in this invention to the region of wavelengths of absorption intrinsic to silver halide largely depends on the grain size of silver halide crystals. Even between the photographic emulsions having the same halogen composition, the sensitizing effect differs according to the grain size of silver halide crystals. Especially, in the case of a photographic emulsion containing silver halide crystals whose mean particle diameter by number is more than 0.18 micron, the sensitizing effect in the region of wavelengths of absorption intrinsic to silver halide decreases greatly.

An example using the hemicyanine dye (18) is given below in Table 1:

TABLE 1

Mean particle diameter (μ)	0.07	0.1	0.15	0.20	0.60
Sensitization ratio	5.0	3	1.3	1.0	0.45

The sensitization ratio is given as the ratio based on the sensitivity value without adding the hemicyanine dye to the silver halide emulsion, which is calculated as 1.

It can be understood from Table 1 that the influence of the grain size of the silver halide crystal is quite great.

In order to prepare spectrally sensitized photographic emulsions according to this invention, one or several of

the sensitizing dyes are added in a usual manner to a silver halide photographic emulsion previously sensitized by the chemical sensitization using one or more of unstable sulfur compounds, precious metal complex compounds and reducing compounds.

In practice, the hemicyanine dye is usually dissolved in a suitable solvent such as methanol, ethanol, etc., then added to an emulsion. The amount of the hemicyanine dye contained in an emulsion can be varied widely in the range of from 5 mg. to 500 mg. per 1 kg. of emulsion according to the desired effect.

The photographic emulsions of this invention can further be hypersensitized and supersensitized.

The photographic silver halide emulsions of this invention are, for example, employed for IC plate, holography, electrobeam records, etc.

In the production of the photographic emulsions of this invention, conventional additives such as other chemical sensitizing agents, stabilizers, anti-fogging agents, tone-adjusting agents, hardeners, surface active agents, plasticizers, antistatic agents, lubricants, development accelerators, color couplers and fluorescent brightening agents can be used together in a conventional manner.

This invention will be further explained by the following example.

Photographic emulsions were prepared by adding the hemicyanine dyes given in Table 3 to silver bromide emulsion ($\text{AgI}:\text{AgBr}=1$ mol:99 mols). The resulting emulsions were coated on the film base of cellulose triacetate and dried, which were then exposed to 1000 lux electric light (2666° K.) through Wratten No. 47B filter and developed. The developer having the composition described in Table 2 was used.

TABLE 2

	G.
Metol	2
Hydroquinone	8.8
Anhydrous sodium sulfite	96
Anhydrous sodium carbonate	48
Potassium bromide	5
Water, enough to make 1 liter.	

In Table 3, the sensitization ratio of silver halide, when each of the hemicyanine dyes was added to the silver halide emulsions containing silver halide crystals whose mean particle diameter by number was 0.07 micron or 0.6 micron, in the region of wavelengths of absorption intrinsic to silver halide is given.

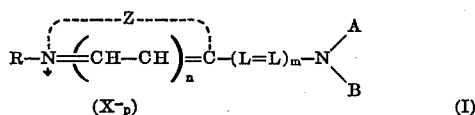
The sensitization ratio was shown as the ratio based on the sensitivity value without adding the hemicyanine dye, which was calculated as 1.

TABLE 3

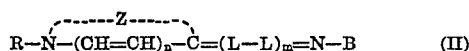
Ex. No.	Dye No.	Amount of dye added/kg. emulsion, mol-gram	Emul-sion	Mean parti-cle diam-eter	Sensiti-zation ratio	Com-par-ison mark	Mean parti-cle diam-eter	Sensiti-zation ratio
1.....	1	10-5/6	AgBrI	0.07	3.0	a	0.6	0.50
2.....	2	10-5/6	AgBrI	0.07	3.2	b	0.6	0.45
3.....	3	10-5/6	AgBrI	0.07	3.4	c	0.6	0.49
4.....	4	10-5/6	AgBrI	0.07	3.0	d	0.6	0.46
5.....	5	10-5/6	AgBrI	0.07	3.1	e	0.6	0.45
6.....	6	10-5/6	AgBrI	0.07	3.0	f	0.6	0.48
7.....	7	10-5/6	AgBrI	0.07	5	g	0.6	0.30
8.....	8	10-5/6	AgBrI	0.07	4.5	h	0.6	0.80
9.....	9	10-5/6	AgBrI	0.07	4.5	i	0.6	0.75
10.....	10	10-5/6	AgBrI	0.07	4.0	j	0.6	0.55
11.....	11	10-5/6	AgBrI	0.07	4.2	k	0.6	0.42
12.....	12	10-5/6	AgBrI	0.07	4.2	l	0.6	0.48
13.....	13	10-5/6	AgBrI	0.07	4.5	m	0.6	0.37
14.....	14	10-5/6	AgBrI	0.07	3.7	n	0.6	0.48
15.....	15	10-5/6	AgBrI	0.07	3.0	o	0.6	0.40
16.....	16	10-5/6	AgBrI	0.07	4.0	p	0.6	0.45
17.....	17	10-5/6	AgBrI	0.07	4.5	q	0.6	0.50
18.....	18	10-5/6	AgBrI	0.07	5.0	r	0.6	0.45
19.....	19	10-5/6	AgBrI	0.07	4.2	s	0.6	0.45
20.....	20	10-5/6	AgBrI	0.07	3.6	t	0.6	0.48
21.....	21	10-5/6	AgBrI	0.07	4.0	u	0.6	0.46
22.....	22	10-5/6	AgBrI	0.07	4.0	v	0.6	0.46
23.....	23	10-5/6	AgBrI	0.07	4.5	w	0.6	0.46
24.....	24	10-5/6	AgBrI	0.07	5.0	x	0.6	0.45
25.....	25	10-5/6	AgBrI	0.07	4.8	y	0.6	0.40
26.....	26	10-5/6	AgBrI	0.07	4.0	z	0.6	0.37
27.....	27	10-5/6	AgBrI	0.07	4.2	a'	0.6	0.35
28.....	28	10-5/6	AgBrI	0.07	4.0	b'	0.6	0.42
29.....	29	10-5/6	AgBrI	0.07	4.5	c'	0.6	0.14
30.....	30	10-5/6	AgBrI	0.07	4.0	d'	0.6	0.38

What is claimed is:

1. A silver halide photographic emulsion comprising at least one of the hemicyanine dyes represented by the following general Formulae I or II and silver halide crystals, at least 95% by number of which are no more than 0.2 micron in diameter, or whose mean particle diameter by number is no more than 0.18 micron:

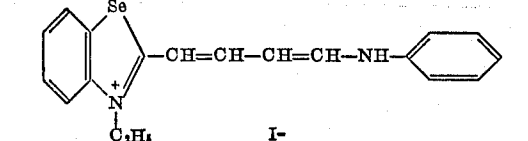
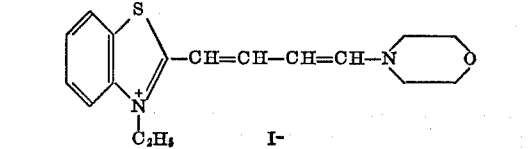
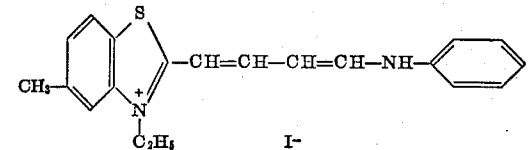
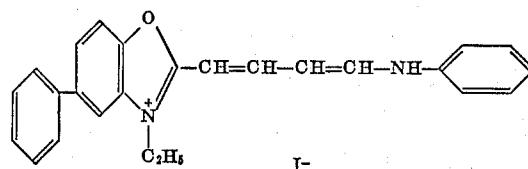
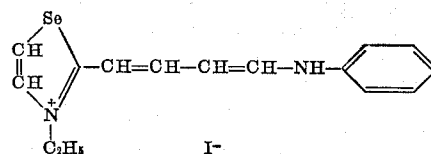
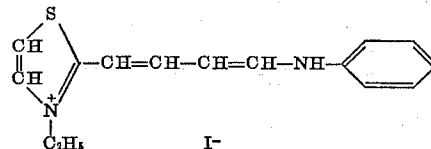
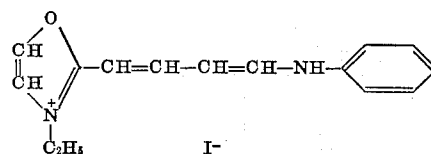
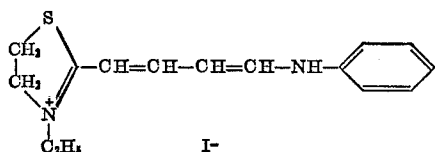
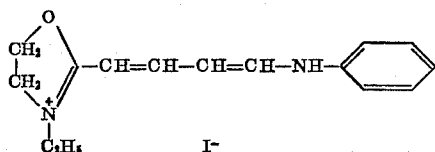


wherein Z represents a group of atoms necessary to complete a five- or six-membered heterocyclic ring, R represents a lower alkyl group, A represents a hydrogen atom, B represents an aryl group, or A and B taken together may represent groups of atoms necessary to complete a ring containing at least one heterocyclic atom connected through a polymethylene chain, L represents a methine chain such that L and R may be connected with each other through a polymethylene chain, X represents an anion, m represents 1, 2 or 3, n represents 0 or 1, p represents 0 or 1, and p=0 if an intramolecular salt thereof is formed;

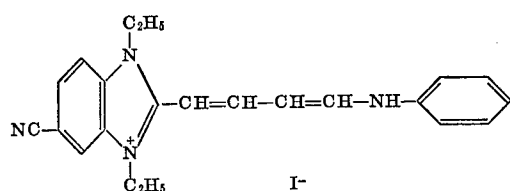
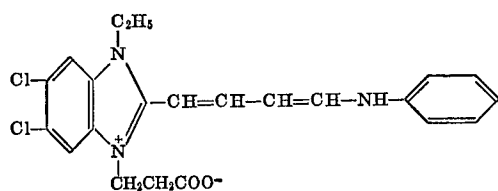
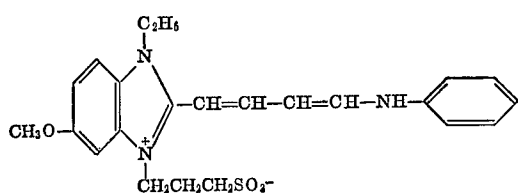
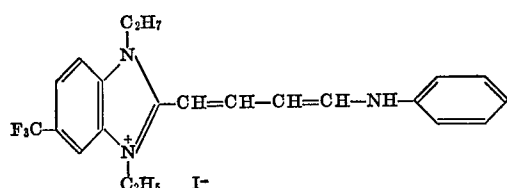
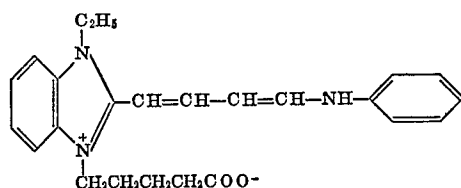
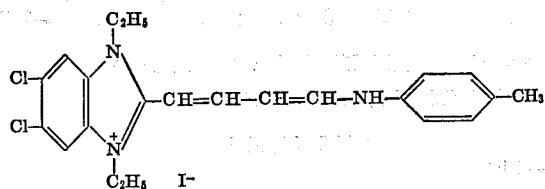
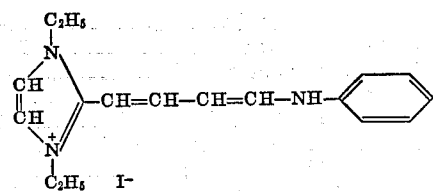
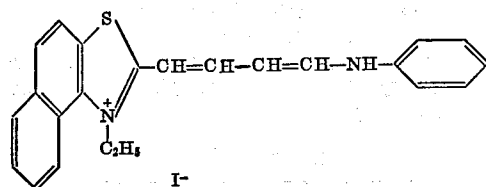
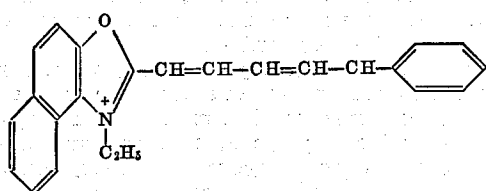


wherein Z, R, L, n and m are the same meanings as those in general Formula I, B represents an aryl group.

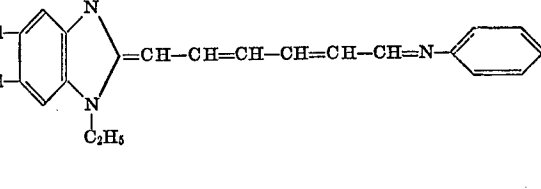
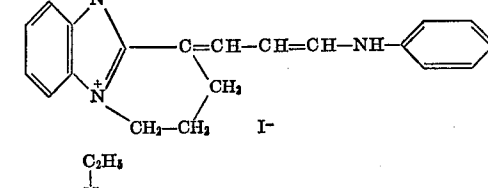
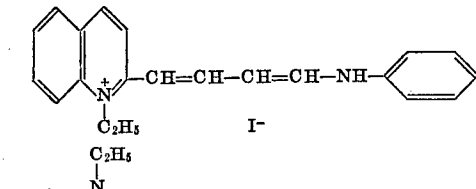
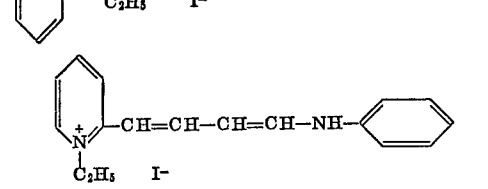
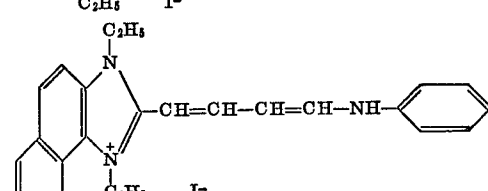
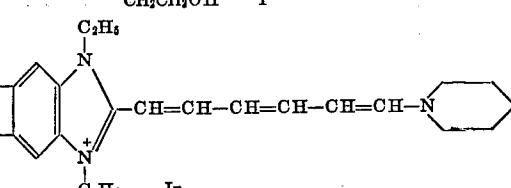
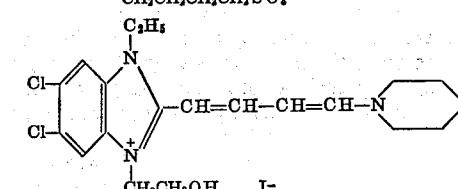
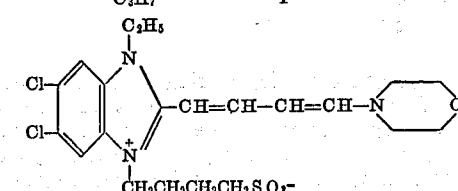
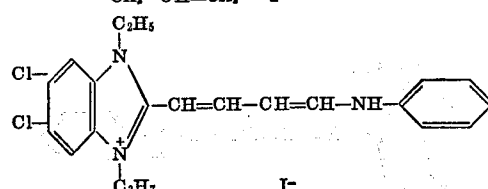
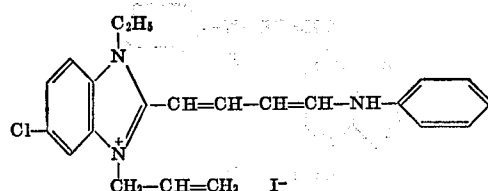
2. The emulsion according to claim 1 wherein said dye is selected from the group consisting of



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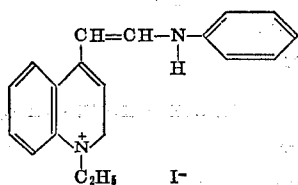


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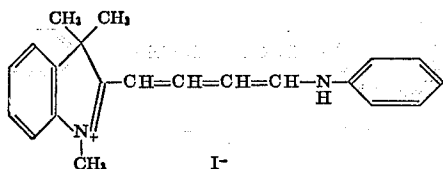


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and



3. The emulsion according to claim 1 wherein said Z is selected from the group consisting of oxazolines, thiazolines, oxazoles, thiazoles, selenazoles, benzoxazoles, benzothiazoles, benzoselenozoles, naphthoxazoles, naphthothiazoles, indolinines, imidazoles, benzimidazoles, naphthoimidazoles, pyridines, and quinolines.

4. The emulsion according to claim 1 wherein said R is selected from the group consisting of methyl, ethyl, n-propyl, hydroxyalkyl, acetoxyalkyl, alkyl groups containing a carboxy group, alkyl groups containing a sulfo group, vinylmethyl and aralkyl groups

5. The emulsion according to claim 1 wherein X is selected from the group consisting of chloride, bromide, iodide, and perchlorate.

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6. The emulsion according to claim 1 wherein the amount of said dye in the emulsion is in the range of 5-500 mg. per 1 kg. of emulsion.

7. The emulsion according to claim 1 wherein said emulsion also contains at least one member selected from the group consisting of chemical stabilizing agents, stabilizers, anti-fogging agents, tone adjusting agents, hardeners, surface active agents, plasticizers, antistatic agents, lubricants, development accelerators, color couplers and fluorescent brightening agents.

8. The emulsion according to claim 1 wherein said ring containing at least one heterocyclic atom is selected from the group consisting of morpholine, pyrrolidine, piperazine, and piperadine.

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