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Beretta et al.

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[45] Sept. 17, 1974

[54] MEROCYANINIC DYES AND THEIR USE IN SILVER HALIDES PHOTOGRAPHIC EMULSIONS CONTAINING THE SAME

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[21] Appl. No.: **232,724**

[30] **Foreign Application Priority Data**

Mar. 9, 1971 Italy 48919/71

[52] **U.S. Cl.** **96/127,** 96/139, 96/141, 260/240.1, 260/240.4

[51] **Int. Cl.** **G03c 1/10**

[58] **Field of Search** 96/127, 140, 141

[56] **References Cited**

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[57] **ABSTRACT**

Merocyanine dyes comprising a heterocyclic nitrogenous nucleus and a heterocyclic ketomethylene nucleus, and silver halide emulsions containing such dyes.

5 Claims, 8 Drawing Figures

Fig. 1

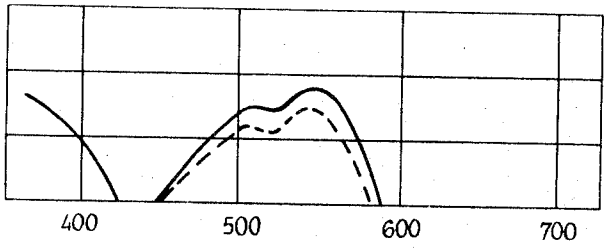


Fig. 2

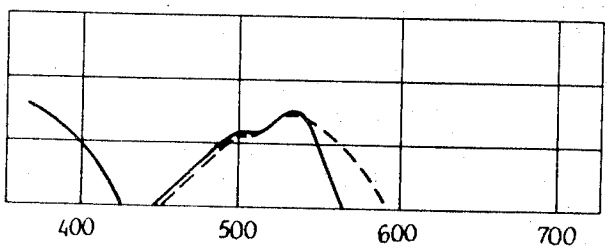
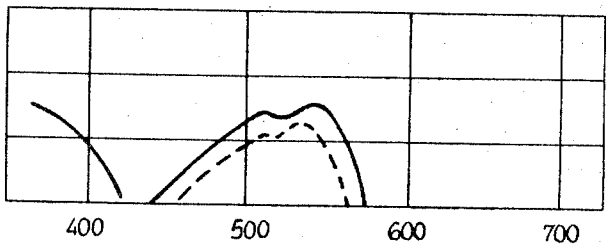


Fig. 3



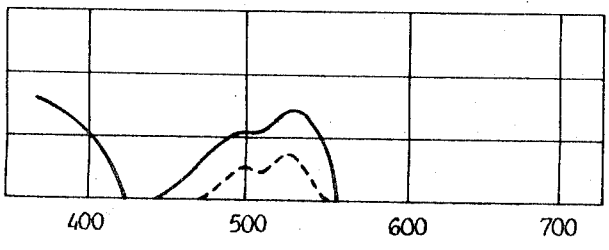


Fig. 4

Fig. 5

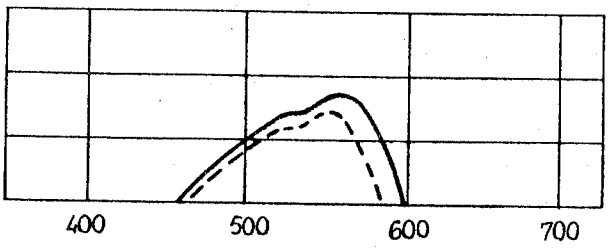
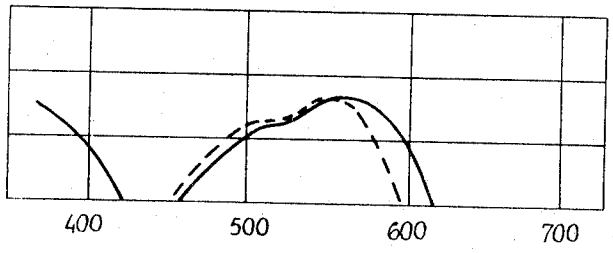


Fig. 6



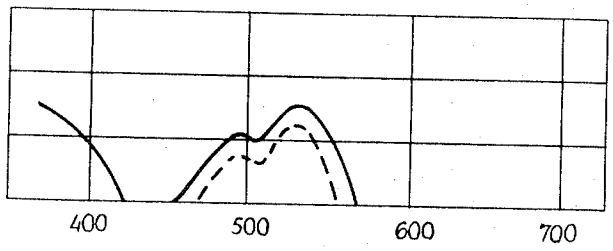
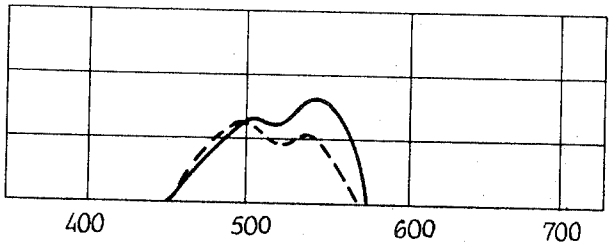


Fig. 7

Fig. 8



MEROCYANINIC DYES AND THEIR USE IN SILVER HALIDES PHOTOGRAPHIC EMULSIONS CONTAINING THE SAME

The present invention relates to merocyaninic dyes and to silver halides emulsions containing the same and to photographic elements containing such dyes.

Silver halides, by themselves, are substantially insensitive to the visible radiations with the exception of those having a lower wave length. The sensitivity of the silver halides emulsions has been extended to higher wave lengths by the introduction into them of various dyeing sensitizers such as those of the merocyaninic class. These dyes are now of common use in the black and white photographic emulsions and in the colored photographic emulsions. For example, a useful photographic element for colored photography may contain layers of silver halides emulsion which have been sensitized to the red, green and blue light. The dyeing sensitizers used in the above photography must exhibit, according to what hereinabove said, the sensitization characteristics required and moreover they must be completely removable from the photographic elements during the processing so as to impart the least residual coloration possible to the final colored image.

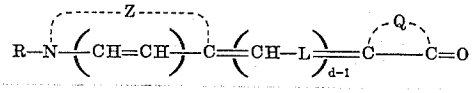
A summary of the technology of the dyeing sensitizers and examples of various dyeing sensitizers may be found in Mees and James, "The Theory of the Photographic Process," Third Edition, The McMillan Company, New York, 1966, Chapter 11. For the desensitizers re same Chapter 11 and 8 and e.g. British Patent 1,186,713.

In brief the present invention relates to merocyaninic dyes comprising on one side a heterocyclic, nitrogeneous nucleus and on the other one of a heterocyclic ketomethylenic nucleus.

These merocyaninic dyes are characterized by the ketomethylenic group containing at least a nitrogen atom, carrying, as a substituent, a furfuryl- or a tetrahydrofurfuryl group. The invention relates moreover to photographic silver halides emulsions containing such dyes, as sensitizers and desensitizers, and to photographic elements prepared with them.

In its preferred realization, the present invention refers to merocyaninic dyes representatable by the following formula:

(1)



In the hereinabove formula,

R represents a substituted and a non substituted alkyl having from one to eight carbon atoms such as for example methyl, ethyl, hydroxyethyl, sulphoethyl, carboxyethyl, hydroxyethyl, hydroxypropyl, sulphobutyl, carboxybutyl, benzyl, paracarboxyphenylmethyl;

L represents a non substitituted methinic group and, when *d* is equal to 2, a methinic group substituted with a monovalent group R_1 such as low alkyl group from one to three carbon atoms as for example methyl, ethyl, propyl, and alkoxy group having from one to three carbon atoms as for example methoxy and ethoxy, and alkylmercapto having from one to three carbon atoms as for example methylmercapto, ethylmercapto and propylmercapto;

Z represents the non metallic atoms required to complete a heterocyclic nucleus.

Q represents the non metallic atoms necessary to complete a heterocyclic nucleus comprising at least a nitrogen atom carrying, as a substituent, a furfuryl or a tetrahydrofurfuryl group.

n is 1 or 2 and *d* is 1, 2 or 3.

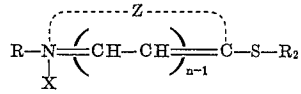
Examples of heterocyclic rings which are completed by the non metallic atoms represented by Z in the hereinabove formula (1) are those of the thiazole series (thiazole, 4-methyl-thiazole, 4-phenylthiazole, 5-methyl-thiazole, 5-phenyl-thiazole, 4,5-dimethyl-thiazole, 4,5-diphenyl-thiazole); those of the benzothiazole series (benzothiazole, 4-chlorobenzothiazole, 5-chloro-benzothiazole, 6-chloro-benzothiazole, 7-chloro-benzothiazole, 4-nitro-benzothiazole, 5-nitro-benzothiazole, 6-nitro-benzothiazole, 5-chloro-6-nitro-benzothiazole, 5-bromo-6-nitrobenzothiazole, 4-methyl-benzothiazole, 5-methyl-benzothiazole, 6-methylbenzothiazole, 5-bromo-benzothiazole, 6-bromo-benzothiazole, 4-phenylbenzothiazole, 5-phenyl-benzothiazole, 4-methoxy-benzothiazole, 5-methoxybenzothiazole, 6-methoxy-benzothiazole, 5-methyl-6-methoxy-benzothiazole, 5-iodo-benzothiazole, 6-iodo-benzothiazole, 4-ethoxy-benzothiazole, 5-ethoxy-benzothiazole, 4,5,6,7-tetrahydro-benzothiazole, 5,6-hydroxymethylen-benzothiazole, 5-hydroxy-benzothiazole, 6-hydroxy-benzothiazole, 5,6-dimethyl-benzothiazole, 5,6-dimethoxy-benzothiazole); those of the naphthothiazole series ([1,2-d]-naphthothiazole, [2,1-d]-naphthothiazole, 5-methoxy-[1,2-d]-naphthothiazole, 5-ethoxy-[1,2-d]-naphthothiazole, 8-methoxy-[2,1-d]-naphthothiazole, 7-methoxy-[2,1-d]-naphthothiazole); those of the oxazole series (4 -methyl-oxazole, 5-methyl-oxazole, 4-phenyl-oxazole, 4,5-diphenyl-oxazole, 4-ethyl-oxazole, 4,5-dimethyl-oxazole, 5-phenyl-oxazole; those of the benzoxazole series (5-chloro-benzoxazole, 5-methyl-benzoxazole, 5-phenyl-benzoxazole, 6-methyl-benzoxazole, 5,6-dimethyl-benzoxazole, 4,6-dimethyl-benzoxazole, 5-metoxy-benzoxazole, 5-hydroxy-benzoxazole, 6-hydroxy-benzoxazole, 4-nitro-benzoxazole, 5-nitro-benzoxazole, 6-nitro-benzoxazole, 5-chloro-6-nitro-benzoxazole, 5-bromo-6-nitro-benzoxazole; those of the naphthoxazole series ([2,1-d]-naphthoxazole, [1,2-d]-naphthoxazole); those of the selenazole series (4-methyl-selenazole, 4-phenyl-selenazole); those of the benzoselenazole series (benzoselenazole, 5-chloro-benzoselenazole, 5-metoxy-benzoselenazole, 5-hydroxy-benzoselenazole, 6-metoxy-benzoselenazole, 5,6-dimetoxy-benzoselenazole, 4-nitro-benzoselenazole, 5-nitro-benzoselenazole, 6-nitro-benzoselenazole, 5-chloro-6-nitro-benzoselenazole, 5-bromo-6-nitro-benzoselenazole; those of the naphthoselenazole ([1,2-d]-naphthoselenazole, [2,1-d]-naphthoselenazole); those of the thiazoline series (thiazoline, 4-methyl-thiazoline, 4-hydroxymethyl-thiazoline, 4,4-bis-hydroxymethyl-thiazoline, 4-acetoxymethyl-4-methyl-thiazoline, 4,4-bis-acetoxymethyl-thiazoline); those of the oxazoline series (oxazoline, 4-hydroxymethyl-4-methyl-oxazoline, 4,4-bis-acetoxymethyl-oxazoline); those of the selenazoline series, those of the 2-quinoline series (quinoline, 3-methyl-quinoline, 5-methyl-quinoline, 7-methyl-quinoline, 3-methyl-quinoline, 6-chloro-quinoline, 8-chloro-quinoline, 6-methoxy-quinoline, 6-etoxy-

quinoline, 6-hydroxy-quinoline, 8-hydroxy-quinoline); those of 4-quinoline series (quinoline, 6-methoxy-quinoline, 7-metoxy-quinoline, 8-methyl-quinoline); those of the 1-isoquinoline series (isoquinoline, 3,4-diisoquinoline); those of the 3-isoquinoline series; those of the 3,3-dialkyl-indolenine series (3,3-dimethyl-indolenine, 3,3,5-trimethyl-indolenine, 3,3,7-trimethyl-indolenine); those of the 2-pyridine series (such as for example 2-pyridine, 5-methyl-2-pyridine, etc.); those of the 4-pyridine series (4-pyridine, 3-methyl-4-pyridine, etc.); those of the imidazole series (for example imidazole, 1-alkyl-imidazole, 1-alkyl-4-phenyl-imidazole, 1-alkyl-4,5-dimethyl-imidazole, etc.); those of the benzimidazole series (for example benzimidazole, 1-alkyl-benzimidazole, 1-alkyl-5,6-dichloro-benzimidazole, 1-phenyl-benzimidazole, 1-hydroxyethyl,5,6-dichloro-benzimidazole, 1-ethyl-5-chloro-benzimidazole, 1-acetoxyethyl-5,6-dichloro-benzimidazole, 1-ethyl-5-chloro-6-amino-benzimidazole, 1-ethyl-5-chloro-6-bromo-benzimidazole, 1-ethyl-5-acetyl-benzimidazole, etc.).

Examples of nuclei which are completed by atoms represented by Q in the hereinabove formula (1) are the nucleus of the thiazole, for example 2,4-thiazole-dione, 4-thiazolidone, 2-thio-2,4-thiazole-dione (rodanine); nuclei of the oxazolone type, for example 2-thio-2,4-oxazole-dione and 2-imino-2,4 oxazole-dione (pseudo-hydantoin); nuclei of the imidazolone type, such as the 2,4-imidazole-dione (hydantoin, for example 2-thio-2,4-imidazolo-dione (2-thio-hydantoin); nuclei of the pyrazolone type, oxindole (2,3-dihydroketoindole), 2,4,6-triketo-hexahydropyrimidine (barbituric or thiobarbituric acid); nuclei of the 3,4-dihydro-quinoline, 3,4-dihydro-quinoxazolone, 1,4-morpholine-3-one and 2H-1,4-benzothiazine-3-one.

The merocyaninic dyes of the present invention represented by the general formula (1), wherein d is equal to 1, can be prepared by reacting an ammonium salt chosen among those known to the skilled in the art, represented by the formula:

(2)

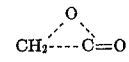


wherein R and Z have the hereinabove reported values;

R_2 represents an alkyl group (such as for example methyl, ethyl, etc.) or an aryl group (such as for example phenyl, o-, m-, p-tolyl, etc.);

X represents an acid anion such as chloride, bromide, iodide, thiocyanate, sulfamate, methylsulfate, ethylsulfate, perchlorate, benzensulfonate, p-toluenesulfonate, etc. with a compound chosen among those represented by the following formula:

(3)

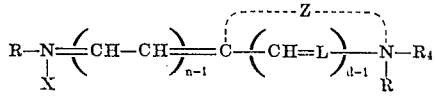


where Q has the hereinabove reported meaning.

The compounds (3) not known before the present invention, as they contain the furfuryl- or the tetrahydrofurfuryl substituent, can be prepared in a way known to the skilled in the art, as it results from the hereinafter following description and examples.

The dyes according to the invention represented by the general formula (1) where $d = 2, 3$ can be prepared by condensing a compound of the general formula (3) with a compound chosen among those known to the skilled in the art, represented by the general formula:

(4)



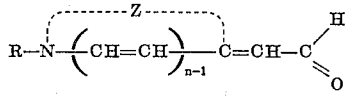
wherein R, Z, X, L and d have the same hereinabove reported values;

R_3 represents an acyl group, for example acetyl, propionyl, benzoyl, and

R_4 represents an aryl group such as, for example phenyl, o-, m-, p-tolyl etc.

A process which can be usefully employed to prepare cyaninic dyes of the general formula (1) with L equal to methinic non substituted group and $d = 2$, consists of condensing a compound of general formula (3) with a ω-aldehyde, known to the skilled in the art, represented by formula:

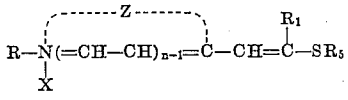
(5)



wherein R, Z and n have the meanings hereinabove reported.

Another process usefully employed in the synthesis of the merocyaninic dyes of the general formula (1) with $d = 2$ and L equal to substituted methinic group as hereinabove reported, consists of the condensation of a compound of the general formula (3) with a compound chosen among the class known to the skilled in the art, represented by the formula:

(6)

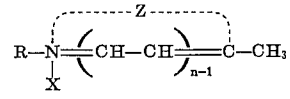


where R, R_1, X, Z and n have the meaning hereinabove reported and

R_5 is equivalent to monovalent alkyl group such as methyl, ethyl, etc.

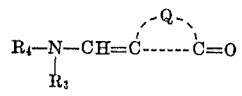
Another method to prepare the merocyaninic dyes of the general formula (1), where $d = 2$ and L is equal to non substituted methinic group consists of reacting a quaternary salt belonging to the class of the compounds known to the skilled in the art, represented by the following formula:

(7)



where R, X, Z, n have the hereinabove cited meanings, with a compound belonging to the class represented by the following formula:

(8)



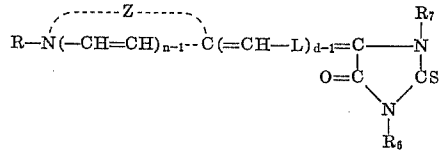
where Q, R_3, R_4, have the hereinabove cited meanings.

The compounds of the formula (8), not know before the present invention, as they contain the furfuryl- or the tetrahydrofurfuryl substituent, can be prepared in a way known to the skilled in the art, from compound of formula (3), as it results also from the examples following hereinafter.

The condensations of which hereinabove, can be advantageously performed by heating the reacting mixture at temperatures ranging between room temperature (about 20°C) and that of boiling of the mixture itself. The condensation can be performed in presence of an inert solvent such as pyridine, nitro-benzene, ethanol, n-propanol, isopropanol, n-butanol, and in the presence of a basic condensing agent such as the trialkylamines (for example triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-n-amylamine, etc.); N-alkyl-pyperidines (for example N-methyl-pyperidine, N-ethyl-pyperidine, etc.); N,N,-dialkyl-anilines (for example N,N-dimethyl-aniline, diethyl-aniline, etc.).

Among the merocyanines according to the invention, represented by formula (1), particularly useful are those represented by the following formula:

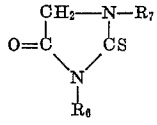
(9)



where R, L, Z, n and *d* have the meanings hereinabove reported and where at least one among the substituents R_6 and R_7 is a furfuryl- or tetrahydrofurfuryl group, while the other one is an alkyl group (for example methyl, ethyl, n-propyl, n-butyl, n-amyl, n-hexyl, n-heptyl, benzyl (phenylmethylene), allyl, cyclo-pentyl, cyclo-hexyl, etc.; a substituted alkyl group such as carboxyethyl, carboxymethyl, sulfo-propyl, dialkylaminoalkyl, etc.; an aryl group such as phenyl, o-, m-, p-tolyl.

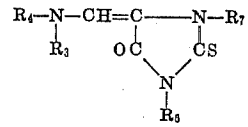
The compounds (9) are prepared according to the above indicated general methods, from compounds not known before the present invention, having the formula:

(10)



where R_6 and R_7 have the hereinabove reported meanings, obtained in a known way, for example according to Wheeler and Al, J.A.C.S. (1911), 45, 456–474, and from compounds not known before the present invention, having the formula

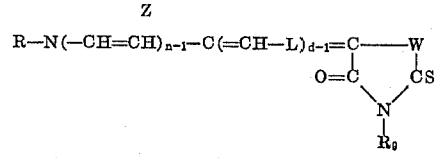
(11)



obtained in a way known to the skilled in the art from compounds having the formula (10) as it results from the following examples.

Among the compounds represented by formula (1), particularly useful are also the merocyanines represented by the following formula:

(12)



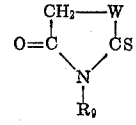
where R, L, Z, *n*, *d*, have the hereinabove said meanings

W is equal to S and O and

R_9 represents a furfuryl or tetrahydrofurfuryl radical.

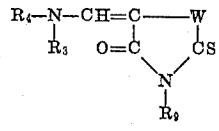
The compounds (12) are prepared according to the most general methods hereinabove reported, from compounds not known before the present invention, having the formula:

(12) bis



where W and R_9 have the hereinabove reported meanings, obtained in a way known to the skilled in the art, for example according to Holberg and Al in K. Prakt, Chemie, 81 (1910) 451 and Andreasch and Zizsser in monatschr. fur Chemie 24 (1903) 504 and 25 (1904) 167 and according to A. Ahlquist in Journ. Prakt. Chemie [2], 84 (1911), 662–675, and from compounds, not known before the present invention, having the formula:

(13)



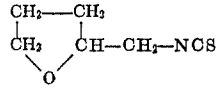
obtained in a way known to the skilled in the art from compound having the formula (12 bis) as it results also from the following examples.

The sensitizers of the present invention introduced into the silver halides photographic emulsions have the advantage of imparting to them and to the photographic element containing them a more extended spectral sensitization (and therefore a greater sensitivity) and of not presenting any residual coloring.

The present invention will be more easily understood, by referring to the following illustrative examples.

Example 1

Tetrahydrofurfuryl-isothiocyanate



24 g of NaOH drops were dissolved in 120 cc of water and to this solution 52.5 g of tetrahydrofurfurylamine were added. The stirred mixture was brought by cooling to +4°C and then 60.3 g of carbon sulfide were added in small portions. The temperature was maintained below 10°C during the whole period of the addition. The mixture was left under stirring for 7 hours and then allowed to stand at rest overnight. A solution of 228 g of lead acetate in 240 cc of water was poured into the reaction mixture under stirring at room temperature and the semisolid black mass obtained was diluted with 200 cc of water and furtherly stirred for 2 hours. The mixture was steam distilled until 3 liters of distillate were obtained; the distillate was then extracted with ethyl ether. The ethereal solution was dried with Na_2SO_4 and evaporated to dryness. A dark dense oil (34 g) was obtained, which was distilled under vacuum. The fraction distilled at 110°–115°C/27 mm Hg was collected.

The yield was 16 g.

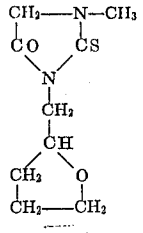
Example 2

furfuryl-senfol

This compound has been prepared similarly to the preceeding one by using 50 g of furfurylamine, 22.8 g of NaOH in 114 cc of water, 60.3 g of CS_2 and a solution of 240 g of lead acetate in 600 cc of water. At the end a dark dense oil was obtained which was immediately used without further purification, since it decomposed very easily (even if stored under vacuum).

Example 3

1-methyl-3-tetrahydro-furfuryl-2-thio-hydantoin



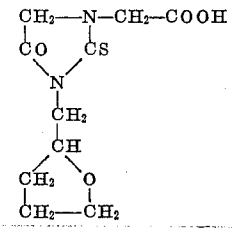
10 g of sarcosine, 15.5. g of tetrahydrofurfuryl-senfol (example 1), 1 cc of acetic anhydride and 5 cc of absolute ethyl alcohol, were introduced into a 100 cc flask and were heated at reflux for 25', then the mixture was poured into 160 cc of iced water. The oil formed was extracted with ether, the ethereal solution was dried with Na_2SO_4 and evaporated under vacuum. The residual oil was distilled under vacuum and the fraction distilled at 216°–220°C/2.5 mm Hg was collected.

The yield was 10 g.

	Centesimal analysis
Found:	C% = 50.78; H% = 6.82; N% = 12.87 S% = 14.75
Calculated:	C% = 50.51; H% = 6.59; N% = 13.09 S% = 14.98

Example 4

1-carboxymethyl-3-tetrahydrofurfuryl-2-thiohydantoin



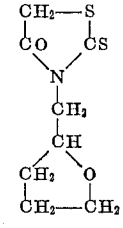
37.6 g of the iminoacetic acid diethyl ester were introduced in a flask supplied with reflux and dropper. From the latter 28.5 g of tetrahydrofurfuryl-senfol (example 1) were allowed to drop in and then the mixture was boiled for 10 minutes. The reaction mixture was poured in a vessel containing 200 cc of cold water; an oil was separated which was extracted with ethyl ether. The ethereal solution was treated with bone black, dried with Na_2SO_4 and evaporated ultil dryness.

The yield was 55.4 g and thus it was obtained the 1-carboxyethoxymethyl-3-(tetrahydrofurfuryl)-2-thiohydantoin. This product was treated with 186 cc of a 10 percent sodium hydroxide solution, heating to boiling for 10' and thus obtaining a complete solution. After acidification with HCl and cooling, the mixture was extracted with ethyl ether. The solution was dried with Na_2SO_4 and evaporated.

A dark oil (9.5 g) was obtained, which was used immediately for the synthesis of the dyes without further purification.

Example 5

N-tetrahydrofurfuryl-rodanine



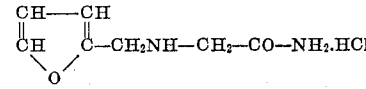
18 g of tetrahydrofurfuryl-senfol, 32 g of absolute alcohol and 16 g of thioglycolic acid were introduced into a 250 cc flask and placed on an oil bath at 110°C. After 1 hour, 2 cc of acetic anhydride were added and the heating was continued for 24 hours. A yellow solution was obtained which was concentrated under vacuum until the formation of a solid which was filtered on a buckner.

The yield was 10.7 g of dried product. The raw product was crystallized from 425 cc of ligroin and 9.4 g of pure product having a M.P. 88°–89°C was obtained.

	Centesimal analysis
Found:	C%=44.21; H%=5.03; N%=29.34; S%=6.40
Calculated:	C%=44.28; H%=N%=29.55; S%=6.46

Example 6

Acetamidofurfurylamine hydrochloride



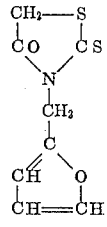
510 g of furfurylamine, 486.4 g of chloroacetamide and 1600 cc of absolute alcohol, were heated at 50°–50°C on a steam bath for 2 hours and then at reflux for 4 hours. The mixture was cooled and allowed to stand. A brown solid was separated and was filtered on a buckner. The solid was mashed with acetone several times until it became white; it was collected on a buckner and washed with ethyl ether. The flaky white product obtained was dried and gave a yield of 186 g M.P. 180.5° – 181.5°C.

Example 7

1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin In a refluxing flask placed in an oil bath at 100°C, 52.5 g of acetamido-furfurylamine hydrochloride, 100 cc of methyl alcohol and 39 g of -di-methylaminopropyl-senfol were introduced. A vivacious reaction occurred which was quenched by immerging the flask into a bath of water and ice. 200 cc more of methyl alcohol were added and to the dark resulting mixture 16.6 g of potassium hydroxide dissolved in 110 cc of water were added and the mixture was boiled for 3 hours, making sure once in a while that the pH remained alkaline. When the heat was termined, to the likewarm solution 137 cc of concentrated HCl were added in small portions. When the addition was terminated, the mixture was brought to ebullition again for 3 hours making sure that the pH remained acid; then it was allowed to stand overnight. A solid was separated and was eliminated by gravity filtering. The mixture was evaporated under vacuum until a solid remained. It was diluted with water, alkalized to pH = 9 with 20 percent sodium carbonate, extracted with ethyl ether and finally the ethereal soluion was dried. The mixture was heated with bone black and was evaporated. A dark oil remained, the yield of which was 59.5 g. The product, which was difficult to purify was immediately used for the dye synthesis.

Example 8

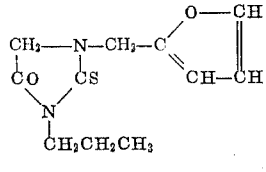
N-furfuryl-rodanine



The reaction was performed similarly to that one of Example 5. The amounts used were 40 g of furfuryl-senfol, 73 cc of ethyl alcohol, 4.5 cc of acetic anhydride and 36 g of thioglycolic acid. The obtained yield was 7.2 g of oil which was distilled under reduced pressure. B.P. 116°–120°C/1 mm Hg.

Example 9

1-furfuryl-3-propyl-thiohydantoin

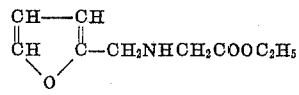


52.5 g of acetamido-furfurylamine hydrochloride, 300 cc of methyl alcohol, 27.8 g of propyl-senfol and 16.6 g of KOH dissolved in 110 cc of water, were mixed in a 1 l flask. The mixture was boiled for 3 hours then 137 cc of concentrated HCl were added after cooling the flask with water and ice. The mixture was then boiled for half an hour and then 200 cc of solvent were distilled off. The mixture was diluted with 200 cc of water and was extracted with ethyl ether, drying the ethereal solution with Na_2SO_4. After evaporation of the ether, 53 g of a dark yellow oil remained which was distilled under vacuum collecting the fraction distilled at 168°–170°C/1 mm Hg. The yield was 45.5 g of a slightly yellow oil.

	Centesimal analysis
Calculated:	C%=55.25; H%=5.90; N%=11.72; S%=13.42
Found:	C%=55.28; H%=6.05; N%=11.71; S%=13.20

Example 10

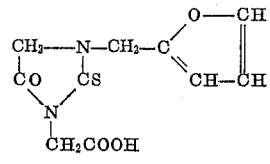
N-furfurylglycine ethyl ester



30 g of furfurylamine, together with 70 cc of absolute ethyl alcohol, were introduced in a flask and from a reflux 54 g of ethyl bromo-acetate were added. A dark solution was obtained and 32 g of triethylamina were added to it. A white solid separated. The mixture was brought to ebullition and was allowed to react for 15 hours while the solid went completely into solution. By cooling and standing a solid tri-ethylamine hydrobromide separated, which was separated from the solution by filtration on a buckner. To the solution was added more ethyl ether to complete the triethylamine hydrobromide precipitation. The ethereal solution was concentrated under reduced pressure and the remained dark oil was diluted under vacuum collecting the fraction having a B.P. 160°–170°C/2 mm Hg. The obtained yield was 33.6 g.

Example 11

1-furfuryl-3-carboxymethyl-2-thiohydantoin



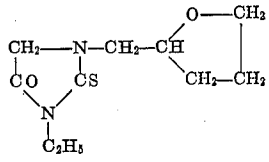
21 g of N-furfuryl-glycine-ethyl ester and 16 g of carboetoxymethyl-senfol were reacted for 15 minutes by bringing the mixture by boiling and the reacted mixture was poured into water (250 cc). The separated oil was extracted with ether and, after drying with anhydrous sodium sulfate, the ethereal solution was evaporated to dryness. The residual yellow oily liquid gave a yield of 33.4 g and the product turned out to be 1-furfuryl-3-carboethoxymethyl-2-thiohydantoin. 33.4 g

of this product were boiled for 10 minutes with 82 cc of a 10 percent sodium hydroxide. The dark yellow solution obtained was cooled and acidified with HCl. Then it was extracted with ether, the ethereal solution was dried with anhydrous sodium sulfate and then was evaporated under vacuum. The residual yellow oil by standing a few days in the dessiccator, solidified and was crystallized from ethyl alcohol. Yield 23 g M.P. 125°–126°C.

	Centesimal analysis
Calculated:	C% = 47.24; H% = 3.94; N% = 11.02
Found:	C% = 47.36; H% = 4.09; N% = 10.79

Example 12

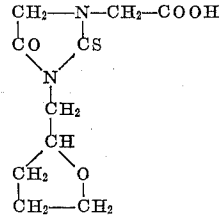
1-tetrahydrofurfuryl-3-ethyl-2thiohydantoin



9.8 g of N-tetrahydrofurfuryl-glycine-ethyl ether (Example 11) and 4.45 g of ethylsenfol were heated at 150°C for 36 hours. The obtained dense liquid was distilled under vacuum and a yellow oil having a B.P. 168°–172°C/12 mm Hg was obtained. The yield was 7.1 g.

Example 13

1-carboxymethyl-3-tetrahydrofurfuryl-2-thiohydantoin

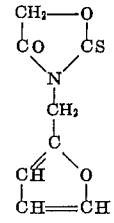


37.6 g of ethyl iminodiacetate were introduced into a flask. Then from a dropper, with caution, 28.5 g of tetrahydrofurfurylsenfol were introduced. The mixture was boiled for 10 minutes and then was poured into a beaker containing 200 cc of cold water; an oil was obtained and was extracted with ethyl ether. The ethereal solution was treated with bone black, dried with anhydrous sodium sulfate, filtered and evaporated to dryness. 55.4 g of 1-carboethoxy-methyl-3-tetrahydrofurfuryl-2-thiohydantoin were obtained and were dissolved in 186 cc of 10 percent sodium hydroxide by boiling for 5 minutes. The solution was poured into a beaker containing 200 cc of water and while cooling in a bath of water and ice was acidified with concentrated HCl and was extracted with ethyl ether. The ethereal solution dried with anhydrous sodium sulfate was evaporated obtaining an oil which solidified after some days. The product was used as such for the synthesis of the dyes.

Example 14

N-furfuryl-2-thio-oxazolidone

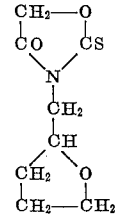
26.1 g of furfuryl-amine and a solution consisting of 21.19 g of potassium hydroxyde dissolved in 81.8 cc of water were mixed in a keller. Under fast stirring 57 g of acetamido-carbodithioloneglycolic acid (prepared according to what has been reported in J. Prakt. Chem./2/99 (1919) p. 45 and following), were added in small portions. The mixture was allowed to stand overnight, was diluted with 271 cc of water and was stirred again for 2 hours then was acidified with HCl. A separated oil was extracted with ethyl and the ethereal solution was dried with anhydrous sodium sulfate. The solution was filtered by gravity and the solvent was evaporated. A yellow oil remained giving a yield of 63 g. It was distilled under reduced pressure and the fraction distilled at 168°–170°C /1mm Hg was collected; its weight totaled 38.6 g. after a little while it solidified in a crystalline mass which was crystallized from ethyl alcohol. 26.5 g of shining white scales were obtained, having M.P. = 68.5°–69°C. The compound was found to comply with the formula:



	Centesimal analysis
Calculated:	C% = 48.77; H% = 3.58; N% = 7.11
Found:	C% = 48.74; H% = 3.76; N% = 7.12

Example 15:

N-tetrahydrofurfuryl-2-thio-oxazolidone.



It was prepared analogously to Example 14, by using 27.1 g of tetrahydrofurfuryl-amine, 21.19 g of potassium hydroxide, 81.8 cc of water and 37.5 g of acetamido-carbodithiolone-glycolic acid. By evaporation of the ethereal solution 37 g of reddish oil were obtained; the oil was distilled under vacuum and the fraction distilled at 180°–182°C/ 1 mm Hg was collected. The yield was 20.15 g.

	Centesimal analysis
Calculated:	C%=48.77; H%=3.56; N%=7.07; S%=16.19
Found:	C%=48.50; H%=3.76; N%=6.82; S%=16.15

Example 16

5-acetanilido-methylene-3-furfuryl-2-thio-oxazolidone.

9.85 g of N-furfuryl-2-thio-oxazolidone, 9.80 g of diphenyl-formamidine and 3 cc of kerosene were reacted for 2 and a half hours at 120°C. An oil separated and solidified after standing overnight. The yield of the pure product, having M.P. 165°–167°C was 5.7 g. 4.7 g of this product (5-anilino-methylene-3-furfuryl-2-thio-oxazolidone) were refluxed with 15 cc of acetic anhydride and 3 cc of trimethylamine for an hour. The solution was poured into a beaker containing 250 cc of water. The obtained solidified oil was crystallized from ethyl alcohol. A yield of 4 g of yellow needless having M.P. 137°–138°C was obtained.

Example 17

5-acetanilido-methylene-3-tetrahydrofurfuryl-2-thio-oxazolidone

It was prepared analogously to the intermediate **16**, using the N-tetrahydrofurfuryl-2-thio-oxazolidone instead of the N-furfuryl-2-thio-oxazolidone. At the end of the operation, 3,5 g of crystallized product having M.P. 174°–175°C were obtained.

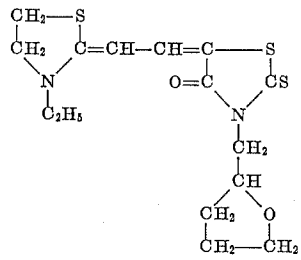
Example 18

5-acetanilido-methylene-1-furfuryl-3-propyl-2-thio-hydantoin

The reaction was analogous to that of Example 16.15 g of 1-furfuryl-3-propyl-2-thiohydantoin, 12.3 g of diphenyl-formamidine and 45 cc of kerosene were used. The 5-anilino-methylene-1-furfuryl-3-propyl-2-thiohydantoin obtained (8.5 g - M.P. 124°–5°C) was boiled with acetic anydride and triethylamine. The yield of the crystallized product was 3.5 g, M.P. 167°–9°C.

Example 19

5-(3-ethyl-thioazolidine-2-ylidene-ethylidene)-3-tetrahydrofurfuryl-rodanine



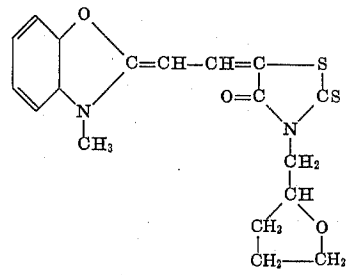
1,39 g of tetrahydro-furfuryl-rodanine, 2 g of 2-(ω-acetanilido-vinyl)thioazoline-iodo-ethylate, 15 cc of ethyl alcohol and 1 cc of triethylamine, were boiled for 20 minutes obtaining an orange solution. The solution was cooled and precipitated with water. A fluid pitch separated and it hardened after standing. It was boiled twice with water and crystallized from ethyl alcohol. Shining violaceous scales were obtained having M.P. 148°C.

(λ max of absorption is ethanol: 485 nm)

Centesimal analysis	
Calculated	C%=50.60; H%=5.66; N%=7.87; S%=27.02
Found:	C%=50.87; H%=5.74; N%=7.50; S%=26.62

Example 20

5-(3-methyl-benzoxaline-2-ylidene-ethylene-)-3-tetrahydrofurfuryl-rodanine



2.78 g of N-tetrahydrofurfuryl-rodanine, 4.2 g of 2-(ω-acetanilidovinyl)benzoxazole-iodo-methylate, 30 cc of ethylic alcohol and 3 cc of triethylamine, were boiled for 20 minutes, obtaining an orange solution. By cooling it separated the dye which was crystallized from a mixture of pyridine and ethyl alcohol in the ratio 2:1.

Red shining crystals having M.P. 212-215°C were obtained.

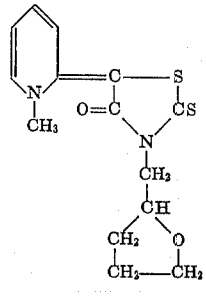
(λ max of absorption in ethanol: 493 nm)

Centesimal analysis	
Calculated:	C%=57.80; H%=4.85; N=7.49; S=17.15
Found:	C%=57.76; H%=5.03; N%=7.38; S%=17.10

Example 21

5-(1:2-dihydro-1-methyl-pyridine-2-ylidene)-3-tetrahydrofurfuryl-rodanine.

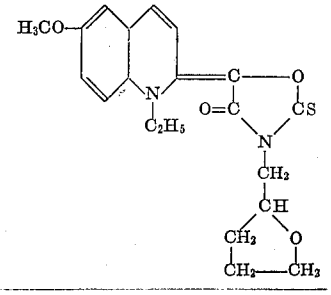
1.2 g of N-methyl-2-thyo-pyridone were salified with 1.5 cc of diethyl-sulfate and by heating at 120°C for 10 minutes the resulting product was made to react with 2.14 g of N-(tetrahydro-furfuryl-rodanine, 10 cc of ethyl alcohol and 1.5 cc of triethylamine boiling the whole mixture for 10 minutes. By cooling it separated the dye which was filtered, washed with ethyl alcohol and ethyl ether, boiled with water and crystallized from ethyl alcohol. Orange crystals having M.P. 139.5°–141.5°C were obtained. The obtained dye corresponded to the formula:



(λ max of absorption in ethanol: 456 nm)

Example 22

5-(1:2-dihydro-1-methyl-6-metoxiquinoline-2-ylidene)-3-tetrahydro-furfuryl-2-thio-oxazolidone

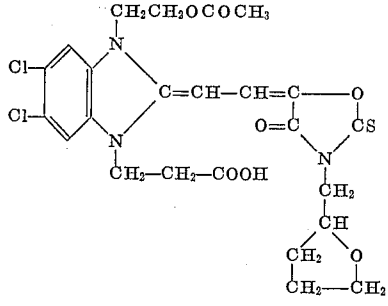


2 g of N-tetrahydrofurfuryl-2-thio-oxazolidone, 3.28 g of 2-ethylmercapto-6-methoxyquinoline-bromo-ethylate, 25 cc of ethyl alcohol, 0.5 cc of triethylamine, were boiled for 15 minutes. The orange dye separated out in the hot and was filtered and washed with ethyl alcohol and ethyl ether. The product was boiled with water and crystallized from ethyl alcohol and needle-like crystals having golden reflexes were obtained. The yield was 1.7 g, the M.P. 194°–5°C.
(λ max of absorption in ethanol: 458–486 nm):

	Centesimal analysis
Calculated:	C% = 62.09; H% = 5.95; N% = 7.24
Found:	C% = 61.96; H% = 5.91; N% = 7.10

Example 23

5-(1-β-acetoxyethyl-3-carboxyethyl-5.6-dichloro-benzimidazoline-2-ylidene-ethylidene)-3-tetrahydrofurfuryl-2-thio-oxazolidone

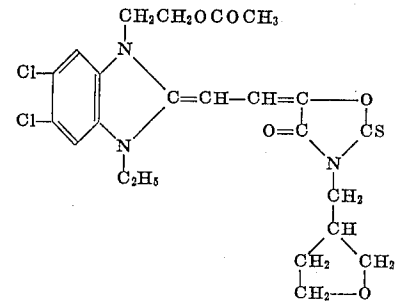


0.86 g of 5-acetanilido-methylene-3-tetrahydrofurfuryl-2-thioxazolidone, 1.1 g of 1-β-acetoxy-ethyl-2-methyl-5.6-dichlorobenzimidazole-3-carboxyethyl bromide, 30 cc of butyl alcohol and 3 cc of triethylamine were boiled for 2 hours. The mixture was concentrated under vacuum and was boiled in water; finally it was crystallized from ethyl alcohol. Red microcrystals having M.P. 209°–210°C were obtained.

(λ max of absorption in ethanol = 498 nm)

Example 24

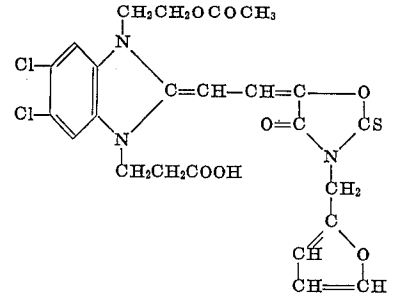
5-(1-β-acetoxyethyl-3-ethyl-5.6-dichloro-benzimidazoline-2-ylideneethyldene)-3-tetrahydrofurfuryl-2-thio-oxazolidone



0.86 g of 5-acetanilido-methylene-3-tetrahydrofurfuryl-2-thiooxazolidone, 1.1 g of 1-β-acetoxyethyl-2-methyl-5.6-dichlorobenzimidazole-iodo-ethylate, 30 cc of butyl alcohol and 3 cc of trimethylamine were boiled for 2 hours. The mixture was concentrated under vacuum. The solid product separated was boiled with water, crystallized from ethyl alcohol and allowed to stand at room temperature. Violet crystals M.P. 180°–181°C were obtained.
(λ max of absorption in ethanol: 497 nm).

Example 25

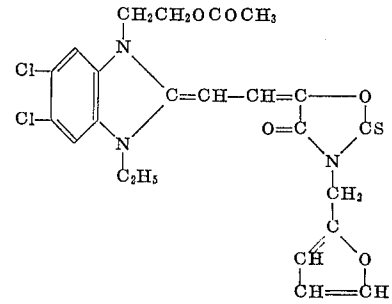
5-[-β-acetoxyethyl-3-carboxyethyl-5.6dichloro-benzimidazoline-2-ylidene]-3-furfuryl-2-thio-oxazolidone



0.8 g of 5-acetanilido-methylene-3-furfuryl-2-thio-oxazolidone, 1.1 g of 1-(β-acetoxyethyl)2-methyl-5.6-dichloro-benzimidazole-3-carboxyethyl bromide, 15 cc of butyl alcohol, 1.5 cc of triethylamine were boiled for 20 minutes. The mixture was poured into water and the precipitate formed was filtered and crystallized from ethyl alcohol. An orange amorphus product having M.P. 284°-5°C was obtained.
(λ max of absorption in ethanol: 498 nm)

Example 26

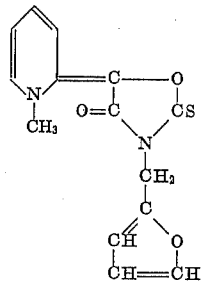
5-[(1-β-acetoxyethyl)-3-ethyl-5.6-dichloro-benzimidazoline-2-ylidene-ethylene]-3-furfuryl-2-thio-oxazolidone.



0.8 g of 5-acetanilidomethylen-3-furfuryl-2-thio-oxazolidone, 1.1 g of 1-β-acetoxyethyl-2-methyl-5.6-dichlorobenzimidazoleiodo-ethylate, 15 cc of butyl alcohol and 1.5 cc of triethylamine were boiled for 30 minutes. The mixture was poured into water and the precipitate thus obtained was filtered and crystallized from N,N-dimethyl-formamide. Red-brick crystals having M.P. 174°–5°C were obtained.
(λ max of absorption in ethanol: 497 nm)

Example 27

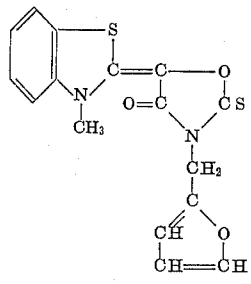
5-(1-2-dihydro-1-methyl-pyridin-2-ylidene)-3-furfuryl-2-thiooxazolidone



1.97 g of N-furfuryl-2-thio-oxazolidone, 2.67 g of 2-methylmercapto-pyridine-iodoethylate, 25 cc of ethyl alcohol, 2.5 cc of triethylamine were boiled for 15 minutes. By cooling the orange solution thus obtained, the raw dye separated out; the dye was crystallized from ethyl alcohol. Yellow needles were obtained.
(λ max of absorption in ethanol: 430 nm).

Example 28

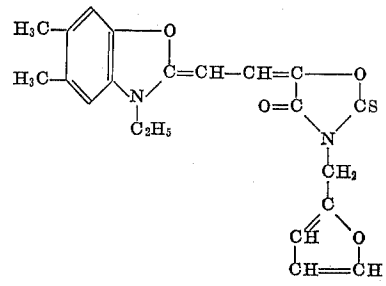
5-(3-methyl-benzothiazoline-2-ylidene)-3-furfuryl-2-thiooxazolidone



0.98 g of N-furfuryl-2-thio-oxazolidone, 1.61 g of 2-methylmercapto-benzothiazole-iodo-methylate, 20 cc of ethyl alcohol, 2 cc of triethylamine were boiled for 5 minutes. The dye separated immediately and was crystallized from N,N-dimethyl-formamide. Yellow needles having a M.P. 280°–1°C were obtained.
(λ max of absorption: 405 nm).

Example 29

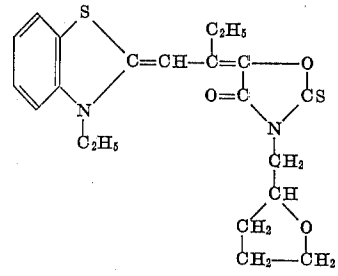
5-(3-ethyl-5,6-dimethyl-benzoxazoline-2-ylidene-ethylene)-2-thio-3-furfuryl oxazolidone



0.98 g of 3-furfuryl-2-thio-oxazolidone, 2.23 g of 2-(ω-acetanilidovinyl)-5,6-dimethyl-benzothiazole-iodo-ethylate, 10 cc of ethyl alcohol and 1 cc of triethylamine were boiled for 30 minutes. The mixture was filtered and the product was crystallized from pyridine. An orange amorphous product having M.P. 276°-7°C was obtained.
(λ max of absorption in ethanol: 472 nm).

Example 30

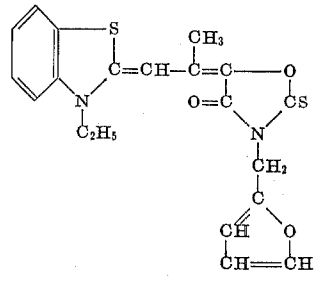
5(3-ethyl-benzothiazoline-2-ylidene-isobutilidene-3-tetrahydrofurfuryl-2-thio-oxazolidone



0.4 g of N-tetrahydrofurfuryl-2-thio-oxazolidone, 0.8 g of 2-(2'-ethylmercapto-3-butenyl)-benzothiazole-iodo-ethylate, 8 cc of ethyl alcohol, 0.8 cc of triethylamine were boiled for 10 minutes. The mixture was cooled and diluted with acidified water. A dark pitchy material with violaceus reflexes separated out. It was crystallized from ethyl alcohol and red violaceus crystals having M.P. 134°–135°C were obtained.
(λ max of absorption in ethanol: 502 nm).

Example 31

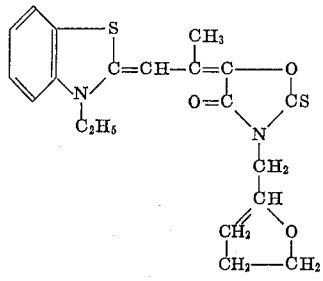
5-(3-ethyl-benzothiazoline-2-ylidene-isopropylidene)-3-furfuryl-2-thio-oxazolidone



0.4 g of N-furfuryl-2-thio-oxazolidone, 0.87 g of 2-(2-ethylmercapto-propenyl)-benzothiazole-ethylparatoluenesulfonate, 8 cc of ethyl alcohol, 0.8 cc of triethylamine were boiled for 5 minutes. The dye separated out and was crystallized from pyridine. Red violet crystals having M.P. 224°–5°C were obtained.
(λ max of absorption in ethanol: 497 nm).

Example 32

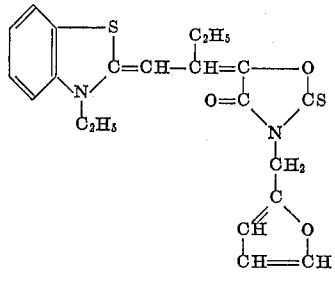
5-(3-ethyl-benzothiazoline-2-ylidene-isopropylidene)-3-tetrahydrofurfuryl-2-thio-oxazolidone



0.8 g of N-tetrahydrofurfuryl-2-thio-oxazolidone, 0.94 g of 2-(2'-ethyl-mercapto-propenyl)-benzothiazole ethyl-p-toluensulfonate, 8 cc of ethyl alcohol, 0.8 cc of triethylamine, were boiled for 10 minutes. the dye separated out and was crystallized from a mixture of pyridine and ethyl alcohol 1:1. Red mycrocrystals of the dye having M.P. 197°–9°C were obtained.
(λ max of absorption in ethanol: 499 nm).

Example 33

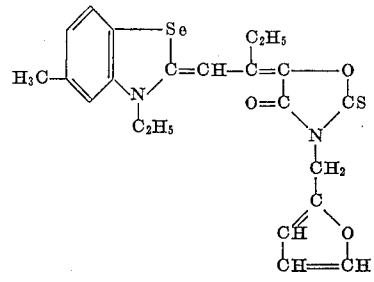
5-(3-ethyl-benzothiazoline-2-ylidene-isobutylidene)-3-furfuryl-2-thio-oxazolidone



0.4 g of N-furfuryl-2-thio-oxazolidone, 0.8 g of 2-(2'-ethylmercapto-butenyl)-benzothiazole-iodoethylate, 8 cc of ethyl alcohol and 0.8 cc of triethylamine, were boiled for 5 minutes. By standing the dye separated out and was crystallized from ethyl alcohol. Purplish pink crystals of the dye, having M.P. 167°–9°C were obtained.
(λ max of absorption in ethanol: 500 nm)

Example 34

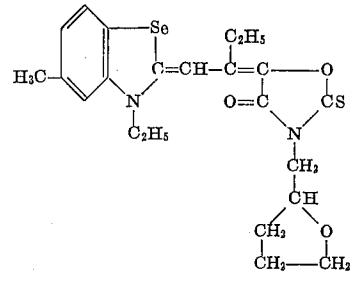
5-(3-ethyl-5-methyl-benzoselenazoline-2-ylidene-isobutylidene)-3-furfuryl-2-thio-oxazolidone



0.59 g of N-furfuryl-2-thio-oxazolidone, 0.93 g of 2-(2'-ethylmercapto-3-butenyl)-5-methyl-benzoselenazole ethyl p. toluensulfonate, 8 cc of ethyl alcohol and 0.8 cc of triethylamine were boiled for 15 minutes. By cooling the dye separated out and was crystallized from a large amount of ethyl alcohol. An orange amorphous product was obtained having M.P. 183.5°–184.5°C
(λ max of absorption in ethanol: 507 nm)

Example 35

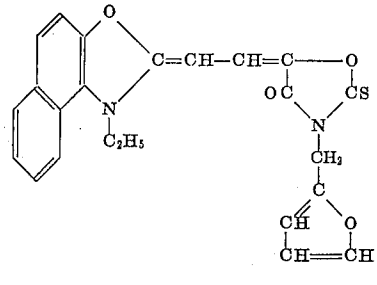
5-(3-ethyl-5-methyl-benzoselenazoline-2-ylidene-isobutylidene)-3-tetrahydrofurfuryl-2-thio-oxazolidone



0.6 g of N-tetrahydrofurfuryl-2-thio-oxazolidone, 1.5 g of 2-(2'-ethylmercapto-3-butenyl)-5-methylbenzoselenazole ethyl p-toluenesulfonate, 8 cc of ethyl alcohol, 0.8 cc of triethylamine, were boiled for 10 minutes. The mixture was precipitated with water. The dye was separated and crystallized from ethyl alcohol. Orange crystals having M.P. 215°–7°C were obtained.
(λ max of absorption in ethanol: 506 nm).

Example 36

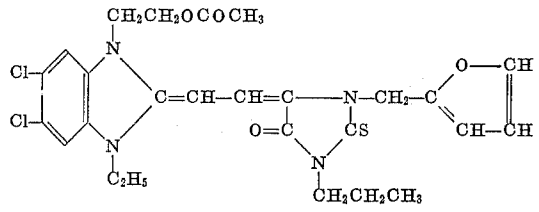
5-(3-ethyl-naphtho-1',2'-4,5-oxazoline-2-ylidene-ethylidene)-3-furfuryl-2-thiooxazolidone



1.97 g of N-furfuryl-2-thio-oxazolidone, 4.84 g of 2-(ω-acetanilidovinyl)-β-naphthooxazole-iodo-ethylate, 40 cc of ethyl alcohol and 4 cc of triethylamine, were boiled for 10 minutes. The orange dye separated in the hot. It was filtered and crystallized from pyridine. Red orange crystals having M.P. 285°–6°C;
(λ max of absorption in ethanol: 486 nm)

Example 37

5-(1-β-acetoxyethyl-3-ethyl-5,6-dichloro-benzimidazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thio-hydantoin

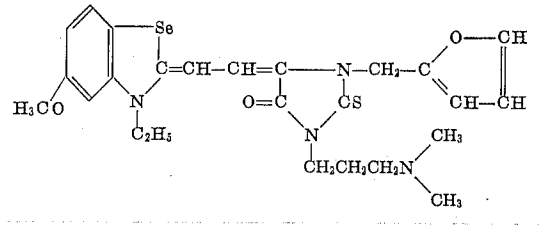


3.83 g of 5-acetanilido-methylene-3-propyl-2-thiodantoin, 4.42 g of 1-β-acetoxyethyl-2-methyl-5,6-dichloro-benzimidazoleiodo-ethylate, 30 cc of N,N-dimethylformamide and 3 cc of triethylamine were reacted for 30 minutes at 150°C. The hot mixture was poured into hot water then decanted and the washing was repeated several times. The product was dissolved in boiling ethyl alcohol and was allowed to stand. The obtained dye weighed 2.3 g and had a M.P. 173°–5°C (Purplish pink crystals).
(λ max of absorption in ethanol: 522 nm)

Centesimal analysis	
Calculated:	C%=55.46;H%=5.01;N%=9.95;Cl%=12.60;S%=5.70
Found:	C%=55.18;H%=5.04;N%=9.80;Cl%=12.75;S%=5.61

Example 38

5-(3-ethyl-5-methoxy-benzoselenazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin

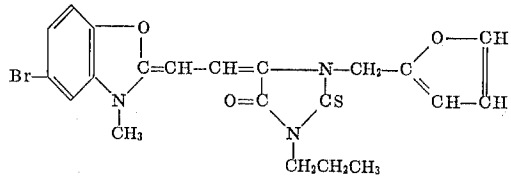


5.62 g of 1-(furfuryl)-3(γ-dimethylaminopropyl)-2thiohydantoin, 5.06 g of 2 (ω-aldehydomethylene)-3-ethyl-5-methoxy-benzoselenazolidene, 20 cc of pyridine, 2 cc of acetic anhydride were boiled for 15 minutes. By standing overnight the dye separated out; it was filtered and crystallized from pyridine. Purplish red crystal of dye having M.P. 194°–5°C were obtained.
(λ max of absorption in ethanol: 528 nm)

Centesimal analysis	
Calculated:	C%=55.14;H%=5.60;N=10.28;S%=5.88;Se%=14.49
Found:	C%=55.09;H%=5.77;N%=10.20;S%=6.31;Se%=14.36

Example 39

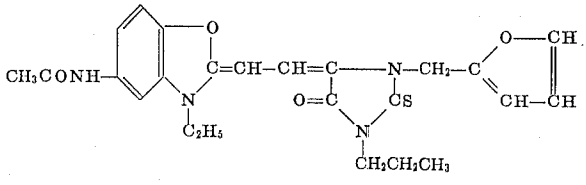
5-(3-methyl-5-bromo-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thio-hydantoin



2.39 g of 1-furfuryl-3-propyl-2-tiohydantoin, 4.83 g of 2-(ω-acetanilidevinyl)-5-bromo-benzoxazole-iodo-methylate, 30 cc of ethyl alcohol and 3 cc of triethyl-amine were boiled for 10 minutes. The dye separated by cooling and was crystallized from pyridine. Red orange crystals having M.P. 254°–5°C were obtained.
(λ max of absorption in ethanol: 479 nm)

Example 40

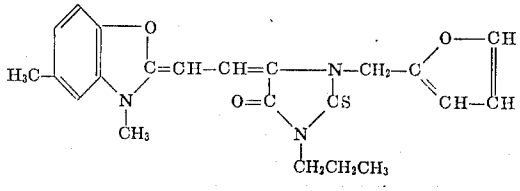
5-(3-ethyl-5-acetylamino-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 4.1 g of 2-(ω-acetanilidovinyl)-3-ethyl-5-acetylamino-benzoxazole-iodo-ethylate, 20 cc of butyl alcohol and 4 cc of piperidine were boiled 20 minutes. The dye separated by standing was filtered and crystallized from ethyl alcohol.
(λ max of absorption in ethanol: 488 nm)

Example 41

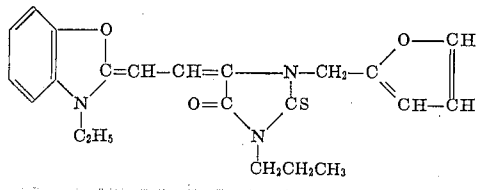
5-(3,5-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thyo-hydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 4.3 g of 2-(ω-acetanilido-vinyl)-5-methyl-benzoxazole-iodo-methylate, 20 cc of butyl alcohol and 4 cc of piperidine were boiled for 20 minutes; the dye separated by standing and was filtered, washed with hot water and crystallized from pyridine. Red crystals of the dye having M.P. 235°–7°C were obtained.
(λ max of absorption in ethanol: 487 nm)

Example 42

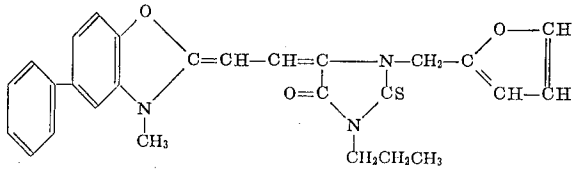
5-(3-ethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 4.3 of 2-(ω-acetanilidovinyl)-benzoxazole-iodo-ethylate, 60 cc of butyl alcohol, 5 cc of piperidine, were boiled for 15 minutes. The dye separated by standing was crystallized from pyridine. Ocre crystals having M.P. 186.5°–187°C were obtained.
(λ max of absorption in ethanol: 481 nm).

Example 43

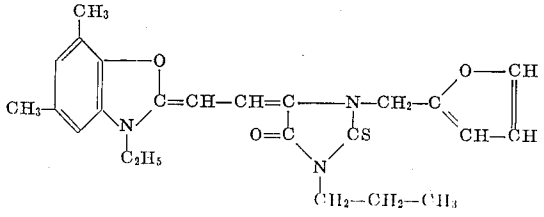
5-(3-methyl-5-phenyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 4.96 g of 2-(ω-acetanilidovinyl)-5-phenyl-benzoxazole-iodo-methylate, 80 cc of butyl alcohol, 8 cc of piperidine were boiled for 1 hour. The dye separated by cooling and was crystallized from piperidine. A light brown amorphous product having M.P. 262°–4° C was obtained.
(λ max absorption in ethanol: 485 nm)

Example 44

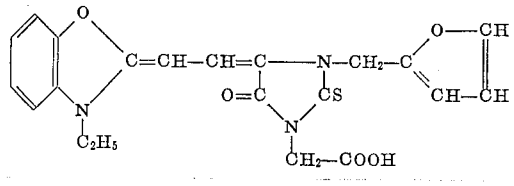
5-(3-ethyl-5,7-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 4.62 g of 2-(λ-acetanilidovinyl)-5,7-dimethylbenzoxazole-iodo-ethylate, 20 cc of butyl alcohol and 4 cc of piperidine were boiled for 20 minutes. The dye separated by cooling and was crystallized from pyridine. Red orange crystals of the dye having M.P. 197°–9°C were obtained.
(λ max of absorption in ethanol: 492 nm)

Example 45

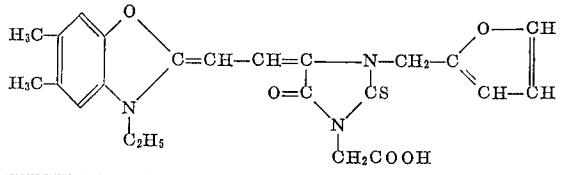
5-(3-ethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-carboxymethyl-2-thiohydantoin



0.508 g of 1-furfuryl-3-carboxymethyl-2-thiohydantoin, 0.868 g of 2-(ω-acetanilidovinyl)-benzoxazole-iodo-ethylate, 7 cc of pyridine and 1 cc of triethylamine were boiled for 10 minutes. After cooling water was added and the mixture was acidified with acetic acid. The dye separated out and was crystallized from pyridine acidified with acetic acid. Dark orange crystals having M.P. 263°–4°C were obtained.
(λ max of absorption in ethanol: 479 nm).

Example 46

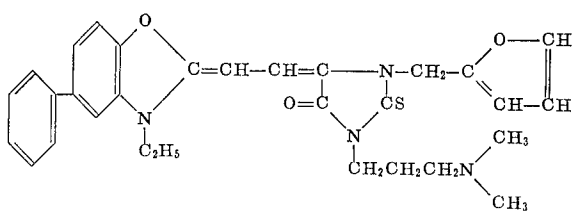
5-(3-ethyl-5,6-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-carboxymethyl-2-thiohydantoin



0.508 g of 1-furfuryl-3-carboxymethyl-2-thiohydantoin, 0.892 g of 2-(λ-acetanilidovinyl)-5,6-dimethyl-benzoxazole-iodo-ethylate, 7 cc of pyridine and 1 cc of trimethylamine were boiled for 10 minutes. After cooling water was added and the mixture was slightly acidified with acetic acid. Purple pink crystals of the dye having M.P. 258°–260°C. were obtained
(λ max of absorption in ethanol: 490 nm).

Example 47

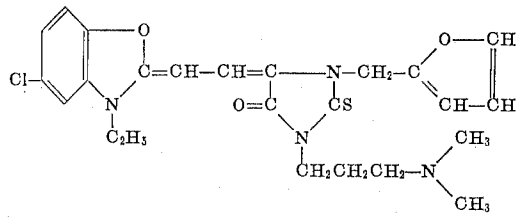
5-(3-ethyl-5-phenyl-benzoxazoline-2-ylidene-ethylidene-1-furfuryl-3(γ-dimethylamino-propyl)-2-thiohydantoin



1.4 g of 1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin, 2.55 g of 2-(ω-acetanilidovinyl)-5-phenyl-benzoxazole-iodoethylate, 5 cc of ethyl alcohol and 1.5 cc of piperidine were boiled for 10 minutes. The dye separated out and was crystallized from pyridine. Red orange crystals of dye having M.P. 225°–7°C were obtained.
(λ max of absorption in ethanol: 490 nm)

Example 48

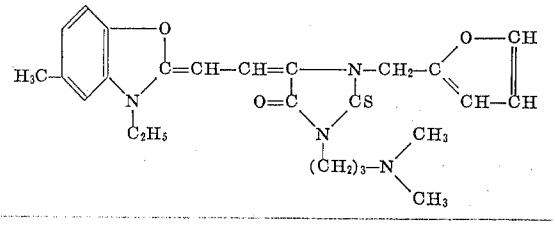
5-(3-ethyl-5-chloro-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



1.4 g of 1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin, 2.34 g of 2-(ω-acetanilidovinyl)-5-chloro-benzoxazole-iodoethylate, 4 cc of pyridine and 0.5 cc of triethylamine were boiled by 10 minutes. The dye separated by cooling and was crystallized from pyridine. An orange amorphous product having M.P. 210°–2°C was obtained.
(λ max of absorption in ethanol: 480 nm).

Example 49

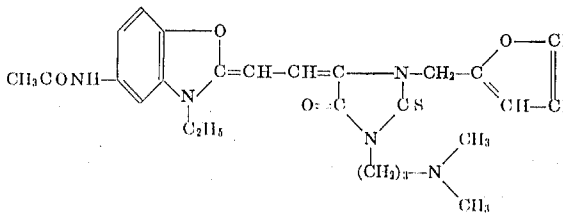
5-(3-ethyl-5-methyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



The compound was prepared analogously to Example 48 using the 5-methyl derivative of the benzoxazole instead of the 5-chloro derivative. Red orange crystals. M.P. 192°–4°C.
(λ max of absorption in ethanol: 488 nm)

Example 50

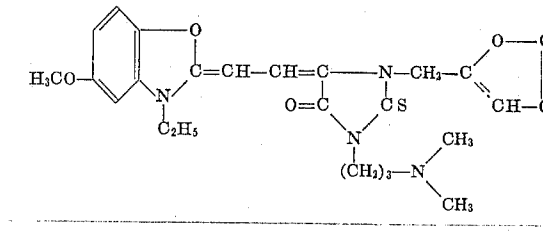
5-(3-ethyl-5-acetylamino-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



The compound was prepared analogously to Example 48 using the 5-acetylamino derivative of the benzoxazole instead of the 5-chloro derivative. Violet crystals. M.P. 151°–2°C.
(λ max of absorption in ethanol: 494 nm)

Example 51

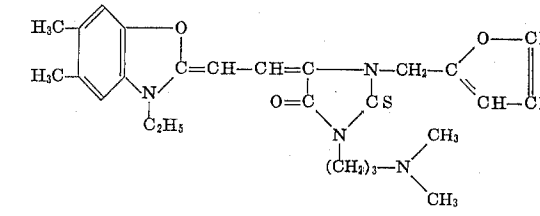
5-(3-ethyl-5-metoxy-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



The compound was prepared analogously to Example 48, using the 5-methoxy derivative of the benzoxazole instead of the 5-chloro derivative. Orange amorphous product. M.P. 227°–8°C.
(γ max of absorption in ethanol: 491 nm)

Example 52

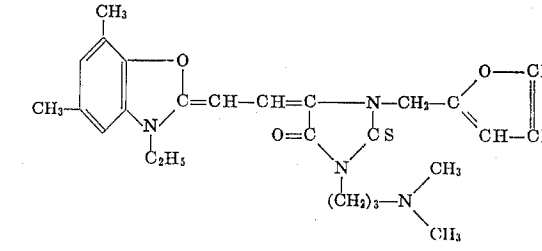
5-(3-ethyl-5,6-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thioydantoin



The compound was prepared analogously to Example 48, using the 5,6-dimethyl derivative instead of the 5-chloro derivative.
(λ max of absorption in ethanol: 493 nm)

Example 53

5-(3-ethyl-5,7-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thioydantoin

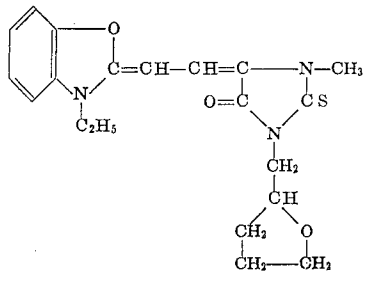


The compound was prepared according to what reported for

Example 48, using the 5,7-dimethyl derivative of the benzoxazole instead of the 5-chloro derivative. M.P. 221°–3°C. Red brick amorphous product.
(λ max of absorption in ethanol: 489 nm)

Example 54

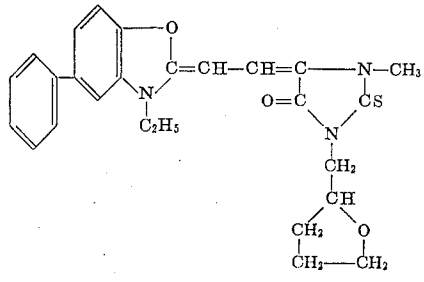
5-(3-ethyl-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



0.53 g of 1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin, 1.02 g of 2-(ω-acetanilidovinyl-benzoxazole-iodo-ethylate, 7 cc of ethyl alcohol and 1 cc of triethylamine were boiled for 10 minutes. The dye separated by cooling and was crystallized from pyridine. Red orange crystals of dye, having M.P. 215°–7°C were obtained.
(λ max of absorption in ethanol: 480 nm)

Example 55

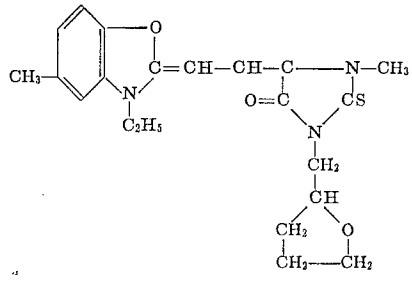
5-(3-ethyl-5-phenyl-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was obtained analogously to Example 54, using the 5-phenyl derivative of the benzoxazole. M.P. 218°–9°C. Purple pink crystals.
(λ max of absorption in ethanol: 486 nm)

Example 56

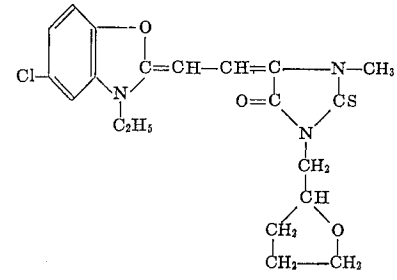
5-(3-ethyl-5-methyl-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was obtained analogously to Example 54, using the 5-methyl derivative of the benzoxazole. The product was orange and amorphous with M.P. 240°–1°C.
(λ max of absorption in ethanol: 484 nm)

Example 57

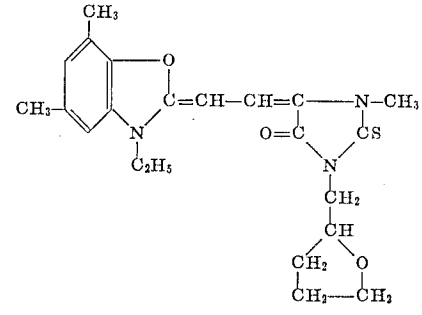
5-(3-ethyl-5-chloro-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was obtained analogously to Example 54 using the 5-chloro derivative of the benzoxazole. The product was orange and amorphous, with M.P. 250.5°–251.5°C.
(λ max of absorption in ethanol: 478 nm)

Example 58

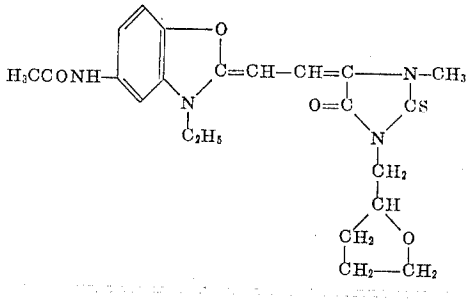
5-(3-ethyl-5,7-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was prepared analogously to Example 54 using the 5,7-dimethyl derivative of the benzoxazole; the product was in orange crystals with M.P. 239.5°–240°C.
(λ max of absorption in ethanol: 492 nm)

Example 59

5-(3-ethyl-5-acetylamino-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin

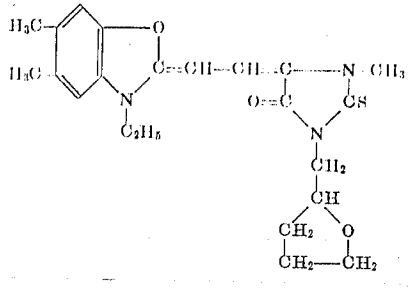


The compound was prepared analogously to Example 54, using the 5-acetylamino derivative of the benzoxazole, in red orange microcrystals having M.P. 280°–1°C.

(λ max of absorption in ethanol: 487 nm).

Example 60

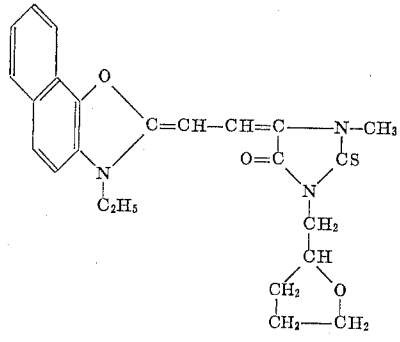
5-(3-ethyl-5,6-dimethyl-benzoxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was prepared analogously to Example 54, using the 5,6-dimethyl derivative of the benzoxazole. An orange amorphous product having M.P. 259°–261°C was obtained.
(λ max of absorption in ethanol: 495 nm).

Example 61

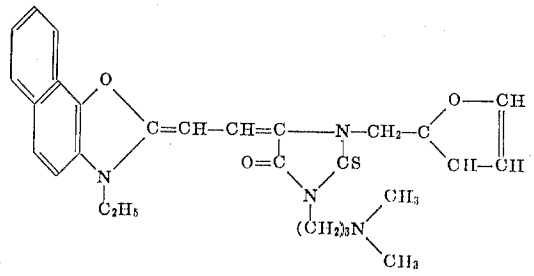
5-(3-ethyl-naphtho-2',1'-4,5-oxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was prepared analogously to Example 54, using the naphto-2',1'-4,5-oxazole derivative. M.P. 270°–3°272°C. Dark red crystals.
(λ max of absorption in ethanol: 496 nm).

Example 62

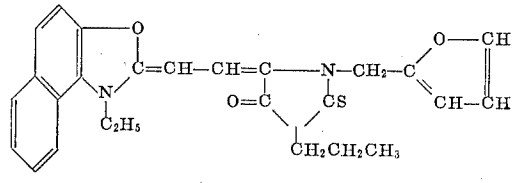
5-(3-ethyl-naphtho-2',1'-4,5-oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



1.4 g of 1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin, 2.42 g of 2-(ω-acetanilidovinyl)-napththo-2',1'-4,5-oxazole-iodo-ethylate, 8 cc of ethyl alcohol, 2 cc of piperidine were boiled for 20 minutes. Water was added to the reaction mixture and the latter was allowed to stand. The dye separated out was filtered and crystallized from pyridine. Red crystals of the dye having a M.P. 195–7°C were obtained. (λ max of absorption in ethanol: 505 nm).

Example 63

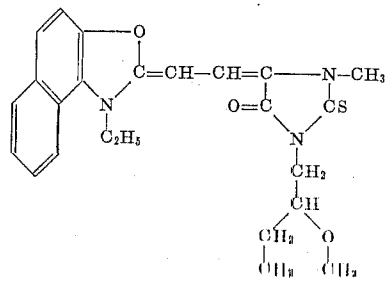
5-(3-ethyl-naphtho-1',2'-4,5 oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



0.239 g of 1-furfuryl-3-propyl-2-thiohydantoin, 0.48 g of 2-(ω-acetanilidovinyl)-naphtho-1',2'-4,5-oxazole-iodo-ethylate, 4 cc of ethyl alcohol, 0.4 cc of triethylamine were boiled for 1 minute. The dye separated immediately and was crystallized from pyridine. An orange amorphous product having M.P. 242°–4°C was obtained.
(λ max of absorption in ethanol: 504 nm).

Example 64

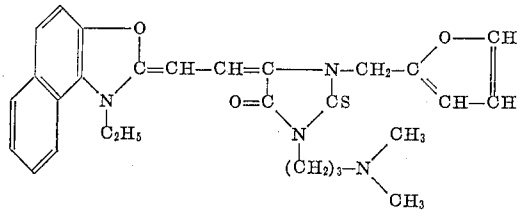
5-(3-ethyl-naphtho-1',2'-4,5-oxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



The compound was prepared analogously to Example 54 using the naphtho-1',2'-4,5-oxazole.
(λ max of absorption in ethanol: 502 nm).

Example 65

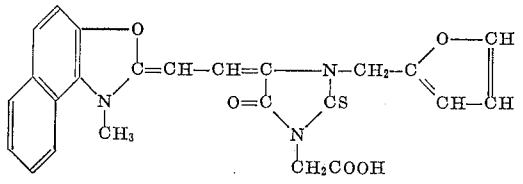
5-(3-ethyl-naphtho-1',2'-4,5-oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



1.4 g of 1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin, 2.42 g of 2-(ω-acetanilidovinyl)-naphtho-1',2'-4,5-oxazoleiodo-ethylate, 5 cc of pyridine, 1 cc of triethylamine were boiled 20 minutes. A crystalline solid separated out and was crystallized from pyridine.
(λ max of absorption in ethanol: 504 nm)

Example 66

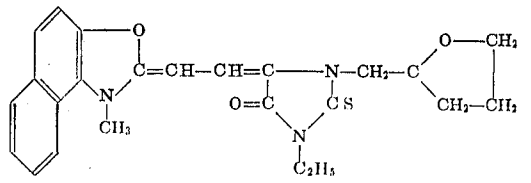
5-(3-methyl-naphtho-1',2'-4,5-oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-carboxymethyl-2-thiohydantoin



0.508 g of 1-furfuryl-3-carboxymethyl-2-thiohydantoin, 0.968 g of 2-(ω-acetanilidovinyl)-naphtho-1',2'-4,5-oxazole-iodoethylate, 7 cc of pyridine and 1 cc of triethylamine were boiled for 10 minutes. By addition of water and of acetic acid the dye separated out and was purified by hot-dissolving in pyridine and acidification with acetic acid. The dye obtained presented a M.P. 259°–61°C.
(λ max of absorption in ethanol: 500 nm).

Example 67

5-(3-methylnaphtho-1',2'-4,5-oxazoline-2-ylidene-ethylidene)-1-tetrahydrofurfuryl-3-ethyl -2-thiohydantoin

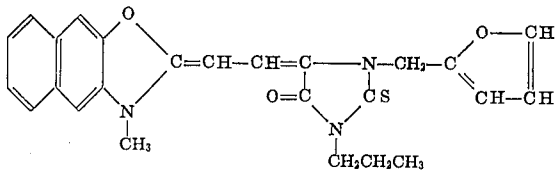


1.14 g of 1-(tetrahydrofurfuryl)-3-ethyl-2-thiohydantoin, 2.35 g of 2-(ω-aldehydomethylene)-naphtho-1',2'-4,5-oxazoleiodo-ethylate, 5 cc of ethyl alcohol and 0.5 cc of triethylamine were boiled for 10 minutes.

The separated dye was crystallized from ethyl alcohol.
(λ max of absorption in ethanol: 504 nm).

Example 68

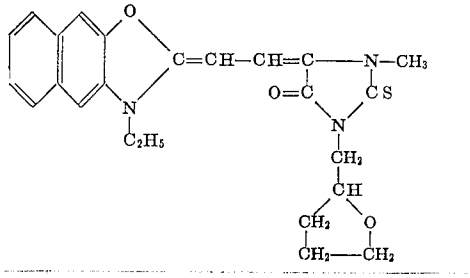
5-(3-methyl-naphtho-4,5-oxazoline-2-ylidene-ethylidene)-1-(furfuryl)-3-propyl-2-thiohydantoin



0.239 g of 1-(furfuryl)-3-propyl-2-thiohydantoin, 0.47 g of 2-(ω-acetanilidovinyl)-naphtho-4,5-oxazole-iodo-ethylate, 3,5 cc of butyl alcohol, 0.5 cc of piperidine were boiled for 15 minutes. The dye separated out and was crystallized from pyridine. The dye dried in the oven has M.P. 253°–5°C. Dark red crystals.
(λ max of absorption in ethanol: 486 nm)

Example 69

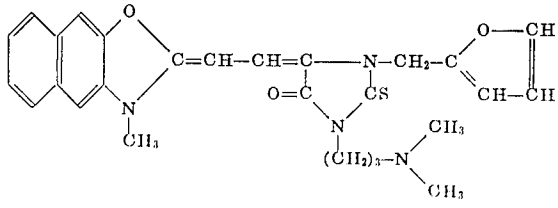
5-(3-ethyl-naphtho-4,5-oxazoline-2-ylidene-ethylidene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



0.53 g of 1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin, 1.17 g of 2-(ω-acetanilidovinyl)-naphtho-4,5-oxazole-iodo-ethylate, 7 cc of ethyl alcohol and 1 cc of triethylamine were boiled for 4 minutes. The separated dye, cristallized from pyridine in pink microcrystals. M.P. 276°–8°C.
(λ max of absorption in ethanol: 487 nm)

Example 70

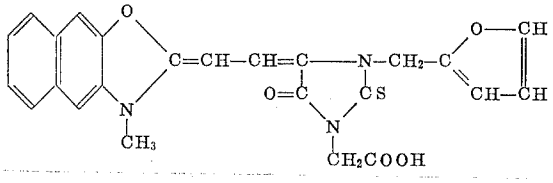
5-(3-methylnaphtho-4,5-oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin



1.4 g of 1furfuryl-3-(γ-dimethylaminopropyl)-2-thiohydantoin, 2.3 g of 2-(ω-acetanilidovinyl)-naphtho-4,5-oxazole-iodo-ethylate, 5 cc of pyridine, 1 cc of triethylamine were boiled at reflux for 20 minutes. The separated dye crystallized from pyridine and the pure dye obtained had a M.P. 235–6°C. (λ max of absorption in ethanol: 485 nm).

Example 71

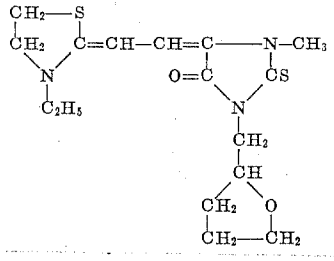
5-(3-methyl-naphtho-4,5-oxazoline-2-ylidene-ethylidene)-1-furfuryl-3-carboxylmethyl-2-thiohydantoin



0.508 g of 1-furfuryl-3-carboxymethyl-2-thiohydantoin, 0.940 g of 2-(ω-acetanilidrovinyl)-naphtho-4,5-oxazoline-iodo-ethylate, 7 cc of pyridine and 1 cc of triethylamine were boiled for 10 minutes. Water was added to the mixture, and the latter was acidified with acetic acid obtaining the dye having M.P. 265°–70°C.
(λ max of absorption is ethanol: 480 nm)

Example 72

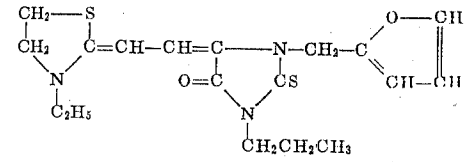
5-(3-ethyl-thiazolidine-2-ylidene-ethylene)-1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin



2.14 g of 1-methyl-3-tetrahydrofurfuryl-2-thiohydantoin, 1.57 g of 2-ω-aldehydo-methylene-3-ethyl-thiazolidine, 1.5 cc of ethyl alcohol and 0.7 cc of acetic anhydride were reacted for half an hour on a steam bath. Then 4.5 cc of ethyl alcohol were added and the mixture was allowed to standing. The solvent was evaporated under vacuum and water was added to the residue. A pitchy material separated out and was boiled again some times with water until it hardened. The solid was dissolved in a small amount of ethyl alcohol and allowed to stand. The dye separated out in red crystals having M.P. 188°–9°C.
(λ max of absorption in ethanol: 472 nm).

Example 73

5-(3-ethyl-thiazolidine-2-ylidene-ethylidene)-1-furfuryl-3-propyl-2-thiohydantoin



2.39 g of 1-furfuryl-3-propyl-2-thiohydantoin, 1.57 g of 2-aldehydo-methylene-3-ethyl-thiazolidine, 2 cc of pyridine and 0.2 cc of acetic anhydride were boiled for 5 minutes. After standing overnight the mixture was precipitated with water. A pitchy material separated out and by long standing it became solid. The solid obtained was purified by ebullition with alcohol and by crystallization from pyridine. Red violet crystals of dye were obtained having M.P. 176.5°–178.5°C.
(80 max of absorption in ethanol 483 nm).

The cyaninic dyes, which are the object of the present invention can be introduced into the silver halides photographic emulsions in a way very well known by the skilled in the art. These emulsions essentially consist of a natural and/or synthetic colloid, permeable to the acqueous media and of silver halide or halides. Moreover they can contain other compounds commonly used for specific purposes, such as, for example, other spectral sensibilizers, chemical sensibilizers, supersensibilizers, antifogging agents, stabilizers, surface active agents, couplers. The thus obtained emulsions can be spread on various supports such as, for example, cellulose triacetate, polyesters, glass, paper and similar materials.

Example 74

The dyeing sensibilizers according to the present invention were dissolved in methyl alcohol containing some toluene, and each of them was added to a photographic emulsion having the same composition, containing 91.5 moles per cent of AgCl and 8.5 moles per cent of AgBr. The resulting emulsions were spread on a cellulose triacetate support, then they were dried and exposed to a Zeiss spectrophotograph and developed for 5′ at 18°C in the Ferrania developer R 6 having the following composition:

Metal	g	1
Anhydrous sodium sulfite	g	25
Idroquinone	g	3.5
Anhydrous sodium carbonate	g	25
Potassium bromide	g	0.75
Water to	cc	1000

None of the sample showed any residual coloration after the development.

In table 1 the sensibilization maxima and limits corresponding to the various obtained emulsions are reported:

TABLE NO. 1

Compound	Sensibilization max nm	Sensibilization limits nm
19	545	475 - 580
20	545	455 - 590
21	475	430 - 510

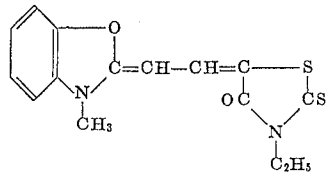
TABLE NO. 1-Continued

Compound	Sensibilization max nm	Sensibilization limits nm
22	—	435 - 525
23	535	460 - 590
24	535	450 - 590
26	535	450 - 560
27	—	420 - 470
34	565	460 - 600
35	570	470 - 610
37	550	465 - 580
38	580	495 - 615
39	515 (480)	440 - 550
40	520 (490)	440 - 550
42	515	435 - 560
43	525	445 - 560
44	530	430 - 560
45	520 (485)	435 - 550
46	530	450 - 555
47	525 (495)	440 - 560
48	520 - 525	440 - 550
49	525 (490)	435 - 555
50	525	440 - 560
51	530 (495)	445 - 555
52	530 (490)	440 - 555
53	525 (495)	445 - 555
54	520	430 - 560
55	530	445 - 565
56	525	430 - 560
57	520	440 - 560
58	525 (490)	440 - 560
59	525 (490)	440 - 565
61	450	455 - 570
63	535 (495)	440 - 570
64	540	460 - 570
65	540 (500)	450 - 570
66	535	490 - 555
68	535 (490)	440 - 580
69	535	455 - 560
70	535	450 - 565
71	530	480 - 555
72	510	435 - 540
73	510	440 - 540

Example 75

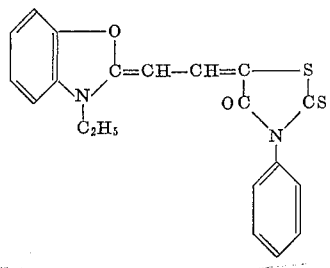
To several samples of the same photographic emulsion of Example 74, were added two sensibilizers not included in the present invention, respectively corresponding to the following formula:

75.1



5-(3-methyl-benzoxazoline-2-ylidene-ethylidene)-3-ethyl-rodanine

75.2



5-(3-ethyl-benzoxazoline-2-ylidene-ethylidene)-3-phenyl-rodanine and the sensibilizer of example 20 according to the present invention. Some samples were exposed to a Zeiss spectrograph and developed for 5 minutes at 18°C in the Ferrania R 6 developer. Some other samples were exposed to a steps-shaped wedge and developed 5 minutes at 18°C in the Ferrania developer R6, then they were read at the densitometer.

In the hereinafter reported Table the sensibilization maxima, the sensibilization limits and the relative sensitivities of the samples containing the three different sensibilizers are indicated. The sample containing the 75.1 sensibilizer is taken as a reference, and the variations of sensitivity as compared to this sample are expressed in - Δ log E for a certain density (having a value of about 1).

TABLE No. 2

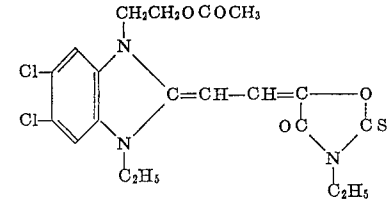
Compound	−Δ log E	Sensibilization Max	Sensibilization limits
75.1	—	540 nm	455–585 nm
75.2	+0.01	545 nm	455–585 nm
20	+0.10	545 nm	455–590 nm

The spectral sensibilization curves corresponding to the sensibilizers 75.1 and 20 are shown in FIG. 1, respectively as dotted and continuous lines.

Example 76

A test completely analogous to the test described in Example 75 was performed with the sensibilizer

76.1



5(-1-β-acetoxyethyl-3-ethyl-5,6-dichloro-benzimidazoline-2-ylidene-ethylidene)-3-ethyl-2-thio-oxazolidone, not included in the present invention, taken as a reference, and the sensibilizer of example 24, according to the present invention. The results are reported in the following table.

TABLE No. 3

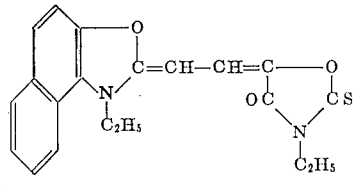
Compound	−Δ log E	Sensibilization Maxima	Sensibilization limits
76.1	—	535 nm	450 560 nm
24	+0.05	535 nm	450–590 nm

The spectral sensibilization curves are reported in FIG. 2. The dotted curve is related to the sensibilizer 24 and the continuous curve to the sensibilizer 76.1.

Example 77

A test completely analogous to the test described in example 75 was performed with the sensibilizer

77.1



5-(3-ethyl-naphtho-1', 2'-4,5-oxazoline-2-ylidene-ethylidene)-3-ethyl-2-thio-oxazolidone not included in the present invention taken as a reference and the sensibilizer of the example 36 according to the present invention. The results are reported in the hereinafter following table and the spectral sensibilization curves are reported in FIG. 3 where the continuous curve is related to the sensibilizer 36 and the dotted curve is related to the sensibilizer 77.1.

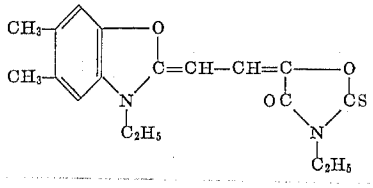
TABLE NO. 4

Compound	−Δ log E	Sensibilization maxima	Sensibilization limits
77.1	—	535 nm	465 - 560 nm
36	+0.14	535 - 40 nm	450 - 565 nm

Example 78

A test completely analogous to the test described in example 75 was performed with the sensibilizer

78.1



5-(3-ethyl-5,6-dimethyl-benzoxazoline-2-ylidene-ethylidene)-3-ethyl-2-thio-oxazolidone, not included in the present invention, taken as a reference and the sensibilizer of example 29 according to the present invention.

The results are reported in the hereinafter following Table 5 and the spectral sensibilization curves are reported in FIG. 4 where the dotted curve is related to the sensibilizer 78.1 and the continuous curve is related to the sensibilizer 29.

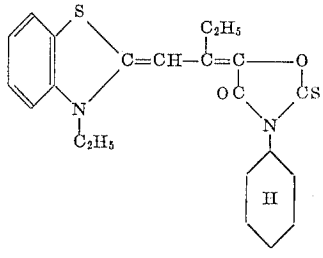
TABLE No. 5

Compound	−Δ log E	Sensibilization maxima	Sensibilization limits
78.1	—	530 nm	475 - 540 nm
29	+0.33	530 nm	465 - 555 nm

Example 79

A test completely analogous to the test described in example 75 was performed with the sensibilizer:

79.1



5-(3-ethyl-benzothiazoline-2-ylidene-isobutenylidene)-3-cyclohexyl-2-thio-oxazolidone, not included in the present invention, taken as a reference and the sensibilizer of example 33 according to the present invention.

The results are reported in the hereinafter following Table 6 and the spectral sensibilization curves are reported in FIG. 5 where the dotted curve is related to the sensibilizer 79.1 and the continuous curve is related to the sensibilizer 33.

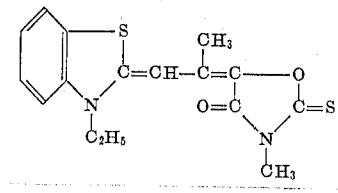
TABLE No. 6

Compound	−Δ log E	Sensibilization maxima	Sensibilization limits
79.1	—	555 nm	475 ÷ 580 nm
33	+0.15	560 nm	475 ÷ 590 nm

Example 80

A test completely analogous to the test described in the example 75 was performed with the sensibilizer

80.1



5-(3-ethyl-benzothiazoline-2-ylidene-isopropylidene)-3-methyl-2-thio-oxazolidone, not included in the present invention, taken as a reference and the sensibilizers of examples 31 and 32 according to the present invention.

The results are reported in the hereinafter following Table 7 and the spectral sensibilization curves corresponding to the sensibilizers 80.1 and 32 are reported in FIG. 6, where the dotted curve is related to sensibilizer 80.1 and the continuous curve is related to sensibilizer 32.

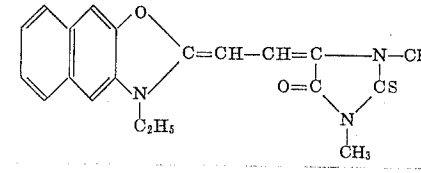
TABLE No. 7

Compound	−Δ log E	Sensibilization maxima	Sensibilization limits
80.1	—	550 nm	450 ÷ 580 nm
31	+0.03	555 nm	450 ÷ 590 nm
32	+0.03	550 - 560 nm	460 ÷ 610 nm

Example 81

A test completely analogous to the test described in the example 75 was performed with the sensibilizer

81.1



5-(3-ethyl-naphtho-4.5-oxazoline-2-ylidene-ethylidene)-1-methyl-3-methyl-2-thiohydantoin, not included in the present invention, taken as a reference and the sensibilizer of example 69, according to the present invention.

The results are reported in the hereinafter following Table 8 and the spectral sensibilization curves are reported in FIG. 7, where the dotted curve is related to

sensibilizer 81.1 and the continuous curve is related to sensibilizer 69.

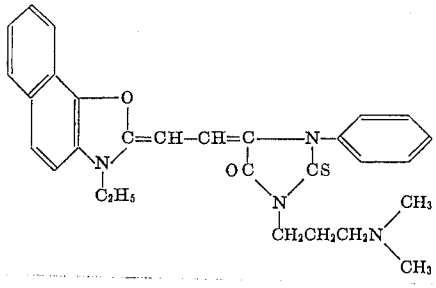
TABLE No. 8

Compound	−Δ log E	Sensibilization maxima	Sensibilization limits
81.1	—	530 nm	470 ÷ 555 nm
69	+0.16	535 nm	460 ÷ 560 nm

Example 82

A test completely analogous to the test described in the example 75 was performed with the sensibilizer

82.1



5-(3-ethyl-naphtho-2',1'-4.5-oxazoline-2-ylidene-ethylidene)-1-phenyl-3-(γ-dimethyl-aminopropyl)-2-thiohydantoin, not included in the present invention, taken as a reference and the sensibilizer of example 62 according to the present invention.

The results are reported in the hereinafter following Table 9 and the sensibilization curves are reported in FIG. 8, where the dotted curve is related to the sensitizer 82.1 and the continuous curve is related to the sensitizer 62.

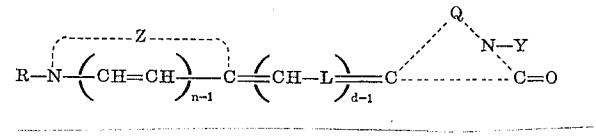
TABLE No. 9

Compound	Δ log E	Sensibilization maxima	Sensibilization. limits
82.1	—	—	440 - 565 nm
62	+0.47	540 nm	465 - 570 nm

The compound 82.1 imparted to the developed emulsion a marked residual coloration, while the compound 62 did not impart any residual coloration.

We claim:

1. A silver halide emulsion containing a dye of the merocyanine class having the formula:



wherein R represents an alkyl group having from one to eight carbon atoms; L represents a non substituted methinic group, and, when $d=2$, a methinic group substituted with a monovalent group R_1 which represents an alkyl group, an alkoxy group and an alkylmercapto group having from one to three carbon atoms; Z represents the non metallic atoms necessary to complete the heterocyclic nucleus; $n=1, 2$; $d=1, 2, 3$; and Q represents the non metallic atoms necessary to complete a ketomethylenic nucleus, and Y represents a furfuryl or tetrahydrofurfuryl group.

2. Photographic element having a photosensitive layer containing the silver halide emulsion according to claim 1.

3. The emulsion of claim 1 wherein the alkyl group R is a hydroxyalkyl, sulfoalkyl, carboxyalkyl or alkaryl.

4. The emulsion of claim 1 wherein R represents benzyl or paracarboxyphenylmethyl.

5. The photographic emulsion of claim 1 wherein Q completes a thiazolone, rhodanine, oxazolone, pseudohydantoin, hydantoin, thiohydantoin, imidazolone, oxindole, 3,4-dihydroquinolone, pyrazolone, 3,4-dihydroquinoxazolone, 2,4,6-triketohexahydropyrimidine, or 1,4-morpholine-3-one nucleus.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,836,370

DATED : September 17, 1974

INVENTOR(S) : Paolo Beretta and Luigi Magnani

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 62, after "group" and before "from" add --having--.

Col. 6, line 37, "Al in K. Prakt" should be --Al in J. Prakt--.

Col. 16, line 54, "2-ylidene-ethylene" should be --2-ylidene-ethylidene--.

Col. 21, line 26, "thiodantoin" should be --thiohydantoin--.

Col. 24, line 2, "λ-acetanilidovinyl" should be --ω-acetanilidovinly--.

Col. 24, line 47, "λ-acetanilidovinyl" should be --ω-acetanilidovinyl--.

Col. 29, line 67, "270°-3°272°C" should be --M.P. 272-3°C--.

Signed and Sealed this

fourteenth Day of *October 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks