

June 15, 1937.

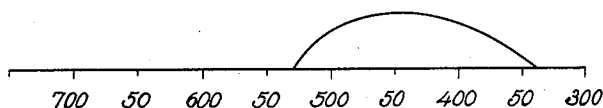
W. ZEH

2,083,804

SENSITIZING PHOTOGRAPHIC EMULSION

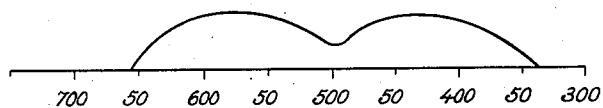
Filed Dec. 7, 1932.

Fig. 1



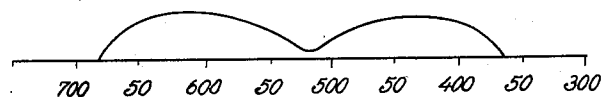
unsensitized silver bromide emulsion containing about 4 per cent of silver iodide

Fig. 2



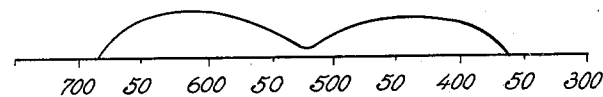
silver bromide emulsion containing about 4 per cent of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]-alpha-gamma-dimethyl-trimethinecyanine iodide

Fig. 3



silver bromide emulsion containing about 4 per cent of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-5-diethylamino-benzthiazole-(2)]-alpha-methyl-trimethinecyanine perchlorate

Fig. 4



silver bromide emulsion containing about 4 per cent of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-naphtho-2'.1':4-5-thiazole-(2)]-alpha-ethyl-trimethinecyanine iodide

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UNITED STATES PATENT OFFICE

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SENSITIZING PHOTOGRAPHIC EMULSION

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Application December 7, 1932, Serial No. 646,215
In Germany December 15, 1931

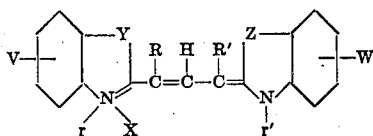
14 Claims. (Cl. 95—7)

My present invention relates to sensitizing of photographic emulsions.

One of its objects is to provide such an emulsion the sensitivity of which is raised over the range of wave lengths to which the emulsion is normally sensitive. Another object is the dyes incorporated in the emulsions in order to increase their sensitivity. Further objects will be seen from the detailed specification following hereafter.

It is known to sensitize silver-halide emulsions by incorporating in the same asymmetrically built trimethinecyanines. Each of these dyes sensitizes the emulsion to which it is added for a definite spectral region which varies according to the ring systems forming the dye.

According to this invention I have found that asymmetrical trimethinecyanines containing two different nuclei linked together by a trimethenyl chain and which have been substituted in the α or α' position (see the following general formula) constitute a class of important sensitizers. By incorporating these dyes corresponding with the following general formula



Y and Z=S, Se, O, $-\text{CH}=\text{CH}-$ or $\text{C}(\text{CH}_3)_2$

V and W=H, alkyl, alkoxy, amino groups, substituted amino groups, benzene or halide,

R and R'=H, alkyl, subject to the condition that R and R' are not both hydrogen

r and r'=alkyl

X=halide, perchlorate, para-toluenesulfonate, alkylsulfate, nitrate.

into a silver-halide emulsion the same is sensitized for wave lengths from about 500μ to about 720μ .

In the general formula Y and Z may represent sulfur, selenium, oxygen, the vinylene group $-\text{CH}=\text{CH}-$ or $\text{C}(\text{CH}_3)_2$. V and W may take any position in the benzene nuclei, however, the 5 and 6 positions, and the 5' and 6' positions are preferred. In the case Y being $\text{CH}=\text{CH}$ the 6 and 7, and 6' and 7' positions are preferred. V and W may represent alkyl such as methyl, ethyl,

etc., or an alkoxy group, for instance, a methoxy or ethoxy group, or halide, or benzene or an amino-group, or a substituted amino group, for instance, alkylated or acylated amino groups. r may be alkyl, for example, methyl, ethyl, propyl, etc. X can be any suitable anion that will precipitate the dye, for instance, a halide, paratoluene sulfonate, alkylsulfate, perchlorate, nitrate or the like. The benzene nuclei may contain one or more of the substituents enumerated. The trimethenyl chain may be substituted by one or two alkyl groups, for instance, methyl groups or ethyl groups but either the α or the α' carbon atom being linked to an alkyl group. The dyes may have an asymmetrical character by linking, for instance, a thiazole to a selenazole, etc., nucleus by a trimethenyl chain or the asymmetrical structure may be due to two differently substituted nuclei of the same base.

In the accompanying drawing there are shown some spectrograms of emulsions sensitized in accordance with the invention.

Fig. 1 shows the spectrogram of an unsensitized silver bromide emulsion containing about 4 per cent of silver iodide,

Fig. 2 shows the spectrogram of the same emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]- α - γ -dimethyl-trimethinecyanine iodide,

Fig. 3 shows the spectrogram of the same emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-5-diethylaminobenzthiazole-(2)]- α -methyl-trimethinecyanine perchlorate, and

Fig. 4 shows the spectrogram of the same emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-naphtho-2'.1':4-5-thiazole-(2)]- α -ethyl-trimethinecyanine iodide.

The dyes are obtainable according to the desired solubility in form of the bromide, iodide, perchlorate, etc., and are used in a quantity as usual for the known sensitizing dyes. This quantity amounts to about 5 to 20 milligrams per 1 kg. of emulsion ready for being cast which contains about 9 per cent of gelatin, 4.5 per cent of silver-halide, the rest being water. However, I do not wish to limit my invention to the quantities just indicated, the most suitable amount will in each case be found by a few comparative experiments. The dyes may be added to the emulsion in form of solutions. Suitable solvents are

the alcohols, for instance, methyl or ethyl alcohol which may be used anhydrous or diluted with water. The dyes are applied to the emulsion during any stage of its production, however, they are preferably added to the finished emulsion before being cast.

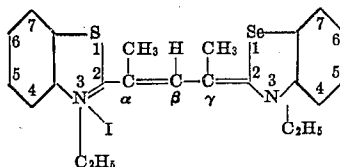
The dyes may likewise be added by coating the emulsion with them or by bathing the finished photographic material in a bath in which the dye is dissolved. Such a treatment may be as follows:—The photographic material to be sensitized is bathed in a solution containing 1 milligram of [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]- α,γ -dimethyl-trimethine-cyanine iodide in 50 to 100 cc. of an aqueous solution of methanol of 50 per cent strength for about 5 minutes. The material is then dried, whereupon it is ready for use.

The dyes are suited for sensitizing an emulsion made according to the boiling process as well as for sensitizing an emulsion made according to the ammonia process.

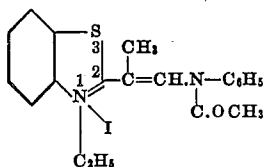
The production of the bases and of the dyes from the bases is analogous to known methods. The production of substituted selenazole bases has been described in the copending application Serial Number 637,131 filed October 10, 1932 by Walter Zeh and the production of bases substituted by an amino group or a substituted amino group has been described in the co-pending application Serial Number 590,940 filed February 4, 1932 by Dieterle et al.

The following examples serve to illustrate my invention.

Example 1.—For producing the dye [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]- α,γ -dimethyl-trimethinecyanine-iodide corresponding to the formula



a mixture of 5 grams of 2-ethylbenzthiazole-ethyl-iodide and 3.5 grams of diphenylformamidine is heated with 15 cc. of acetic anhydride to about 150° C. for about 1 hour. After cooling a yellow crystalline mass separates which is washed with acetic anhydride and ether. The intermediate product thus obtained corresponding probably with the formula



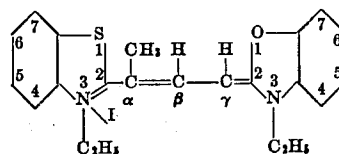
is dissolved in about 15 cc. of pyridine. To this solution there are added 3 grams of 2-ethylbenzselenazole ethiodide and the mixture is heated to 140° C. for about 10 minutes. After cooling the dye precipitates in blue flakes. Recrystallization from alcohol yields a bluish green crystal powder.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 565 μ .

Incorporated in a silver-bromide emulsion con-

taining about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 500 μ to about 680 μ with a maximum at about 605 μ .

Example 2.—The dye [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzoxazole-(2)]- α -methyl-trimethinecyanine-iodide corresponding with the formula

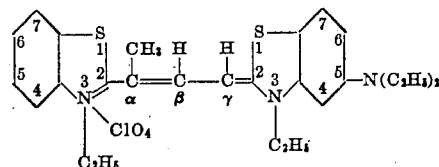


is obtainable by boiling the intermediate product described in Example 1 in 5 cc. of pyridine with 2 grams of 2-methyl-benzoxazole ethiodide and precipitating the dye from the orange red solution by the addition of about 5 cc. of an aqueous solution of potassium iodide of about 10 per cent strength. The dye may be recrystallized from alcohol and is then obtainable in form of orange red crystals.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 525 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 510 μ to about 610 μ with a maximum at about 565 μ .

Example 3.—The dye [3-ethyl-benzthiazole-(2)]-[3-ethyl-5-diethylamino-benzthiazole-(2)]- α -methyl-trimethenecyanine-perchlorate corresponding with the formula

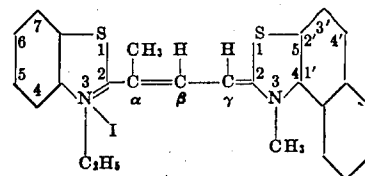


may be made by boiling the intermediate product described in Example 1 dissolved in 10 cc. of pyridine with 3 grams of 2-methyl-5-diethylamino ethiodide. From the blue solution which forms, the dye separates in blue flakes after the addition of about 10 cc. of an aqueous solution of sodium perchlorate of 5 per cent strength.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 600 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 510 μ to about 700 μ with a maximum at about 630 μ .

Example 4.—For producing the dye [3-ethyl-benzthiazole-(2)]-[3-methyl-naphtho-1',2':4,5-thiazole-(2)]- α -methyl-trimethinecyanine-iodide corresponding with the formula



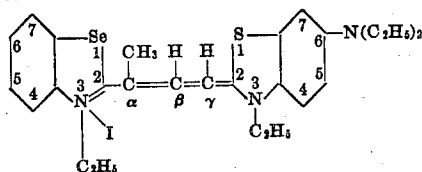
a mixture of the intermediate product made according to Example 1, 3 grams of 2-methyl-4,5-

benzobenzthiazole ethiodide and 10 cc. of pyridine are boiled. After the addition of about 10 cc. of an aqueous solution of potassium iodide the dye precipitates in form of blue flakes.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 585 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 510 μ to 670 μ with a maximum at about 600 μ .

Example 5.—The dye [3-ethyl-benz-selenazole-(2)-1-[3-ethyl-6-diethylamino-benzthiazole-(2)-1- α -methyl-trimethinecyanine-iodide corresponding with the formula

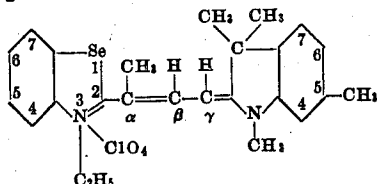


is produced as follows. 5 grams of 2-ethylbenz-selenazole ethiodide in 30 cc. of acetic anhydride are heated with 3.5 grams of diphenylformamidine for about 1 hour to 140–150° C. After cooling the product which has separated is removed by filtration and washed with acetic anhydride and ether. This product is condensed with 2 grams of 2-methyl-6-diethylamino-benzthiazole ethiodide by heating the mixture in 10 cc. of pyridine. The dye precipitates from the blue solution in pyridine after cooling in form of blackish green crystal powder.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 605 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 515 μ to about 720 μ with a maximum at about 630 μ .

Example 6.—When condensing the intermediate product described in Example 5 with 2 grams of 1,2,3,3,6-pentamethylindole-iodide instead of the 2-methyl-6-diethylamino-benzthiazole-ethiodide and adding to the solution in pyridine a few cc. of an aqueous solution of sodium perchlorate the dye [3-ethyl-benz-selenazole-(2)-1-[3-methyl-5-methylindole-(2)-1- α -methyl-trimethinecyanine perchlorate corresponding with the formula

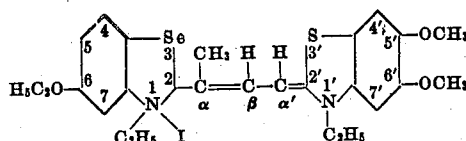


is obtained in form of a brown red crystal powder.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 555 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 505 μ to about 650 μ with a maximum at about 600 μ .

Example 7.—The dye [3-ethyl-5-ethoxy-benz-selenazole-(2)-1-[3-ethyl-5,6-dimethoxy-benzthiazole-(2)-1- α -methyl-trimethinecyanine-iodide corresponding with the formula

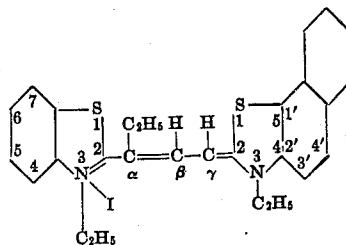


may be obtained as follows. 3 grams of 2-ethoxybenz-selenazole ethiodide are heated with 2 grams of diphenylformamidine in 10 cc. of acetic anhydride for about 1 hour to 140° C. After cooling the intermediate product is precipitated from the red brown mixture. After washing the intermediate product with acetic anhydride and ether it is condensed with 1 gram of 5,6-dimethoxybenzthiazole ethiodide in 5 cc. of pyridine, by boiling these ingredients for about 5 minutes. After the addition of water and cooling the dye precipitates in form of bluish black flakes.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 595 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 520 μ to about 700 μ with a maximum at about 630 μ .

Example 8.—For producing the dye [3-ethyl-benzthiazole-(2)-1-[3-ethyl-naphtho-2':1':4,5-thiazole-(2)-1- α -ethyl-trimethinecyanine-iodide corresponding with the formula



there is first made an intermediate product by heating 3 grams of 2-n-propylbenzthiazole ethiodide with 2 grams of diphenylformamidine in 10 cc. of acetic anhydride for about 1 hour to 140° C. To the reddish yellow mixture there is added ether which is decanted after the separation of the intermediate product. The latter is then washed with ether and hereafter condensed with 1 gram of 2-methyl-6,7-benzobenzthiazole ethiodide by boiling these compounds in 5 cc. of pyridine for a short period of time. On the addition of about 5 cc. of water the dye is precipitated in form of bluish black flakes.

The alcoholic solution of the dye shows an absorption maximum at a wave length of about 585 μ .

Incorporated in a silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 510 μ to about 660 μ with a maximum at about 610 μ .

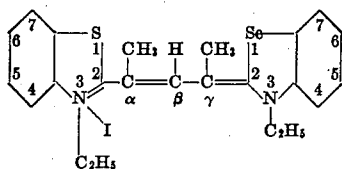
It is to be understood that my invention is not limited to the foregoing examples or to the specific details given therein. Numerous other embodiments are possible and I contemplate as included within my invention all such modifications and equivalents as fall within the scope of the appended claims. So, for instance, the benzene nuclei may contain one or more substituents. The nomenclature used is familiar to every chemist skilled in the art and has the advantage of clearness. Numbering of the bases etc. is begun from the sulfur etc. of the 5 ring, numbering of the quinoline nuclei and of the dyes is begun

from the nitrogen atom. The formulae of the dyes as given herein represent the molecular structure of my new dyes as far as known. If, however, in future it should become evident that the formulae do not exactly correspond to the dyes, this fact will not affect my invention since the dyes will be easily identified by the method of producing the same which has been fully described in the examples and is analogous to known methods.

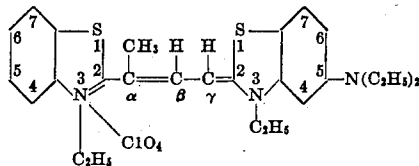
What I claim is:

1. A photographic material comprising a silver-halide emulsion sensitized with an asymmetrical trimethinecyanine containing in its molecule an alkyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

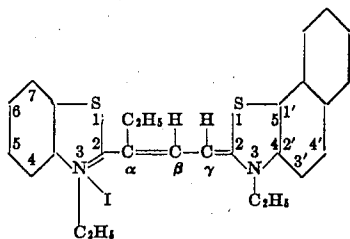
2. A photographic material comprising a silver halide emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]- α,γ -dimethyl-trimethinecyanine iodide corresponding probably to the formula



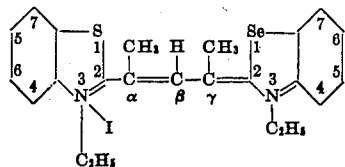
3. A photographic material comprising a silver halide emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-methyl-5-diethylamino-benzthiazole-(2)]- α -methyl-trimethinecyanine perchlorate corresponding probably to the formula



4. A photographic material comprising a silver halide emulsion sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-naphtho-2':1':4,5-thiazole-(2)]- α -ethyl-trimethinecyanine iodide corresponding probably to the formula



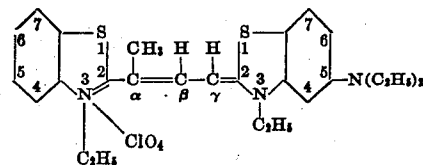
5. A photographic material comprising a gelatino-silver-bromide emulsion containing about 4% of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]- α,γ -dimethyl-trimethinecyanine iodide corresponding probably to the formula



and having a range of sensitivity from about 500 μ to about 680 μ with a maximum at about 605 μ .

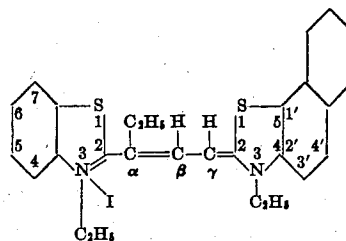
6. A photographic material comprising a ge-

latino-silver bromide emulsion containing about 4% of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-5-diethylamino-benzthiazole-(2)]- α -methyl-trimethinecyanine perchlorate corresponding probably to the formula



and having a range of sensitivity from about 510 μ to about 700 μ with a maximum at about 680 μ .

7. A photographic material comprising a gelatino-silver bromide emulsion containing about 4% of silver iodide sensitized with [3-ethyl-benzthiazole-(2)]-[3-ethyl-naphtho-1':2':4,5-thiazole-(2)]- α -ethyl-trimethinecyanine-iodide corresponding probably to the formula



and having a range of sensitivity from about 510 μ to about 660 μ with a maximum at about 610 μ .

8. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical 3-alkyl-trimethinecyanine salt containing in its molecule an alkyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

9. A photographic material comprising a silver halide emulsion sensitized with a dye selected from the group consisting of 3-alkyl-trimethinecyanine iodides and perchlorates containing in its molecule an alkyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

10. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical 3-alkyl-trimethinecyanine salt containing in its molecule an ethyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

11. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical 3-alkyl-trimethinecyanine salt containing in its molecule a methyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

12. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical 3-alkyl-trimethinecyanine salt containing in its molecule a methyl group linked to both lateral carbon atoms of the trimethenyl chain.

13. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical carbocyanine salt selected from the group consisting of thiazole-trimethinecyanine salts, selenazole-trimethinecyanine salts and oxocarbocyanine salts containing in its molecule an alkyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

14. A photographic material comprising a silver halide emulsion sensitized with an asymmetrical indole-trimethinecyanine salt containing in its molecule an alkyl group linked to at least one of the lateral carbon atoms of the trimethenyl chain.

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