United States Patent

Shiba et al.

[15] **3,649,288**

[45] **Mar. 14, 1972**

[54] SUPERSENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

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[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

[22] Filed: **July 21, 1970**

[21] Appl. No.: **56,959**

[30] **Foreign Application Priority Data**

July 21, 1969 Japan.....44/57545

[52] **U.S. Cl.**.....**96/122,** 96/114, 96/123

[51] **Int. Cl.**.....**G03c 1/22,** G03c 1/28

[58] **Field of Search**.....96/122, 114, 123

[56] **References Cited**

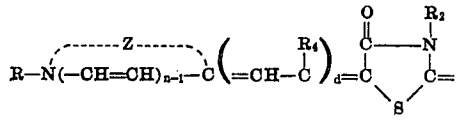
UNITED STATES PATENTS

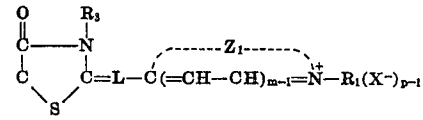
3,416,927 12/1968 Kalenda.....96/122

Primary Examiner—Norman G. Torchin
Assistant Examiner—Alfonso T. Suro Pico
Attorney—Sughrue, Rothwell, Mion, Zinn and MacPeak

[57] **ABSTRACT**

A supersensitized silver halide emulsion comprising a sensitizing dye of the general formula [I]





[I]

wherein R, R_1, R_2 and R_3, which may be same or different, each represents a group of the alkyl series, i.e., an alkyl, a substituted alkyl, or an allyl aralkyl group; L represents a monomethyne group or aliphatic hydrocarbon chain which may combine with the N-atom in the heterocyclic ring containing Z_1 to form a ring; R_4 represents a hydrogen atom or an alkyl or an aryl group m, n and p each represents 1 or 2 and d represents 0, 1 or 2; X^- represents an anion and forms an intramolecular salt when p is 1; and Z and Z_1, which may be same or different, each represents the non-metallic atomic groups necessary to complete a 5- or 6-membered heterocyclic nucleus and a polycyclic aromatic sulfo compound of the general formula [II]

DSO_3M [II]

wherein M represents a hydrogen atom or a cation forming a water-soluble salt of a compound represented by said formula [II], and D represents a polycyclic aromatic radical, is disclosed.

16 Claims, No Drawings

SUPERSENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a silver halide photographic emulsion. More particularly, this invention relates to a so-called "supersensitized" silver halide photographic emulsion.

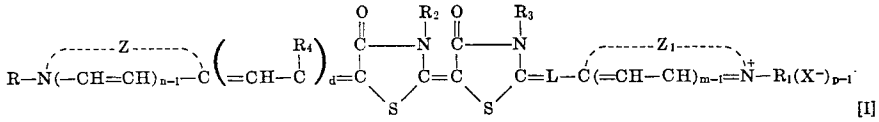
2. Description of the Prior Art

It is well known in the art of the manufacture of silver halide photographic emulsions that the sensitive range of the spectrum of silver halide emulsion can be expanded, that is, the emulsion is spectrally sensitized by addition thereto of a sensitizing dye or a spectral sensitizer.

If a silver halide emulsion is more intensively sensitized, in at least a portion of the spectral range sensitized by a sensitizer, by the addition of the sensitizer in combination with another dye or organic compound the sensitization obtained by the addition of the sensitizer alone at the same combined concentration of the sensitizer and the other dye or organic pigment, then the silver halide emulsion is regarded as being a "supersensitized" silver halide emulsion. The supersensitization often causes a shift in the sensitization maximum.

SUMMARY OF THE INVENTION

We have found that supersensitization is obtained by the addition to a silver halide photographic emulsion of a sensitizing dye represented by the following general formula [I]



[I]

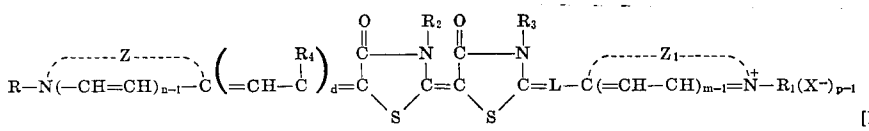
wherein R, R_1, R_2 and R_3, which may be same or different, each represents a group of the alkyl series, i.e., an alkyl, a substituted alkyl, or an allyl aralkyl group; L represents a monomethyne group or aliphatic hydrocarbon chain which may combine with the N-atom in the heterocyclic ring containing Z_1 to form a ring; R_4 represents a hydrogen atom or an alkyl or an aryl group; *m*, *n* and *p* each represents 1 or 2 and *d* represents 0, 1 or 2; X^- represents an anion and forms an intramolecular salt when *p* is 1; and Z and Z_1, which may be same or different, each represents the nonmetallic atomic groups necessary to complete a 5- or 6-membered heterocyclic nucleus, in combination with a polycyclic aromatic compound having at least one sulfo group in the molecule represented by the following general formula [II]

$$DSO_3M \qquad [II]$$

wherein M represents a hydrogen atom or a cation forming a water-soluble salt of a compound represented by said formula [II], and D represents a polycyclic aromatic radical. The combination of the sensitizing dye of the general formula [I] and the sulfo-group-containing polycyclic aromatic compound of the general formula [II] results in a supersensitization when tested in a conventional emulsion.

DETAILED DESCRIPTION OF THE INVENTION

As indicated above the sensitizing dye is one represented by the following general formula [I]



[I]

wherein R, R_1, R_2 and R_3, which may be same or different, each represents a group of the alkyl series, i.e., an alkyl, a substituted alkyl, or an allyl aralkyl group; L represents a monomethyne group or aliphatic hydrocarbon chain which may combine with the N-atom in the heterocyclic ring containing Z_1 to form a ring; R_4 represents a hydrogen atom or an alkyl or an aryl group; *m*, *n* and *p* each represents 1 or 2 and *d* represents 0, 1 or 2; X^- represents an anion and forms an intramolecular salt when *p* is 1; and Z and Z_1, which may be same or different, each represents the nonmetallic atomic groups necessary to complete a 5- or 6-membered heterocyclic nucleus.

R, R_1, R_2 and R_3 in the general formula [I] is a group in the alkyl series, for example, methyl, ethyl, propyl, β-hydroxyethyl, β-acetoxyethyl, sulfoethyl($-C_2H_4SO_4^-$), carboxymethyl, β-carboxyethyl, γ-carboxypropyl, β-sulfoethyl, γ-sulfopropyl, δ-sulfobutyl, allyl, benzyl, phenethyl, p-carboxybenzyl and p-sulfophenethyl.

R_4 in the general formula [I] is, for example, methyl, ethyl, phenyl or the like.

X in the general formula [I]is, for example, a chlorine ion, a bromine ion, a perchlorate ion, a p-toluenesulfonate ion, a benzenesulfonate ion, an ethylsulfate ion, a methylsulfate ion or the like.

The heterocyclic nucleus completed by the Z or Z_1 in the general formula [I], for example, can be of the thiazole series, such as thiazole itself and thiazoles having a substituent on its ring such as methyl or phenyl; of the benzothiazole series, such as benzothiazole itself and benzothiazoles having ring substituents such as, for example, a halogen atom, an alkyl, an alkoxyl or a phenyl group; of the naphthothiazole series, such as α-naphthothiazole, β-naphthothiazole, tetrahydronaphthothiazoles and naphthothiazoles having on either benzene ring substituents such as, for example, an alkoxyl group; of the oxazole series such as substituted oxazoles having ring substituents such as, for example, an alkyl or a phenyl group; of the benzoxazole series, such as benzoxazole itself and benzoxazoles having ring substituents such as, for example, a halogen, a methyl, an ethyl, an ethoxy, a hydroxyl or a phenyl group; of the naphthoxazole series such as α-naphthoxazole and β-naphthoxazole; of the selenazole series, such as 4-methylselenazole and 4-phenylselenazole; of the benzoselenazole series, such as benzoselenazole itself, 5-chlorobenzoselenazole, 5-methylbenzoselenazole, 5-methoxybenzoselenazole and 5-hydroxybenzoselenazole; of the naphthoselenazole series, such as α-naphthoselenazole and β-naphthoselenazole; of the thiazoline series, such as thiazoline itself and 4-methylthiazoline; of the 2-quinoline series, such as quinoline itself and quinolines having on either benzene ring substituents such as, for example, a halogen, a methyl, a methoxy or a hydroxyl (except for the 2-position) group; of the 4-quinoline series such as quinoline itself and 4-quinolines having on either benzene ring substituents such as, for example, methyl or methoxy (except for the 4-position) group; of the benzimidazole series, such as 1,3-dimethylbenzimidazole, 1,3-diethylbenzimidazole, 1,3-diethyl-5-chlorobenzimidazole,

1,3-diethyl-5,6-dichlorobenzimidazole; of the 3,3'-dialkylindolene series, such as 3,3'-dimethylindolene, 3,3',5-trimethylindolene and 3,3',7-trimethylindolene; of the 2-pyridine series such as pyridine itself and pyridines having substituents such as, for example, a methyl group in other than the 2-position; and of the 4-pyridine series such as pyridine itself.

M in the general formula [I] is, for example, a sodium ion, a potassium ion, an ammonium ion, a triethanolammonium ion aNd a pyridinium ion.

The polycyclic aromatic compound having at least one sulfo group in the molecule used in combination with the sensitizing dye having the general formula [I] is of the general formula [II]

$$DSO_3M \qquad [II]$$

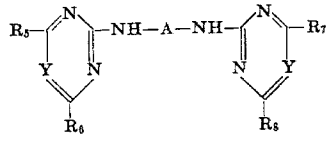
wherein M represents a hydrogen atom or a cation forming a water-soluble salt of a compound represented by said formula [II], and D represents a polycyclic aromatic radical.

The term "polycyclic aromatic radical" as used in the general formula [II] is intended to encompass a "residue of a compound containing at least one condensed aromatic nucleus, such as, for example, a naphthalene or a purene nucleus or a residue of at least two benzene nuclei or other aromatic nuclei, such as, of a triazine, or a purimidine nucleus which are combined directly with each other such as, for example, diphenyl, terphenyl or quaterphenyl or through an aliphatic chain, an atom or an atomic group with each other". Hereinafter, in this specification, the sulfo-group-containing polycyclic aromatic compound of the general formula [II] will be hereinafter designated as "sulfo compound" for convenience.

Separate portions of the emulsion are sensitized with the spectral sensitizer represented by the general formula [I] (hereinafter dye) in a series of concentrations of the sensitizer, and to each is added the "sulfo compound" at various concentrations, for instance, concentrations of 1, 5, 10 and 20 times the concentration of the dye. The so sensitized emulsions are separately applied to supports and dried. The photographic elements thus obtained are subjected to sensitometer testing for determination of the range and degree of spectral sensitivity of the emulsions.

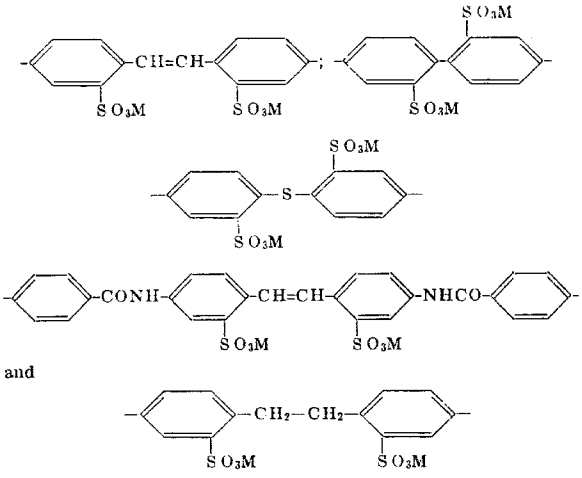
If the sensitivity brought about by the combination of the dye and the sulfo compound exceeds, even if in a least a portion of the range of photosensitization, the sensitivity brought about by the dye alone at the same concentration of the combined concentration of the dye and the sulfo compound in the combination, this is the evidence for a supersensitization effect.

Especially useful sulfo compounds having the general formula [II] are those represented by the following general formula [III].



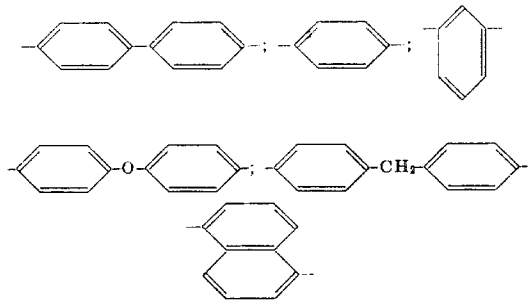
[III]

wherein Y represents =CH— or =N—; R_5, R_6, R_7 and R_8, which may be the same or different, each represents a hydrogen atom, a hydroxyl group, an alkoxyl group, a group of the aryloxyl series, for example, an aryloxyl group and a substituted aryloxyl group (for example, a phenoxy, an o-tolyloxy or a p-sulfophenoxy group), a halogen atom (for example, a chlorine or a bromine atom), a heterocyclic nuclear group (for example, a morphonyl or piperidyl group), an alkylthio group (for example, a methylthio or an ethylthio group), a heterocyclic thio group (for example, benzothiazylthio group), an arylthio group (for example, a phenylthio or a tolylthio group), an amino group, a group of the alkyl amino series, for example, an alkylamino and a substituted alkylamino group (for example, a methylamino, a dimethylamino, an ethylamino, a propylamino, a diethylamino, a dodecylamino, a cyclohexylamino, a β-hydroxyethylamino, a di-β-hydroxyethylamino or a β-sulfoethylamino group), a group of the aryl amino series, for example, an arylamino and a substituted arylamino group (for example, an anilino, an o-sulfoanilino, a m-sulfoanilino, a p-sulfoanilino, an o-anisylamino, a p-anisylamino, a m-anisylamino, an o-toluidino, a m-toluidino, a p-toluidino, an o-carboxyanilino, a m-carboxyanilino, a p-carboxyanilino, a hydroxyanilino, a naphthylamino or a sulfonaphthyl amino group), a heterocyclic amino group (for example, a 2-benzothiazolamino, a 2-pyridylamino group) and an aryl group (for example, a phenyl group); wherein —A— represents a bivalent radical selected from the group consisting of —A_1—and —A_2—, wherein —A_1— represents groups having the following formulas



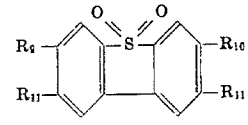
and

wherein —A_2— represents groups having the following formulas



provided that when A is —A_2—, at least one of the R_5, R_6, R_7 and R_8 groups has a substituent containing the —SO_3M group.

Compounds represented by the following general formula [IV] are also useful in the present invention as included within the scope of those compounds of the general formula [II].



[IV]

wherein R_9 and R_{10}, which may be the same or different, each represents a group of the acylamino series (for example, an acetamido, a sulfobenzamido, a 4-methoxy-3-sulfobenzamido, a 2-ethoxybenzamido, a 2,4-diethoxybenzamido, a p-toluylamino, a 4-methyl-2-methoxybenzamido, a 1-naphthoylamino, a 2-naphthoylamino, a 2,4-dimethoxybenzamido or a 2-thienylbenzamido group) or a sulfo group; and wherein R_{11} represents a hydrogen atom or a sulfo group, with at least one of the groups of R_9 to R_{11} being a sulfo group.

The sensitizing dyes of the general formula [I] for use in accordance with the present invention are disclosed by F.M. Hamer in *Cyanin Dyes and Related Compounds*, Chapter 15, p. 671, Interscience Publishers (1964).

Some of the sulfo compounds of the general formula [III] for use in the present invention are disclosed in, for instance, U.S. Pat. No. 2,171,427; 2,660,587; 2,473,475 and 2,595,030.

The sensitizing dye of the general formula [I] for use in the present invention is a dye containing at least four heterocyclic rings in which two ketomethylene nuclei are directly bonded to each other. The sensitizing dye of the general formula [I] differs from dyes containing one ketomethylene nucleus in the center of the molecule and the two basic nuclei and from trinuclear dyes containing two ketomethylene nuclei, not only in chemical structure but also in the following characteristics.

1. The trinuclear dyes containing two ketomethylene nuclei in general have low solubilities in methanol, while the sensitizing dye represented by the general formula [I] has a high solubility in methanol or similar solvents.

2. The sensitizing dye represented by the general formula [I] incorporated in a silver halide photographic emulsion imparts thereto a sensitivity which is reduced only slightly by the addition of conventional additives for photographic emulsions such as, for example, color couplers, antifogging agents and irradiation inhibiting dyes.

3. The sensitizing dye represented by the general formula [I], when used alone, however, is generally inferior in sensitizing power to dyes. having one ketomethylene nucleus in the center of the molecule and two basic nuclei and needs another sensitizing technique to provide a highly sensitive emulsion. This additional sensitization is attained by the combination of the sensitizing dye represented by the general formula [I] with the sulfo compound.

The incorporation of the sulfo compound represented by the general formula [II] in combination with the sensitizer represented by the general formula [I] in a silver halide emulsion results in supersensitization, and, according to the circumstances, a marked reduction of fog in comparison with the incorporation of the sensitizer alone. Although some of the sensitizing dyes represented by the general formula [I] have disadvantages in that they cause a reduction of the sensitivity of emulsion during storage when incorporated in photosensitive materials, the reduction in sensitivity during storage can be minimized by incorporating into the emulsion the sensitizer in combination with a certain one of the sulfo compounds represented by the general formula [II].

The combination of the sensitizer of the general formula [I] and the sulfo compound of the general formula [II] has a super sensitization effect over a wide range of amounts added to a silver halide emulsion. The optimum amount of the sensitizer and of the sulfo compound to give the desired supersensitization can be determined by conventional methods used in photographic emulsion techniques. The extent of the supersensitization can be determined by measuring the sensitivity using a spectral sensitometer.

It is preferred to use the sensitizer at a concentration of from 0.002 to 0.2 g./g.-mol of silver halide and the sulfo compound at a concentration of from 0.01 to 10.0 g./g.-mol of silver halide in the silver halide emulsion. The preferred ratio of the concentration of the sensitizer to the concentration of the sulfo compound ranges from 1:1 to 1:200. Addition of the sensitizer to an emulsion can be performed in the conventional manner well known in the art. The sulfo compound can be added as a solution in water or in a methanol, ethanol or like organic solvent to a silver halide emulsion. It is convenient to add the sensitizer and the sulfo compound to the emulsion before application to a substrate. The sensitizer and the sulfo compound can be added to the emulsion in the order of the sensitizer and then the sulfo compound or, alternately, the sulfo compound and then the sensitizer or they can be added in admixture to the emulsion. The incorporation of the sensitizer and the sulfo compound can also be attained during ageing of the photosensitive element after washing with water.

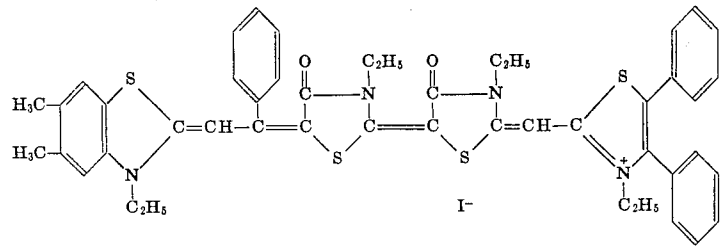
In the preparation of the silver halide emulsion of the present invention, there can be used, in place of gelatin in a gelatin-silver halide emulsion, resinous materials and derivatives having no adverse effects on photosensitive materials.

In the preparation of the emulsions for use in the practice of the present invention silver chloride, silver bromide, silver iodobromide, silver chloroiodide, silver chloroiodobromide and similar silver halides can be used.

Chemical sensitizers, antifogging agents, stabilizers, hardeners, coating assistants, plasticizers, developing promoters, toners, fluorescent whitening agents, anti-air-fogging agents, couplers and other conventional additives can be incorporated in the emulsion of the present invention. Dyes used in the silver-dye bleaching process as disclosed in Japanese Pat. specification No. 35/13093 can also be incorporated in the emulsion. The emulsion can be applied conventionally to a suitable support such as, for example, sheet glass, cellulose derivative films, synthetic resin films or baryta papers.

The sensitizer of the general formula [I] for use in the present invention is exemplified by the following specific examples but is not limited thereto.

I-1



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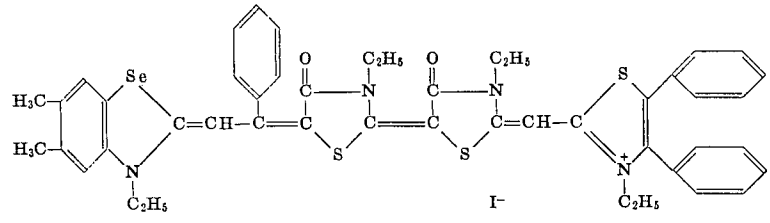

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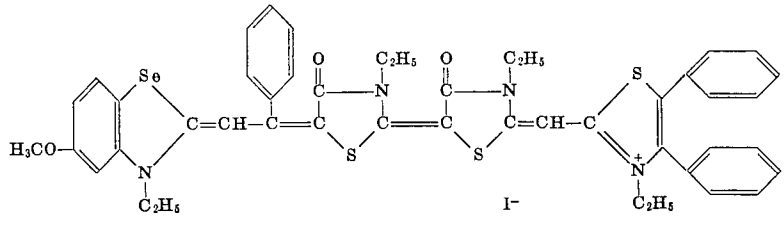

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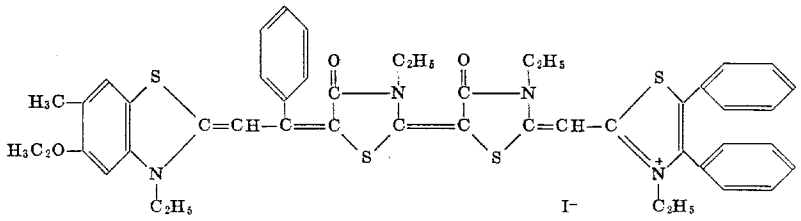

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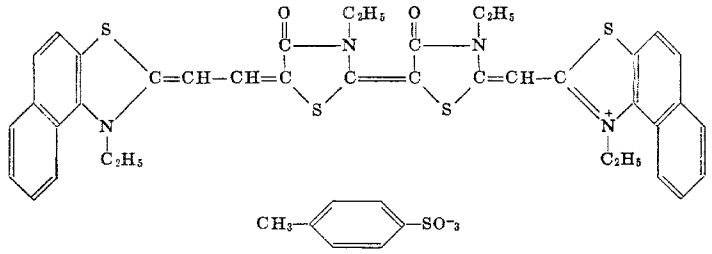

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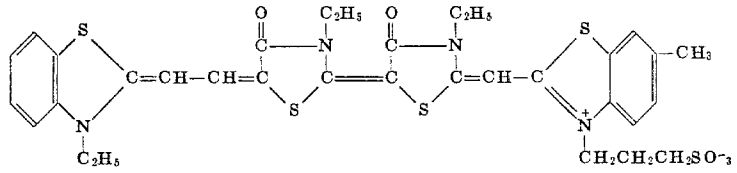

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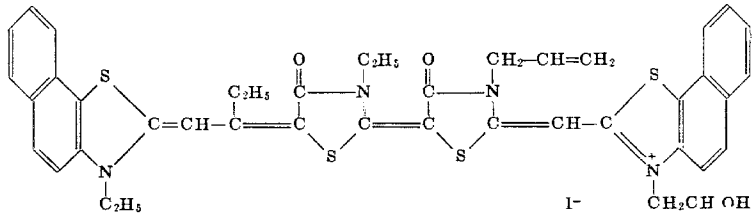

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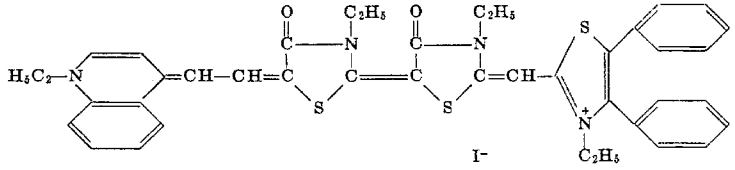

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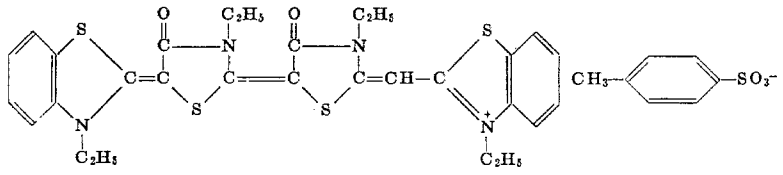
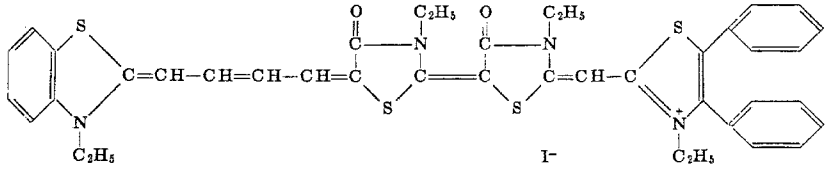


I-10



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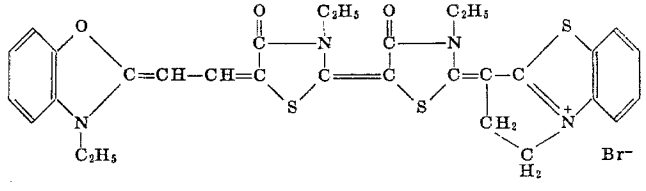
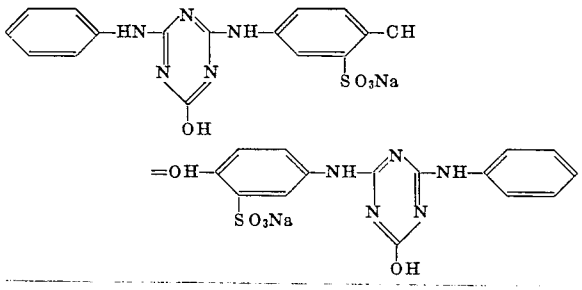
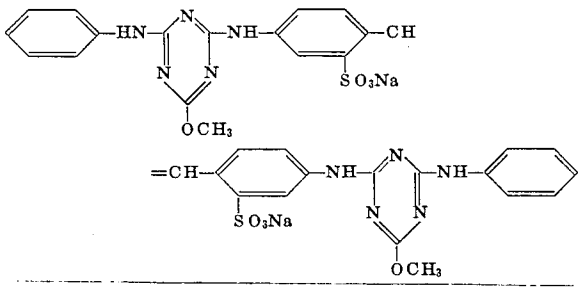


The sulfo compounds of the general formula [II] for use in the present invention are exemplified by the following compounds but are not limited thereto.

II-1



II-2



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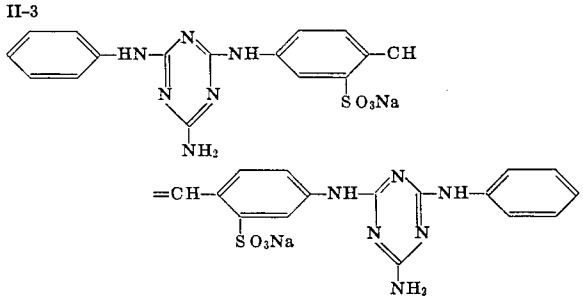

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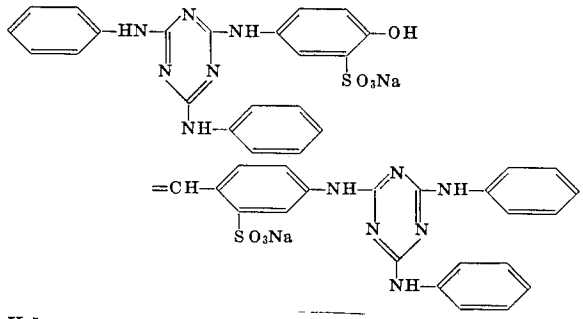

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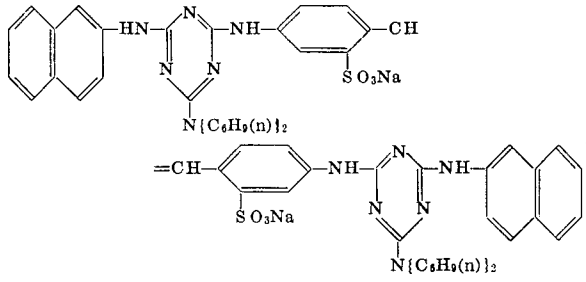
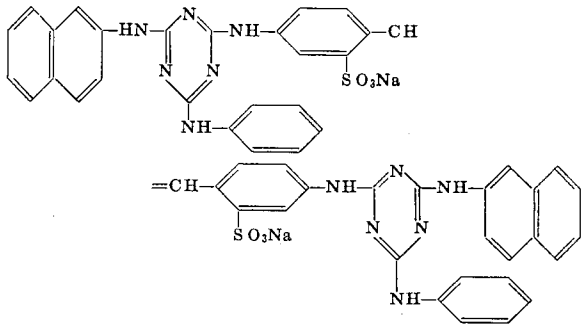
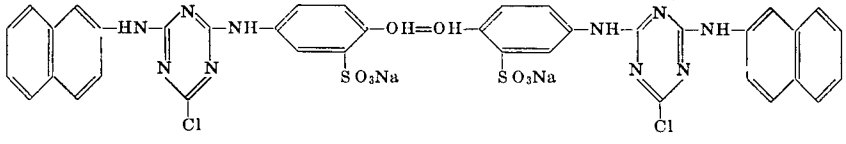


II-6



II-7



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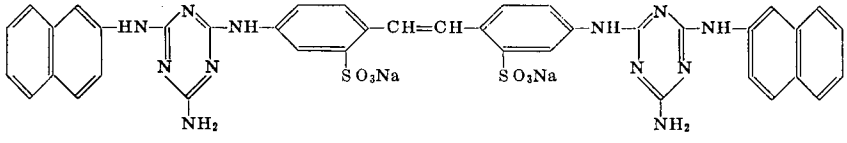

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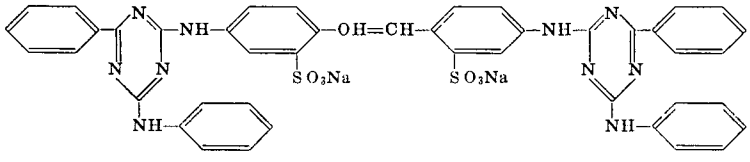

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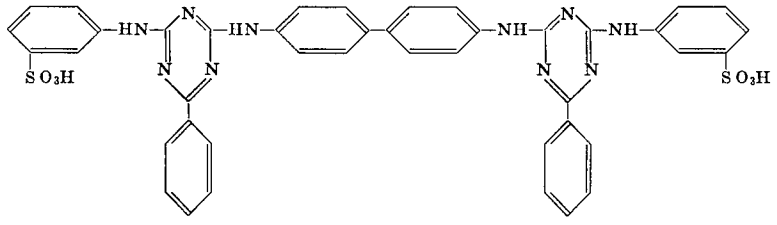

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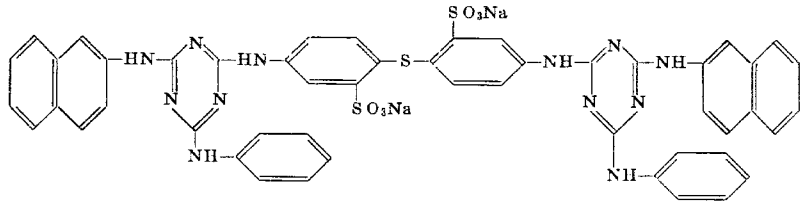

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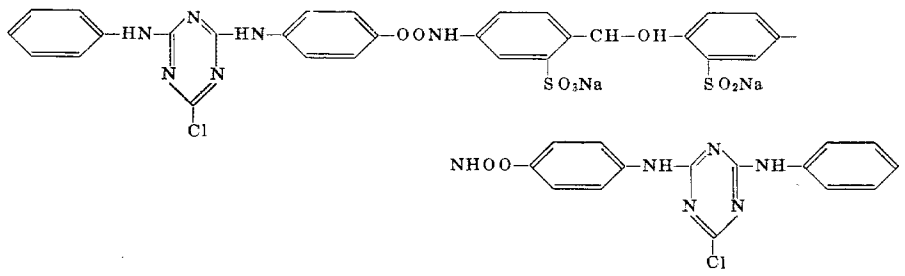

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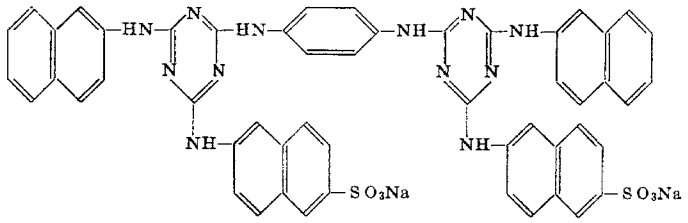

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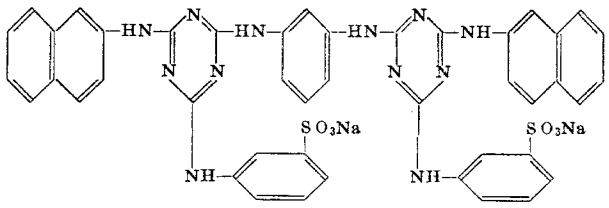

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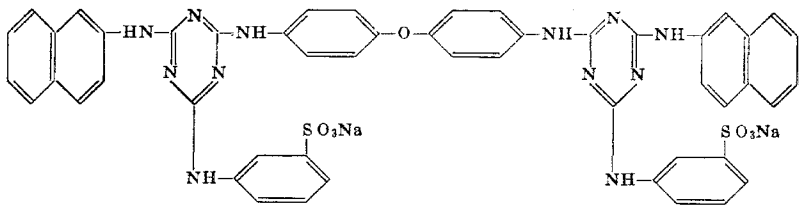

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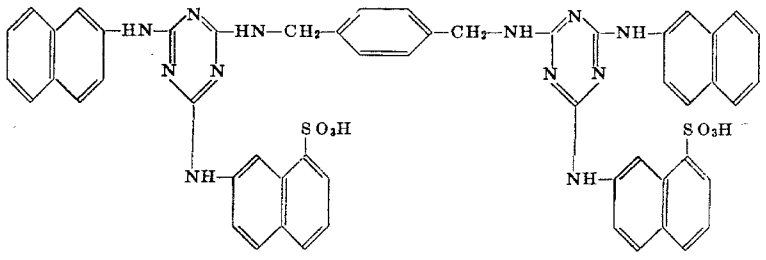

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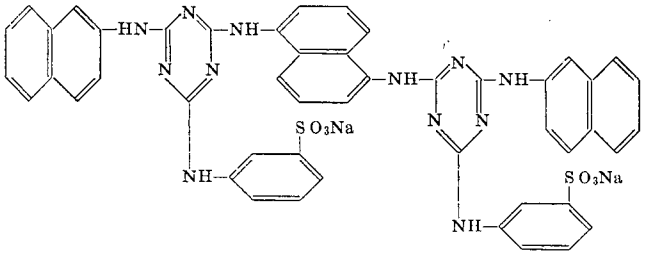

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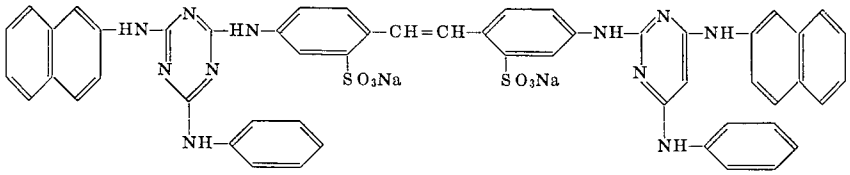

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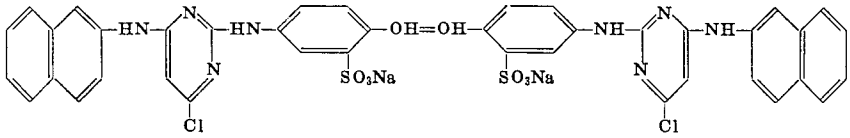

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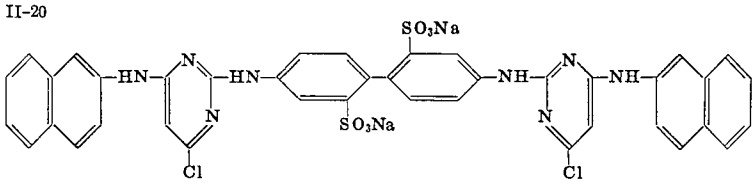

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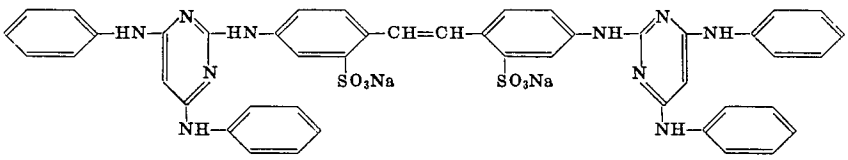

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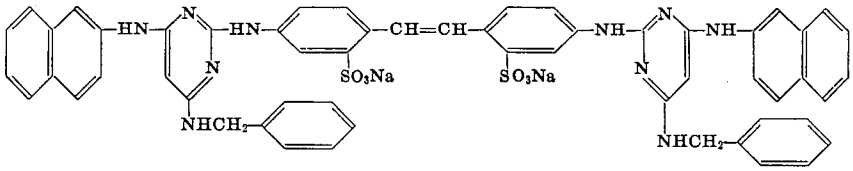

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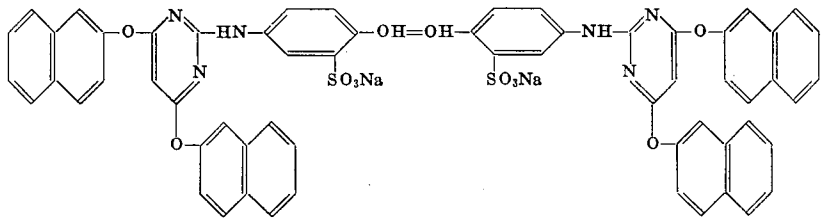

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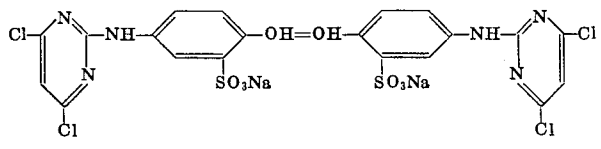

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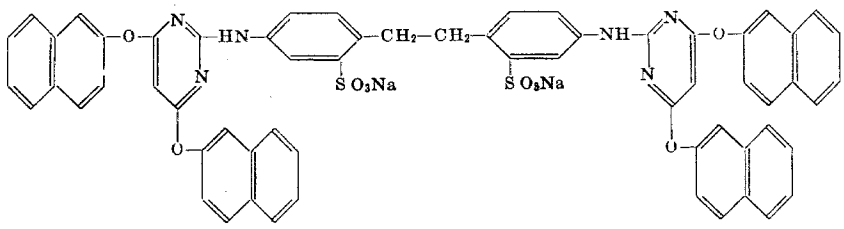

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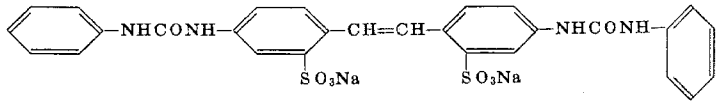

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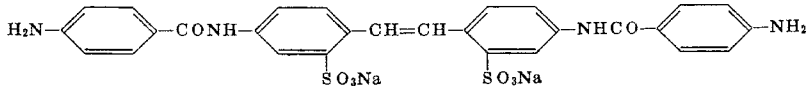

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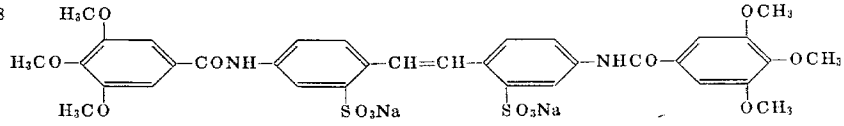

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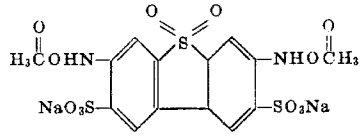

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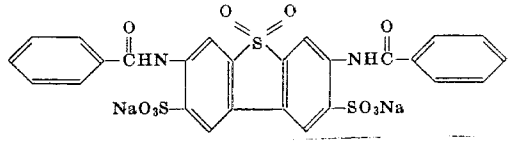

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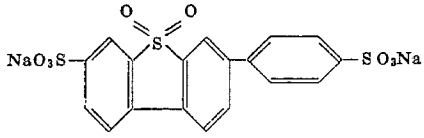

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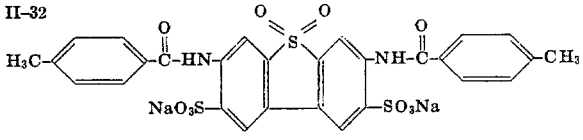

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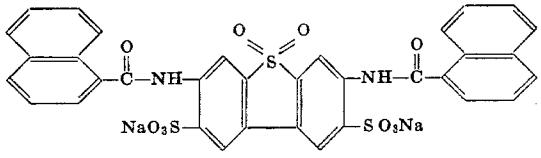

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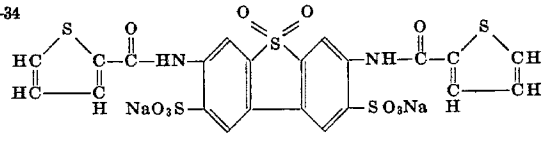

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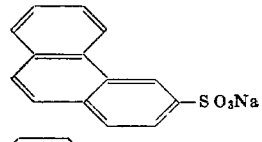

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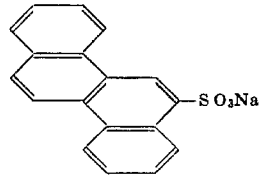

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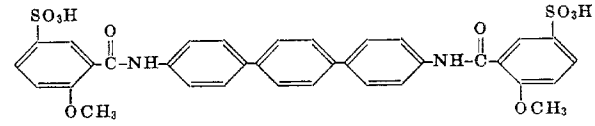


The present invention is illustrated in greater detail by reference to the following examples but is not limited thereby.

EXAMPLES

To separate portions of a silver halide emulsion from the same batch were added (1) a sensitizer represented by the general formula [I] or (2) a combination of a sensitizer represented by the general formula [I] and a sulfo compound represented by the general formula [II]. Each of the separate emulsion portions thus sensitized was applied to an acetyl-cellulose base. The coated film was, after drying, exposed through a Fuji filter No. 7 (Trademark, transmitting light of wavelengths of 590 millimicrons or longer) or a Fuji filter No. 3 (Trademark, transmitting light of wavelengths of 480 millimicrons or longer) and subjected to development.

The value of the sensitivity is the relative value of the amount of exposure needed to give an optical density (including fog) of 0.1 and was calculated by basing the relative sensitivity of an emulsion containing the sensitizer alone as 100.

The values obtained with emulsions containing a sulfo compound alone are not shown because little or no sensitization effect was obtained. Although within runs of the same example an emulsion of the same batch was used, in separate examples there were used the same or different emulsions. The results are summarized in Table 1. In Examples 1 to 4 a silver chlorobromide emulsion of the same batch was used and in Examples 5 to 15 a silver iodobromide emulsion of the same batch was used. The specimens in Example 13 only were exposed through a Fuji filter No. 3. The specimens of Examples 1 to 4 were developed at 20° C. for 2 minutes with a developing solution as indicated in Table 2 and the specimens of Examples 5 to 15 were developed at 20° C. for 4 minutes in a developing solution as indicated in Table 3.

TABLE 2

N-Methyl-p-aminophenol Sulfate	3.1 g.
Sodium Sulfite	45 g.
Hydroquinone	12 g.
Sodium Carbonate (anhydrous)	67.5 g.
Potassium Bromide	1.9 g.
Diluted with water to	1 l.

TABLE 3

N-Methyl-p-aminophenol Sulfate	2.2 g.
Sodium Sulfite	96 g.
Hydroquinone	8.8 g.
Sodium Carbonate	48 g.
Potassium Bromide	5 g.
Diluted with water to	1 l.

Additives (mg.)

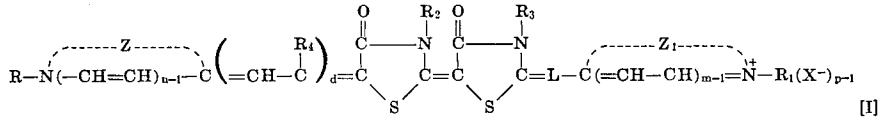
Example No.	Sensitizing Dye	Sulfo Compound	Sensitivity	Fog
1	a. I-4(95.1)—[1]	—	100	0.07
	b. I-4(95.1)	+ II-1(968)	195	0.07
	c. I-4(95.1)	+ II-2(968)	186	0.07
	d. I-4 (95.1)	+ II-3(968)	186	0.07
	e. I-4(95.1)	+ II-4(968)	200	0.06
	f. I-4(95.1)	+ II-5(968)	155	0.07
	g. I-4(95.1)	+ II-6(968)	155	0.05
	h. I-4(95.1)	+ II-7(968)	145	0.07
2	i. I-1(46.0)	—	100	0.07
	j. I-1(46.0)	+ II-8(968)	152	0.07
	k. I-1(46.0)	+ II-9(968)	132	0.07
	l. I-1(46.0)	+ II-10(968)	126	0.07
	m. I-1(46.0)	+ II-11(968)	132	0.06
	n. I-1(46.0)	+ II-12(968)	141	0.07
	o. I-1(46.0)	+ II-13(968)	135	0.07
	p. I-1(46.0)	+ II-14(968)	135	0.07
3	q. I-2(48.3)	+ —	100	0.07
	r. I-2(48.3)	+ II-15(484)	120	0.07
	s. I-2(48.3)	+ II-16(484)	120	0.07
	t. I-2(48.3)	+ II-17(848)	126	0.07
	u. I-2(48.3)	+ II-18(484)	132	0.07
	v. I-2(48.3)	+ II-19(484)	145	0.07
	w. I-2(48.3)	+ II-20(484)	132	0.07
	x. I-2(48.3)	+ II-21(484)	152	0.007
4	y. I-8(40.7)	+ —	100	0.09
	z. I-8(40.7)	+ II-22(968)	186	0.09
	a'. I-8(40.7)	+ II-23(968)	209	0.07
	b'. I-8(40.7)	+ II-25(968)	186	0.08
	c'. I-8(40.7)	+ II-26(968)	170	0.08
	d'. I-8(40.7)	+ II-30(968)	166	0.08
	e'. I-8(40.7)	+ II-35(968)	120	0.09
	f'. I-8(40.7)	+ II-36(968)	120	0.09
5	g'. I-1(92.1)	—	100	0.10
	h'. I-1(92.1)	+ II-4(968)	155	0.09
6	i'. I-2(96.7)	—	100	0.10
	j'. I-2(96.7)	+ II-4(968)	132	0.09
7	k'. I-3(97.0)	—	100	0.10
	l'. I-3(97.0)	+ II-4(968)	112	0.08
8	m'. I-4(95.1)	—	100	0.11
	n'. I-4(95.1)	+ II-4(968)	155	0.08
9	o'. I-5(86.1)	—	100	0.08
	p'. I-5(86.1)	+ II-4(968)	100	0.08
10	q'. I-6(70.3)	—	100	0.08
	r'. I-6(70.3)	+ II-4(968)	132	0.08
11	s'. I-7(87.3)	—	100	0.08
	t'. I-7(87.3)	+ II-4(968)	110	0.08
12	u'. I-8(81.5)	—	100	0.12
	v'. I-8(81.5)	+ II-4(968)	204	0.09
13	w'. I-9(74.0)	—	100	0.08
	x'. I-9(74.0)	+ II-4(968)	145	0.08
14	y'. I-10(84.6)	—	100	0.10
	z'. I-10(84.6)	+ II-4(968)	170	0.09
15	a''. I-11(51.9)	—	100	0.10
	b''. I-11(51.9)	+ II-4(968)	145	0.09

1/ Milligrams of additive per gram mole of silver halide.

What is claimed is:

1. A photographic silver halide emulsion sensitized with a combination of

1. at least one sensitizing dye having the following general formula



[I]

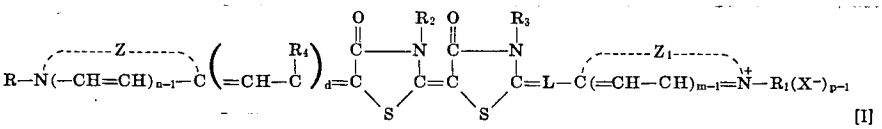
wherein R, R_1, R_2 and R_3, which may be the same or different, each is selected from the group consisting of a group of the alkyl series; R_4 is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group; wherein Z and Z_1, which may be the same or different, each is the non-metallic atomic groups necessary to complete a heterocyclic nucleus selected from the group consisting of the thiazole series, benzothiazole series, naphthothiazole series, oxazole series, benzoxazole series, naphthoxazole series, selenazole series, benzoselenazole series, naphthoselenazole series, thiazoline series, 2-quinoline series, 4-quinoline series, benzimidazole series, 3,3'-dialkylindoleneine series, 2-pyridine series, 4-pyridine series; wherein L is selected from the group consisting of a monomethine group and an aliphatic carbon chain which may combine with the N-atoms in said heterocyclic nucleus containing Z_1 to form a ring; wherein *m*, *n* and *p* each is 1 or 2, and wherein *d* is 0, 1 or 2; and wherein X represents an anion; and

2. at least one sulfo compound having the following general formula

$$D—SO_3M$$

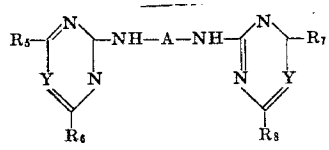
wherein D is a polycyclic aromatic radical, said radical being selected from the group consisting of the residue of a compound containing at least one condensed aromatic nucleus, at least two benzene nuclei, and more than two aromatic nuclei; and M is selected from the group consisting of a hydrogen atom and a cation forming a water-soluble salt of said sulfo compound.

2. The photographic silver halide emulsion of claim 1, sensitized with a combination of at least one sensitizing dye having the general formula

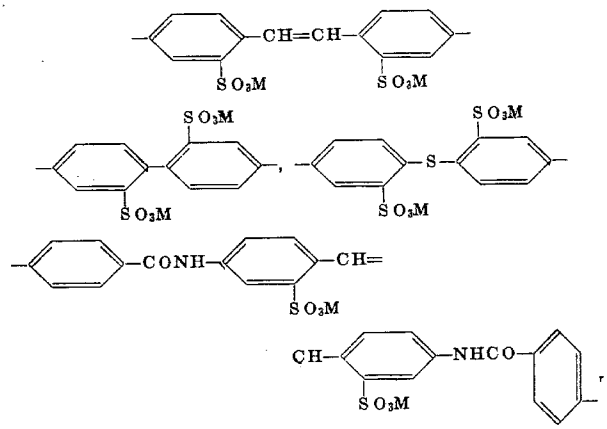


[I]

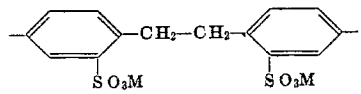
wherein R, R_1, R_2, R_3, R_4, Z, Z_1, L, X^-, *m*, *n*, *d* and *p* are as described in claim 1 and at least one compound having the following general formula



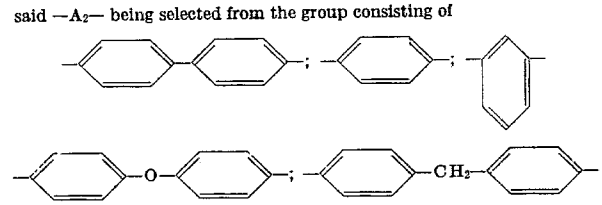
wherein Y is selected from the group consisting of = CH— and = N—; wherein R_5, R_6, R_7 and R_8, which may be the same or different, each is selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxyl group, a group of the aryloxyl series, a heterocyclic nuclear group, an alkyl alkyl thio group, a heterocyclicthio group, an arylthio group, an amino group, a group of the alkylamino series, a group of the arylamino series, a heterocyclicamino group and an aryl group; wherein —A— is a bivalent radical selected from the group consisting of $—A_1—$ and $—A_2—$, said $—A_1—$ being selected from the group consisting of



and



said $—A_2—$ being selected from the group consisting of



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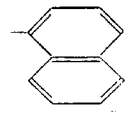
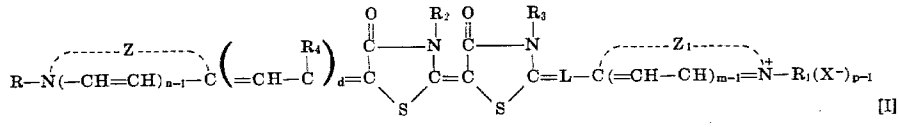


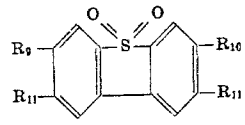
wherein when —A— is $—A_2—$, at least one of R_5, R_6, R_7 and R_8 has a substituent containing an $—SO_3M$ group;

3. The photographic silver halide emulsion of claim 1, sensitized with a combination of at least one sensitizing dye having the general formula



[I]

wherein R, R_1, R_2, R_3, R_4, Z, Z_1, L, X^-, *m*, *n*, *d* and *p* are as described in claim 1 and at least one compound having the general formula



[IV]

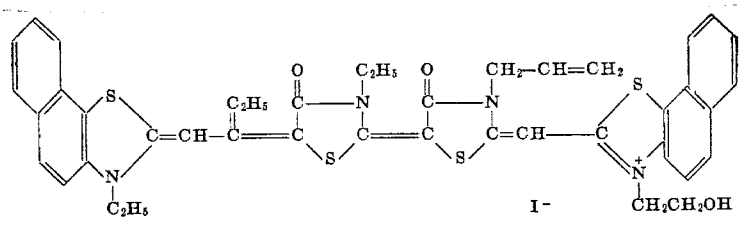
wherein R_9 and R_{10}, which may be the same or different, each is selected from the group consisting of a group of acylamino series and a sulfo group; wherein R_{11} is selected from the group consisting of a hydrogen atom and a sulfo group, wherein at least one of R_9, R_{10}, and R_{11} is a sulfo group.

4. The photographic silver halide emulsion as claimed in claim 1, wherein the group of the alkyl series is selected from the group consisting of an alkyl group, a hydroxy alkyl group, an acetoxy alkyl group, a sulfatoalkyl group, a carboxy alkyl group, a sulfoalkyl group, an allyl group, a benzyl group, a phenethyl group, a carboxybenzyl group, and a sulfophenethyl group.

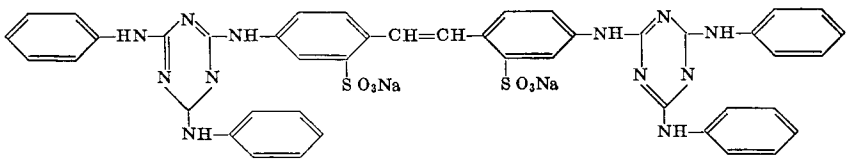
5. The photographic silver halide emulsion as claimed in claim 2, wherein said substituted aryloxyl group is selected from the group consisting of phenoxy, tolyloxy, and sulfophenoxy; wherein said group of the alkyl amino series is selected from the group consisting of an alkyl amino, hydroxyalkyl amino and a sulfoalkyl amino group; wherein the group of the arylamino series is selected from the group consisting of an anilino group, a sulfoanilino group, an anisylamino group, a toluidino group, a carboxyanilino group, a hydroxy anilino group, a naphthylamino group and a sulfonaphthylamino group, wherein the heterocyclic nuclear group is selected from the group consisting of a morphonyl and a piperidyl group; wherein the heterocyclic thio group is a benzothiazylthio group; wherein the heterocyclic amino group is selected from the group consisting of a benzothiazolamino group and a pyridylamino group.

6. The photographic silver halide emulsion as claimed in claim 3 wherein the group of the acylamino series is selected from the group consisting of an acetamido group, a sulfobenzamido group, an alkoxysulfobenzamido group, an alkoxybenzamido group, a toluylamino group, an alkylalkoxybenzamido group, a dialkoxybenzamido group, a naphthoylamino group and a thienylbenzamido group.

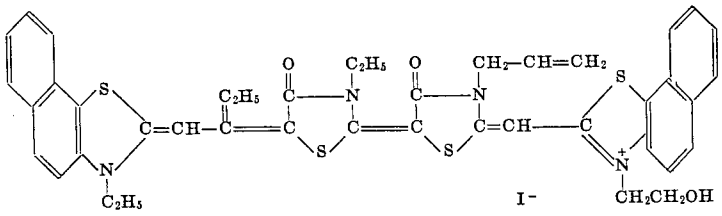
7. A photographic silver halide emulsion sensitized with a combination of



and



8. A photographic silver halide emulsion sensitized with a combination of



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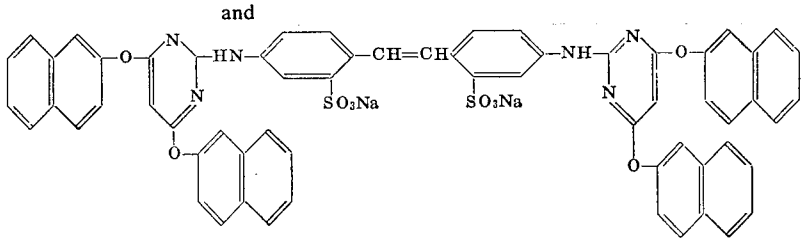
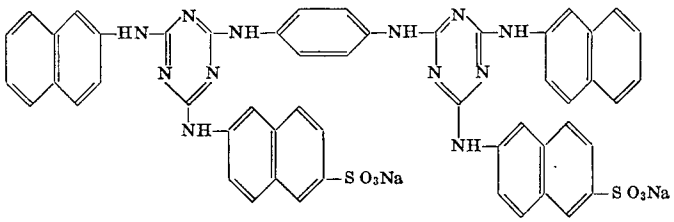
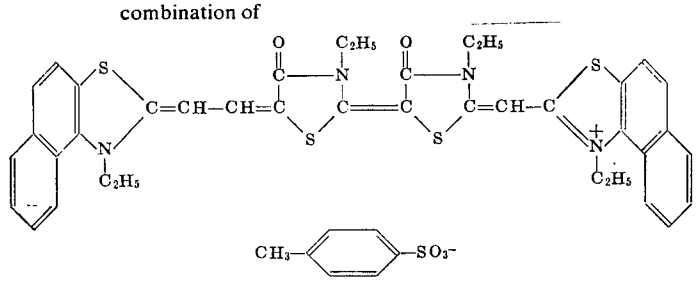


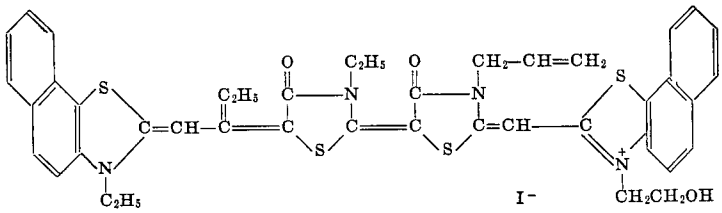
and



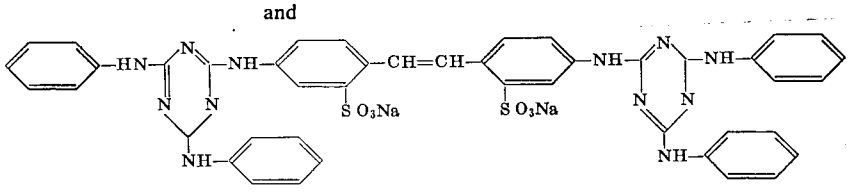
10. A photographic silver halide emulsion sensitized with a combination of



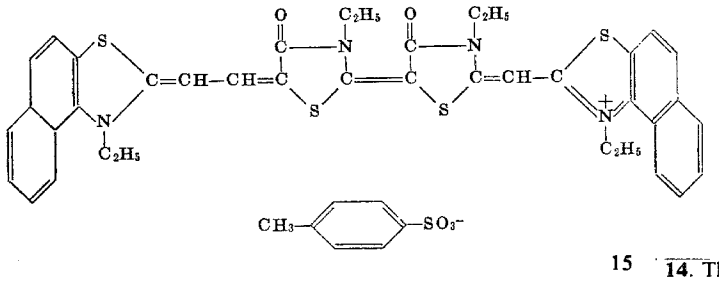
9. A photographic silver halide emulsion sensitized with a combination of



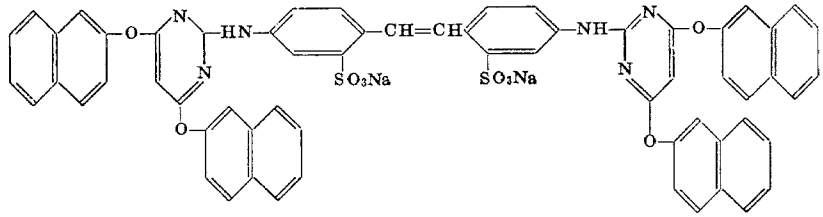
and



11. A photographic silver halide emulsion sensitized with a combination of



and



12. The photographic silver halide emulsion as claimed in claim 1, wherein the sensitizing dye is present at a level ranging from 0.002 to 0.02 grams per gram mol of the silver halide.

13. The photographic silver halide emulsion as claimed in claim 1, wherein the sulfo compound is present at a level ranging from 0.01 to 10.0 grams per gram mol of silver halide.

14. The photographic silver halide emulsion as claimed in claim 12, wherein the weight ratio of said sensitizing dye to the sulfo compound in the emulsion ranges from 1:1 to 1:200.

15. The photographic silver halide emulsion as claimed in claim 13, wherein the weight ratio of said sensitizing dye to the sulfo compound in the emulsion ranges from 1:1 to 1:200.

16. A photographic light-sensitive element comprising a support having thereon at least one layer containing the photographic emulsion as claimed in claim 1.