

United States Patent

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Continuation-in-part of application Ser. No. 757,148, Sept. 3, 1968, now abandoned.		

**[54] SILVER HALIDE PHOTOGRAPHIC EMULSIONS
SUPERSENSITIZED WITH AN OXADIAZOLE AND
A METHINE DYE
9 Claims, No Drawings**

[52] U.S. Cl..... 96/123,
96/122, 96/126
[51] Int. Cl..... G03c 1/28
[50] Field of Search..... 96/104, 109

[56]

References Cited

UNITED STATES PATENTS

2,271,623	2/1942	Carroll	96/104
2,398,778	4/1946	Carroll et al.	96/104
2,411,546	11/1946	Knott	96/104
2,848,329	8/1958	Chechak et al.	96/104
3,017,270	1/1962	Tregillus et al.	96/109
3,113,026	12/1963	Sprung	96/109
3,397,987	8/1968	Luckey et al.	96/109
3,457,078	7/1969	Riester	96/104

FOREIGN PATENTS

861,907	3/1961	Great Britain.....	96/104
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ABSTRACT: Photographic silver halide emulsions are super-sensitized with the combination of a photographic spectral sensitizing methine dye and an oxazole, an oxadiazole, a thiozole or a thiadiazole.

SILVER HALIDE PHOTOGRAPHIC EMULSIONS SUPERSENSITIZED WITH AN OXADIAZOLE AND A METHINE DYE

This application is a continuation-in-part of applicant's pending application Ser. No. 757,148 filed Sept. 3, 1968, now abandoned.

This invention relates to novel photographic silver halide emulsions containing a new supersensitizing combination.

It is well known in the photographic art that certain methine dyes extend the spectral sensitivity of photographic emulsions. It is further known that a number of such dyes in combination with each other or with certain other compounds markedly alter the sensitivity of photographic emulsions, for example in relative speed, compared with the individual dyes by themselves in such emulsions. While supersensitizing combinations of the above kind have been proposed for various uses, only a relatively few have proven entirely satisfactory for commercial photographic applications. Consequently, there is still need in the art for improved supersensitizing combinations comprising methine dyes.

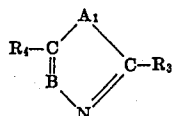
It is, accordingly, an object of this invention to provide a new class of supersensitizing combinations for photographic silver halide emulsions.

Another object of this invention is to provide novel emulsions containing such new supersensitizing combinations and photographic elements prepared therewith.

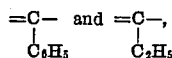
Other objects of the invention will be apparent from this disclosure and the appended claims.

I have now made the important discovery that new and improved supersensitizing combinations for light-sensitive photographic silver halide emulsions are produced with (1) a heterocyclic compound selected from the group consisting of an oxazole, an oxadiazole, a thiazole or a thiadiazole, and (2) a photographic spectral sensitizing methine dye. The new supersensitizing combinations of this invention are compatible with the emulsions giving essentially clear layers with excellent keeping stability and causing relatively little or no fogging in both fresh and incubated condition.

The preferred heterocyclic compounds of above component (1) are represented by the following formula I:



wherein A₁ represents an atom of oxygen or sulfur; B represents a methine group, e.g., =CH-, and substituted methine groups such as



or a nitrogen atom; R₃ represents a lower alkyl group containing from one to four carbon atoms, e.g., methyl, ethyl, isopropyl, butyl, benzyl, phenethyl, etc., an aryl group, e.g., phenyl, tolyl, chlorophenyl, methoxyphenyl, naphthyl, stilbenyl, etc., an amino group including substituted amino, e.g., amino, methylamino, diethylamino, butylamino, phenylamino, diphenylamino, naphthylamino, anisidino, anilino, acetamidophenylsulfonamino, etc., styryl; amido groups such as acetamido or a halogen substituent, e.g., chlorine or bromine; R₄ represents a hydrogen atom or a value given for R₃. Compounds embraced by Formula I above include the various oxazoles, thiazoles, oxadiazoles, thiadiazoles, and the like.

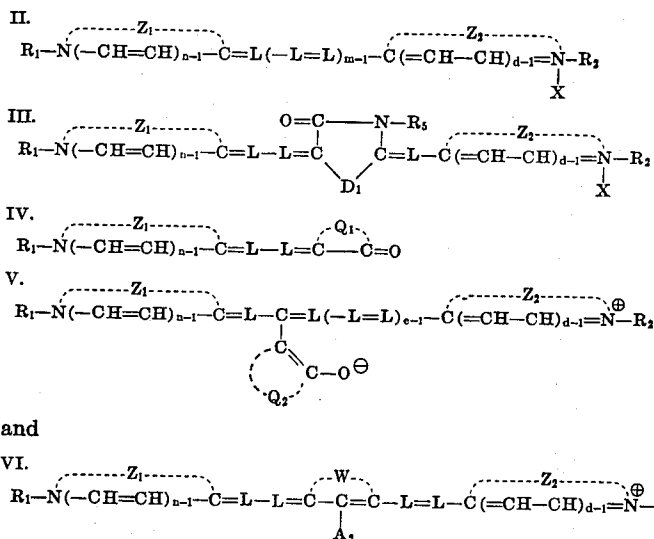
Typical heterocyclic compounds of the invention represented by Formula I above include those listed in the following Table I.

TABLE I

Cpd. No.	Compound
I	2-Methyl-5-phenyl-1,3,4-oxadiazole
II	2-Methyl-5-(α -naphthyl)-1,3,4-oxadiazole
III	2-Methyl-5-p-hydroxyphenyl-1,3,4-oxadiazole
IV	2,5-Di(p-aminophenyl)-1,3,4-oxadiazole
V	2,5-Di(p-aminostyryl)-1,3,4-oxadiazole
VI	5-(p-Ethoxyphenyl)-2-methyl-1,3,4-oxadiazole
VII	2-(p-Biphenyl)-5-phenyl-1,3,4-oxadiazole
VIII	5-Phenyl-2-stilben-4-yl-1,3,4-oxadiazole
IX	2,5-bis(4-Diethylaminophenyl)-1,3,4-oxadiazole
X	2,5-Di(α -naphthyl)-1,3,4-oxadiazole
XII	2-Amino-5-phenyl-1,3,4-thiadiazole
XIII	2-Anilino-5-phenyl-1,3,4-thiadiazole
XIV	2-(p-Acetamidophenylsulfonamino)-5-methyl-1,3,4-thiadiazole
XV	2-Acetamido-5-iodo-1,3,4-thiadiazole
XVI	2-(p-anisidino)-5-methyl-1,3,4-thiadiazole
XVII	1,4-Bis[2-(5-phenyloxazolyl)]benzene
XVIII	2,5-Diphenyloxazole
XIX	2-(α -Naphthyl)-5-phenyloxazole
XX	2-Anilino-4,5-diphenyloxazole
XXI	1,4-Bis[2-(5-p-tolyloxazolyl)]benzene
XXII	2-(p-Aminophenyl)-4-methylthiazole
XXIII	2-Anilino-4-phenylthiazole
XXIV	2,5-Diphenylthiazole

The above class of heterocyclic compounds are well known and methods for their preparations are described in the prior art literature. Some of the more specific references are included herein for illustrative purposes, for example, reference can be had to Chemical Abstracts 29, 5444^a; 30, 4837^a; 32, 556^b; 32, 557^b; 44, 2516^d; 49, 1011^d; 49, 7560^b; 50, 6435^a; 51, PI2983^b; 51, 13580^a; 53, 7800^e; 53, 15064^h; 54, 13100^f; 55, 18297^c; 59, 630^f; etc.

The methine dyes of above component (2) of the invention are represented by the following formulas:



$$\text{—C}=\text{C—O}^{\ominus}$$



m

4

K-

1.

1-
71

e

23

3

4

43

50

55

22

imidazolidinedione, etc.; a 2-imidazolin-5-one nucleus, e.g., 2-propylmercapto-2-imidazolin-5-one, etc.; etc. Preferably, Q₁ and Q₂ each represents the atoms to complete a ring containing from three to four carbon atoms, one nitrogen atom and one atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium.

Typical methine spectral sensitizer dyes of the invention represented by Formulas II to VI above include those listed in the following table 2.

TABLE 2

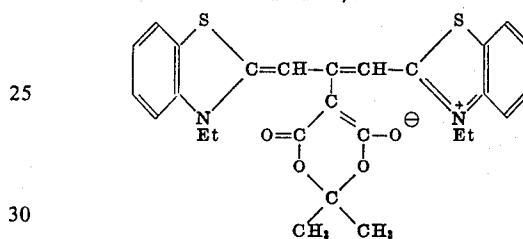
Dye No.	Cyanine Spectral Sensitizer Dyes
A	1,1'-Diethyl-2,2'-cyanine iodide
B	3,3'-Dimethyl-9-ethyl-4,5,4',5'-naphthothiacarbocyanine chloride
C	3,3'-Di-β-hydroxyethylthiadicarbocyanine bromide
D	1'-Butyl-3-ethyl-4-phenylthia-4'-carbocyanine iodide
E	3,3'-Diethyloxathiadicarbocyanine iodide
F	1,3-Diethyl-5-[di(1-ethyl-2(1H)-β-naphthothiazolylidene)-isopropylidene] barbituric acid
G	2-[Di(1-ethyl-2(1H)-β-naphthothiazolylidene)isopropylidene]-1,3-indandione
H	1,3-Diethyl-5-[(1-ethyl-2(1H)-β-naphthothiazolylidene)-isopropylidene] barbituric acid
I	2-[(1-Ethyl-2(1H)-β-naphthothiazolylidene)isopropylidene]-1,3-indandione
J	5-[Di(1-ethyl-2(1H)-β-naphthothiazolylidene)isopropylidene]-1,3-di(β-methoxyethyl)barbituric acid
K	2-[(2-benzothiazolylethylidene)methylene]-2-β-methoxyethyl-5-[(1-methyl-2(1H)naphtho[1,2]thiazolylidene-β-phenyl-ethylidene)-4-thiazolidone]
L	1,3-Diethyl-5-[(1,3-di(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene)indan-2-ylidene] barbituric acid
M	2-Dicyanomethylene-1,3-di[(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]indan
N	1,3-Diethyl-5-[(β-(3-ethyl-2(3H)-benzothiazolylidene)-α-[(3-ethyl-2(3H)benzothiazolylidene)amino]-ethylidene)] barbituric acid
O	1,3-Diethyl-5-[2,5-di[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]cyclopentylidene] barbituric acid
P	Anhydro-3-ethyl-5-phenyl-1'-(4-sulfobutyl)thia-4'-carbocyanine hydroxide
Q	1,3-Diethyl-5-[2-(3-ethyl-2(3H)-benzothiazolylidene)-5-[(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]-cyclopentylidene] barbituric acid
R	5-[Di(3-ethyl-2(3H)-benzothiazolylidene)isopropylidene]-3-ethyl-1-phenyl hydantoin
S	5-[Di(3-ethyl-2(3H)-benzothiazolylidene)isopropylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione
T	2-[(2-Benzothiazolylethylidene)methylene]-3-(3-dimethylaminopropyl)-5-[(1-methylnaphtho[1,2-d]thiazolin-2-ylidene)-1-phenylethylidene]-4-thiazolidinone
U	3-(3-Dimethylaminopropyl)-5-[(3-ethyl-2-benzothiazolylidene)ethylidene]-2-thio-2,4-oxazolidinedione
V	3,3'-Diethylselenadicarbocyanine iodide

The methine dyes of the invention illustrated by those listed in above Table 2 have been previously described in the literature, except for Dye No. K which forms part of and is illustrative of the subject matter of copending application of D. W. Heseltine, Ser. No. 463,024, filed June 10, 1965, now U.S. Pat. No. 3,440,052. Pertinent references include the following: Zeh et al. U.S. Pat. No. 2,068,047, issued 1/19/37 Brooker, U.S. Pat. No. 2,078,233, issued 4/27/37 Koslowsky, U.S. Pat. No. 2,107,379, issued 2/8/38 Mees, U.S. Pat. No. 2,158,883, issued 5/16/39 Brooker et al. U.S. Pat. No. 2,161,331, issued 6/6/39 Brooker U.S. Pat. No. 2,170,807, issued 8/29/39 Brooker U.S. Pat. No. 177,402, issued 10/24/39

Brooker U.S. Pat. No. 2,177,403, issued 10/24/39 Carroll et al. U.S. Pat. No. 2,177,635, issued 10/31/39 Carroll U.S. Pat. No. 2,206,076, issued 7/2/40 Brooker U.S. Pat. No. 2,211,762, issued 8/20/40 Brooker et al. U.S. Pat. No. 2,213,238, issued 9/3/40 Brooker U.S. Pat. No. 2,307,916, issued 1/12/43 Brooker et al. U.S. Pat. No. 2,313,922, issued 3/16/43 Schneider U.S. Pat. No. 2,374,505, issued 4/24/45 Falleson et al. U.S. Pat. No. 2,378,917, issued 6/26/45 Brooker U.S. Pat. No. 2,454,629, issued 1/23/48 Thompson U.S. Pat. No. 2,535,993, issued 12/26/50 Carroll et al. U.S. Pat. No. 2,950,196, issued 8/23/60 Brooker et al. U.S. Pat. No. 2,955,939, issued 10/11/60 Jones U.S. Pat. No. 2,961,318, issued 11/22/60 Brooker et al. U.S. Pat. No. 3,194,805, issued 7/13/65 Tabor et al. U.S. Pat. No. 3,335,010, issued 8/8/67 Brooker et al. U.S. Re. No. 24,292, reissued 3/19/57 I.G., Br. Pat. No. 434,235, accepted 8/28/35

The following example describes the preparation of above mentioned Dye No. S.

20 5-[Bis(3-ethyl-2-benzothiazolylidene)isopropylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione



A mixture of 3-ethyl-2-ethylmer manner well known to those skilled in the art by measuring the sensitivity of a series of test portions of the same emulsion, each portion containing a different concentration of the sensitizing dye. In general, the heterocyclic compounds in my invention have little or no sensitizing action by themselves alone in the emulsions employed. Ordinarily, the optimum or near optimum concentration of the cyanine dyes herein is of the order of from 0.01 to 1.2 g. per mole of silver halide in the emulsion, and that of the heterocyclic compound herein is of the order of from 0.05 to 5.0 g.

The methods of incorporating sensitizing dyes in silver halide emulsions are well known to those skilled in the art and these known techniques are employed in dispersing the dyes of the invention in the emulsions. In practicing my invention the sensitizing dyes and the heterocyclic compounds can be directly dispersed in the emulsions, or they can first be dissolved in some convenient solvent, such as pyridine, methyl alcohol, acetone, etc. (or mixtures or such solvents), or diluted with water in some instances, and added to the emulsions in the form of these solutions. If desired, the components can be separately dissolved in a given solvent and added separately to the emulsion, or they can be dissolved in the same or different solvent and these solutions mixed together before addition is made to the silver halide emulsions. The dyes and heterocyclic compounds of the invention are dispersed in the finished emulsions in such manner as to be uniformly distributed throughout the emulsions prior to coating on a suitable support, such as paper, glass, cellulose ester film, polyvinyl resin film (e.g., polystyrene film, polyvinyl chloride film, etc.) polyester film, etc. The following procedure has been found quite satisfactory: Stock solutions of the heterocyclic compounds of Formula I and the dyes of Formulas II to V above are prepared by separately dissolving these components in appropriate solvents as described above. Then, to the flowable silver halide emulsion, the desired amount of stock solution of one of the dyes is slowly added while stirring the emulsion. Stirring is continued until the dye is thoroughly incorporated in the emulsion. Then, the desired amount of stock solution of one of the heterocyclic compounds is slowly added to the emulsion while stirring. Stirring is continued until the added materials are thoroughly incorporated in the emulsion. The

supersensitized emulsions can then be coated on a suitable support and the coating allowed to dry. In some instances, it may be desirable to heat the supersensitized emulsion for a few minutes before coating onto the suitable support. The details of such coating techniques are well known to those skilled in the art. The foregoing procedure and proportions are to be regarded only as illustrative. Clearly, the invention is directed to any silver halide emulsion containing a supersensitizing combination of the invention, e.g., gelatino-silver chloride, -chlorobromide, -chloriodide, -chlorobromiodide, -bromiodide, etc., emulsions.

Fine grain emulsions can also be employed herein. These may be prepared by precipitating photosensitive silver halide crystals, in an aqueous medium, in the presence of an acid substituted aryl mercaptan, e.g., thiosalicylic acid, dissolved in said medium. Gelatin or other suitable hydrophilic colloid is added and the emulsion obtained is chilled and set. The chilled emulsion is then shredded into small noodles and washed in running tap water. After washing, the emulsion is remelted, and the volume, pH and Pag are adjusted. A fine grain gelatino-silver bromiodide emulsion prepared in the above manner and containing a dye combination of the invention is particularly useful for recording radiations in the region of the spectrum ranging about from 300 to 750 nm. in fine detail. Further details for preparing such fine grain emulsions can be had by reference to copending application of Sutherns, Ser. No. 622,034, filed Mar. 10, 1967, now U.S. Pat. No. 3,519,427.

The emulsions of this invention can contain the chemical sensitizers, speed increasing compounds, plasticizers, hardeners and coating aids, and the silver halide may be dispersed in any of the binders, that are described and referred to in Graham et al. U.S. Pat. No. 3,046,129 issued July 24, 1962.

The following examples are included for a further understanding of the invention.

Examples 1 to 20

These examples illustrate the supersensitization produced with the 1,3,4-oxadiazoles defined by Formula I above in combinations with various cyanine dyes coming under Formulas II to VI above. The testing procedure and the results are set forth in the following description and table 3. The specified cyanine dyes and heterocyclic compounds are identifiable by reference to tables 1 and 2 above.

To different portions of the same batch of melted gelatino-silver bromiodide emulsion, containing 0.77 mole percent iodide, of the type described by Trivelli and Smith Phot. Journal, 79, 330 (1939), are added the individual cyanine dyes and the heterocyclic compounds in the proportions given in table 3 hereinafter. In each case, after being digested at about 50° C. for 10 minutes, the emulsion is coated at a coverage of 432 mg. silver per square foot on a cellulose acetate film support. A sample of each coating is exposed on an Eastman 1B Sensitometer to light from a tungsten source modulated by a step-wedge and Kodak Wratten No. 16 filter and processed for 3 minutes in Kodak Developer D-19 which has the following composition:

N-methyl-p-aminophenol sulfate.	2.0 g.
Hydroquinone	8.0 g.
Sodium sulfite (desiccated)	90.0 g.
Sodium carbonate (monohydrate)	52.5 g.
Potassium bromide	5.0 g.
Water to make	1.0 liter

and then fixed in a conventional sodium thiosulfate fixing bath, washed and dried. Densitometric measurements are then made of the developed images of each coating. The relative speed values are determined by the exposure necessary to produce a density of 0.3 above fog, an arbitrary relative speed of 100 being chosen for the control containing only dye. The

results are listed in the following table together with the values for gamma and fog.

TABLE 3

Supersensitization by 1,3,4-oxadiazoles (Addendum)

Ex. No.	Dye No. and conc. (g./mole silver)	Addendum and conc. (g./mole silver)	Relative speed	γ	Fog
5					
10	1(a)----- V (.04)	None	100	0.92	.04
	(b)----- V (.04)	I (.660)	132	0.90	.04
	(c)----- V (.04)	II (.660)	126	0.85	.04
	(d)----- V (.04)	III (.660)	138	0.90	.04
20	2(a)----- J (.033)	None	100	-----	.04
	(b)----- J (.033)	III (.660)	79,500	1.10	.05
	3(a)----- U (.060)	None	100	2.10	.05
	(b)----- U (.060)	IV (1.1)	261	1.82	.04
	(c)----- U (.060)	VI (1.62)	126	1.84	.04
15	4(a)----- A (.090)	None	100	1.20	.06
	(b)----- A (.090)	IV (1.1)	138	1.02	.05
	(c)----- A (.090)	V (1.3)	132	0.86	.09
	5(a)----- J (.076)	None	100	-----	.06
	(b)----- J (.076)	IV (1.1)	135,000	1.18	.06
	(c)----- J (.076)	V (1.3)	9,330	0.97	.15
	(d)----- J (.076)	VI (1.6)	3,980	1.53	.06
20	6(a)----- N (.076)	None	100	1.12	.04
	(b)----- N (.076)	IV (.660)	148	1.22	.04
	7(a)----- F (.076)	None	100	-----	.07
	(b)----- F (.076)	IV (.660)	1,070	1.45	.05
	8(a)----- L (.033)	None	100	1.56	.05
	(b)----- L (.033)	IV (.660)	776	1.56	.04
	(c)----- L (.033)	IX (.660)	1,410	1.28	.05
25	9(a)----- D (.090)	None	100	0.85	.04
	(b)----- D (.090)	V (1.3)	219	0.71	.04
	10(a)----- G (.076)	None	100	1.42	.05
	(b)----- G (.076)	V (.330)	13,800	0.63	.40
	11(a)----- H (.076)	None	100	-----	.04
	(b)----- H (.076)	V (.330)	1,260	0.74	.46
	12(a)----- I (.076)	None	100	0.92	.06
	(b)----- I (.076)	V (.330)	1,150	0.75	.50
30	13(a)----- Q (.076)	None	100	1.70	.04
	(b)----- Q (.076)	V (.330)	575	1.31	.06
	14(a)----- O (.076)	None	100	1.80	.04
	(b)----- O (.076)	V (.330)	977	1.06	.17
	15(a)----- S (.076)	None	100	1.70	.04
	(b)----- S (.076)	V (.330)	151	0.87	.33
	16(a)----- R (.076)	None	100	1.37	.03
	(b)----- R (.076)	V (.330)	257	1.20	.04
35	17(a)----- B (.090)	None	100	1.46	.06
	(b)----- B (.090)	VI (1.6)	110	1.16	.07
	18(a)----- J (.076)	None	100	-----	.06
	(b)----- J (.076)	VII (3.0)	550	1.20	.06
	(c)----- J (.076)	VIII (.560)	4,360	1.28	.06
	(d)----- J (.076)	IX (.660)	2,140	1.10	.07
40	19(a)----- M (.033)	None	100	-----	.04
	(b)----- M (.033)	IX (.660)	276	1.52	.04
	20(a)----- K (.066)	None	100	1.27	.06
	(b)----- K (.066)	X (2.0)	219	1.15	.05

Referring to above table 3, it will be seen that the relative speed for each of the supersensitizing combinations is markedly greater than that of the same emulsion containing the specified dye but containing no 1,3,4-oxadiazole addendum. Remarkably high relative speeds are shown for examples 2B, 5B, 5C, 5D, 10B, 18C and 18D with no increase in fog in most instances.

Examples 21 to 25

These examples illustrate the supersensitization produced with the 1,3,4-thiadiazoles defined by Formula I above in combinations with various cyanine dyes coming under Formulas II to VI above. The testing procedure is exactly the same as that described in above examples 1 to 20 and the results are tabulated in similar fashion in the following table.

TABLE 4

Supersensitization by 1,3,4-thiadiazoles (Addendum)

Ex. No.	Dye No. and conc. (g./mole silver)	Addendum and conc. (g./mole silver)	Relative speed	γ	Fog
65	21(a)----- J (.076)	None	100	-----	.06
	(b)----- J (.076)	XII (.660)	49,000	1.73	.05
	22(a)----- V (.040)	None	100	0.80	.04
	(b)----- V (.040)	XIII (.660)	145	0.74	.04
	23(a)----- D (.076)	None	100	0.93	.04
	(b)----- D (.076)	XII (.660)	126	0.90	.04
70	24(a)----- K (.053)	None	100	1.41	.04
	(b)----- K (.053)	XVI (.660)	115	1.27	.04
	25(a)----- J (.076)	None	100	-----	.05
	(b)----- J (.076)	XIV (.660)	832	1.66	.04
	(c)----- J (.076)	XV (.185)	224	1.80	.06
	(d)----- J (.076)	XVI (.660)	7,950	1.40	.04

It will be noted from above table 4 that in each instance substantial improvement in relative speed over each dye alone is

shown with the supersensitizing combinations of the invention.

Examples 26-34

These examples illustrate the supersensitizing effect produced with the oxazoles defined by Formula I of the invention in combinations with various cyanine dyes of Formula II to VI above. The testing procedure is exactly the same as that described in above examples 1 to 20 and the results are listed in similar manner in the following table.

TABLE 5
Supersensitization by oxazoles (Addendum)

Ex. No.	Dye No. and conc. (g./mole silver)	Addendum and conc. (g./mole silver)	Relative speed	γ	Fog
26(a)-----	C (.050)	None	100	1.65	.04
(b)-----	C (.050)	XVII (.330)	204	1.65	.04
27(a)-----	V (.040)	None	100	0.80	.04
(b)-----	V (.040)	XVII (.330)	141	1.25	.03
28(a)-----	D (.076)	None	100	0.93	.04
(b)-----	D (.076)	XVII (.330)	159	1.40	.04
(c)-----	D (.076)	XVIII (.330)	174	0.82	.04
29(a)-----	J (.076)	None	100	-----	.05
(b)-----	J (.076)	XVIII (.330)	380	1.93	.05
(c)-----	J (.076)	XXI (.330)	2,000	2.20	.04
30(a)-----	V (.040)	None	100	0.94	.04
(b)-----	V (.040)	XXI (.330)	135	1.00	.04
(c)-----	V (.040)	XX (.660)	302	0.96	.04
31(a)-----	D (.076)	None	100	0.83	.04
(b)-----	D (.076)	XXI (.330)	436	0.65	.04
(c)-----	D (.076)	XX (.660)	457	0.68	.04
32(a)-----	K (.053)	None	100	1.21	.05
(b)-----	K (.053)	XXI (.330)	186	1.11	.05
(c)-----	K (.053)	XX (.660)	178	0.85	.04
33(a)-----	J (.076)	None	100	1.32	.06
(b)-----	J (.076)	XX (.660)	302	1.26	.05
34(a)-----	E (.053)	None	100	0.96	.04
(b)-----	E (.053)	XXI (.990)	209	1.23	.04

Referring to above table 5, it will be noted that the supersensitizing combinations of the invention containing oxazoles defined by Formula I above show substantial improvements in relative speed in each instance as compared with that shown for the individual dye alone in the same emulsion.

Examples 35-40

These examples illustrate the supersensitization produced with the thiazoles defined by Formula I above in combinations with various cyanine dyes coming under the definitions of Formulas II to VI above. The testing procedure is exactly the same as that described in above examples 1 to 20 and the results are tabulated in table 6 in the same manner.

TABLE 6
Supersensitization by thiazoles (Addendum)

Ex. No.	Dye No. and conc. (g./mole silver)	Addendum and conc. (g./mole silver)	Relative speed	γ	Fog
5	35(a)-----	P (.076)	None	100	0.74
	(b)-----	P (.076)	XXII (.330)	269	0.92
	36(a)-----	J (.076)	None	100	1.70
	(b)-----	J (.076)	XXIII (.660)	372	1.86
	(c)-----	J (.076)	XXIV (.660)	2,400	1.58
10	37(a)-----	P (.053)	None	100	1.55
	(b)-----	P (.053)	XXIII (.660)	126	1.38
	(c)-----	P (.053)	XXIV (.660)	145	1.37
	38(a)-----	K (.053)	None	100	1.34
	(b)-----	K (.053)	XXIII (.660)	126	1.33
	39(a)-----	C (.050)	None	100	1.43
	(b)-----	C (.050)	XXIV (.660)	129	1.53
15	40(a)-----	V (.040)	None	100	1.34
	(b)-----	V (.040)	XXIV (.660)	276	1.24

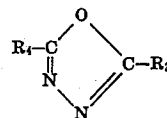
Referring to above table 6, it will be noted that in each instance substantial improvement in relative speed over each dye alone is shown by the supersensitizing combinations of the invention.

It will be apparent from all of the foregoing that still other valuable supersensitizing combinations of the invention can be produced by selecting other heterocyclic compounds embraced by Formula I above and other cyanine dyes embraced by Formulas II to VI above, and that such combinations likewise will give desirably improved supersensitized photographic silver halide emulsions and elements.

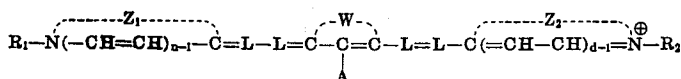
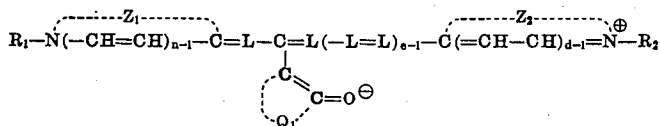
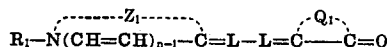
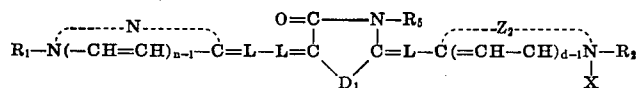
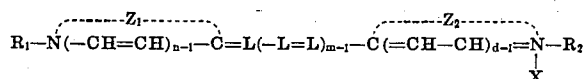
The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention described hereinabove and in the appended claims.

We claim:

1. A photographic silver halide emulsion containing a supersensitizing combination of (1) a heterocyclic compound represented by the following formula:

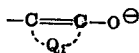


and (2) a methine dye selected from those having one of the following formulas:



wherein d , e and n each represents a positive integer of from 1 to 2; m represents a positive integer of from 1 to 3; L represents a methine linkage; R_1 and R_2 each represents a member selected from the group consisting of an alkyl group and an aryl group; R_3 represents a member selected from the from the group consisting of an alkyl group containing from one to four carbon atoms, an aryl group, an amino group, a styryl group, an amido group, and a halogen atom; R_4

represents a member selected from the group consisting of a hydrogen atom and a value given for R_3 ; X represents an acid anion; R_5 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group and an aryl group; A_2 represents a member selected from the group consisting of a dicyanomethylene group and the group



D_1 represents a member selected from the group consisting of an oxygen atom, a sulfur atom and the nonmetallic atoms necessary to complete a diazole ring; W represents the nonmetallic atoms necessary to complete a ring selected from the group consisting of a cyclopentene ring, a cyclohexene ring and an indan ring; Z and Z_1 represents the nonmetallic atoms necessary to complete a nitrogen containing heterocyclic nucleus of the type used in methine dyes containing from five to six atoms in the heterocyclic ring; and Q_1 and Q_2 each represents the nonmetallic atoms necessary to complete a heterocyclic ketomethylene nucleus of the type used in merocyanine dyes containing from five to six atoms in the heterocyclic ring.

2. A light sensitive photographic silver halide emulsion containing a supersensitizing combination comprising (1) at least one compound selected from the group consisting of 2-methyl-5-phenyl-1,3,4-oxadiazole; 2-methyl-5-(α -naphthyl)-1,3,4-oxadiazole; 2-methyl-5-p-hydroxyphenyl-1,3,4-oxadiazole; 2,5-di-(p-aminophenyl)-1,3,4-oxadiazole; 2,5-di-(p-aminostyryl)-1,3,4-oxadiazole; 5-(p-ethoxyphenyl)-2-methyl-1,3,4-oxadiazole; 2-(p-biphenyl)-5-phenyl-1,3,4-oxadiazole; 5-phenyl-2-stilben-4-yl-1,3,4-oxadiazole; 2,5-bis(4-diethylaminophenyl)-1,3,4-oxadiazole; 2,5-di-(α -naphthyl)-1,3,4-oxadiazole; and (2) at least one methine dye selected from the group consisting of 1,1'-diethyl-2,2'-cyanine salt; 3,3'-dimethyl-9-ethyl-4,5,4',5'-naphthothiacarbocyanine salt; 3,3'-di- β -hydroxyethylthiadibocyanine salt; 1'-butyl-3-ethyl-4-phenylthia-4'-carbocyanine salt; 3,3'-diethyloxathiadicarbocyanine salt; 1,3-diethyl-5-[di(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]barbituric acid; 2-[di(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-indandione; 1,3-diethyl-5-[(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-barbituric acid; 2-[(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-indandione; 5-[di(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-di-(methoxyethyl)barbituric acid; 2-[(2-benzothiazolylethiodide)methylene]-3- β -methox-

yethyl-5-[(1-methyl-2(1H)-naphtho [1,2]thiazolylidene- α -phenylethylidene)-4-thiazolidone; 1,3-diethyl-5-[1,3-di(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]indan-2-ylidene barbituric acid; 2-dicyanomethylene-1,3-di[(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]indan; 1,3-diethyl-5- β -(3-ethyl-2(3H)-benzothiazolylidene)- α -(3-ethyl-2(3H)-benzothiazolylidene)amino]ethylidene barbituric acid; 1,3-diethyl-5-2,5-di[(3-ethyl-2(3H)-benzoxazolylidene)ethylidene]-cyclopentylidene barbituric acid; anhydro-3-ethyl-5-phenyl-1'-(4-sulfobutyl)thia-4'-carbocyanine hydroxide; 1,3-diethyl-5-2-(3-ethyl-2(3H)-benzothiazolylidene)-5-[(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]cyclopentylidene barbituric acid; 5-[di(3-ethyl-2(3H)-benzothiazolylidene)isopropylidene]-3-ethyl-1-phenyl hydantoin; 5-[di(3-ethyl-2(3H)-benzothiazolylidene)isopropylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione; 2-[(2-benzothiazolylethoperchlorate)methylene]-3-(3-dimethylaminopropyl)-5-[(1-methylnaphtho[1,2d]thiazolin-2-ylidene)-1-phenylethylidene]-4-thiazolidinone; 3-(3-dimethylaminopropyl)-5-[(3-ethyl-2-benzothiazolylidene)ethylidene]-2-thio-2,4-oxazolidinedione; and 3,3'-diethylselenadibocyanine salt.

3. A light-sensitive photographic silver halide emulsion supersensitized with the combination comprising (1) 2,5-di(p-aminophenyl)-1,3,4-oxadiazole and (2) 5-[di(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-di(β -methoxyethyl)barbituric acid.

4. A light-sensitive photographic silver halide emulsion supersensitized with the combination comprising (1) 2,5-di(p-aminostyryl)-1,3,4-oxadiazole and (2) 2-[di(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-indandione.

5. A light-sensitive photographic silver halide emulsion supersensitized with combination combination (1) (1) 2,5-di(p-aminophenyl)-1,3,4-oxadiazole (2) (3) 1,1'-diethyl-2,2'-cyanine salt.

6. A light-sensitive photographic silver halide emulsion supersensitized with the combination comprising (1) 2,5-di(p-aminostyryl)-1,3,4-oxadiazole and (2) 2-[(1-ethyl-2(1H)- β -naphthothiazolylidene)isopropylidene]-1,3-indandione.

7. A light-sensitive photographic silver halide emulsion supersensitized with the combination comprising (1) 2,5-di(p-aminostyryl)-1,3,4-oxadiazole and (2) 1,3-diethyl-5-[2-(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]cyclopentylidene] barbituric acid.

8. A photographic element comprising a support having a coating thereon containing an emulsion of claim 1.

9. A photographic element comprising a support having a coating thereon containing an emulsion of claim 2.

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