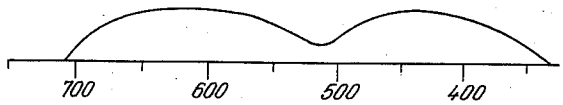
Jan. 5, 1937. W. DIETERLE ET AL 2,066,968

MANUFACTURE OF LIGHT SENSITIVE MATERIALS

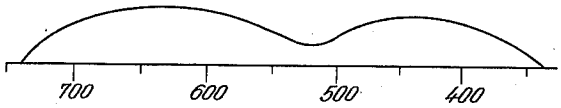
Filed March 10, 1933

Fig. 1



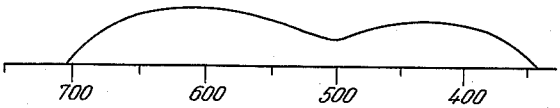
SILVER HALIDE EMULSION SENSITIZED WITH [3-ETHYL-6-DIETHYLAMINO-BENZTHIAZOLE-(2)]-[3-ETHYL-BENZSELENAZOLE-(2)]-TRIMETHINECYANINE IODIDE

Fig. 2



SILVER HALIDE EMULSION SENSITIZED WITH [3-ETHYL-5-DIETHYLAMINO-BENZTHIAZOLE-(2)]-[3-ETHYL-6-DIETHYLAMINO-BENZTHIAZOLE-(2)]-TRIMETHINE CYANINE PERCHLORATE

Fig. 3



SILVER HALIDE EMULSION SENSITIZED WITH [3-ETHYL-5-DIETHYLAMINO-BENZTHIAZOLE-(2)]-[3-ETHYL-6-ETHOXY-BENZTHIAZOLE-(2)]-TRIMETHINE-CYANINE PERCHLORATE

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Patented Jan. 5, 1937 2,066,968

UNITED STATES PATENT OFFICE

2,066,968

MANUFACTURE OF LIGHT-SENSITIVE MATERIALS

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Application March 10, 1933, Serial No. 660,287
In Germany March 27, 1931

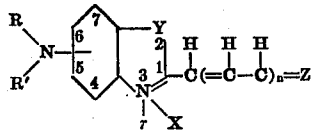
5 Claims. (Cl. 95—7)

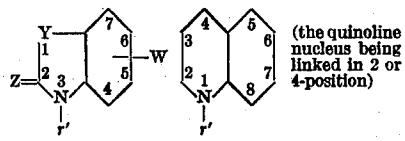
Our present invention relates to sensitizing of photographic emulsions.

It is a continuation-in-part of our application Ser. No. 590,940, filed Feb. 4, 1932.

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. Further objects will be seen from the detailed specification following hereafter.

We have found that the cyanines having introduced in their molecule an amino group or a substituted amino group and corresponding with the general Formula 1





(the quinoline nucleus being linked in 2 or 4-position)

Y=S, Se

Y'=S, Se, $C(CH_3)_2$, O

W=H, , alkyl, alkoxyl,

r and r'=alkyl

R=H, alkyl, aryl, acyl

R'=H, alkyl

n=O or 1

X=halide, perchlorate, alkylosulfate, paratoluene sulfonate, nitrate, or another suitable anion, are particularly suited for sensitizing photographic emulsions. The dyes are characterized by their sensitizing efficiency and their stability against agents used for stabilizing the emulsions, for instance, potassium bromide.

In the appended claims the expression "an amino group" is to be understood as including not only the amino group but also substituted amino groups.

The amino group having the radicals R and R' may be introduced at any position of the nuclei, the 5 and 6 positions are preferred for the nuclei of the kind of the benzthiazole nucleus; in the case of the quinoline nucleus the 6 and 7 positions are preferred. There may further be present in the nuclei monovalent radicals, e. g. alkyl, alkoxyl, halide in any possible position.

The unsymmetrical character of the dyes may have various causes. For instance, Y may differ from Y', or if Y and Y' represent the same radical, W may be different from the group



for instance, H; or if Y and Y' represent the same radical and W represents



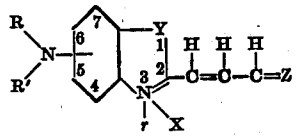
the two

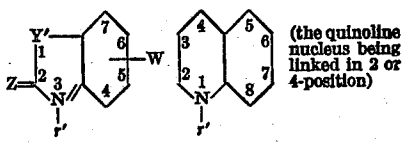


groups may be linked in different positions. These possibilities are of course only a few of those which are included within this invention.

The general Formula 1 comprises three principal groups of cyanines dyes:

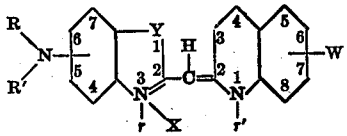
Trimethinecyanines of the Formula 2,



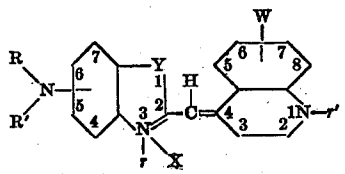


(the quinoline nucleus being linked in 2 or 4-position)

pseudocyanines of the Formula 3,



and isocyanines of the Formula 4,



In the Formulae 2, 3 and 4 the amino group may take the places 4, 5, 6 and 7. The radical R

may represent H; or alkyl, for instance, methyl or ethyl; or aryl, for instance, phenyl, naphthyl; or a substituted aryl; or acyl, for instance, benzoyl, acetyl, propionyl or butyryl. R' may be alkyl in the case of R being alkyl or aryl, or R' is hydrogen in the case of R being hydrogen or acyl. X may represent any suitable anion that will precipitate the dye, for instance, a halide, perchlorate, alkylosulfate, paratoluene sulfonate, nitrate. r and r' represent alkyl, for instance, methyl, ethyl, propyl, butyl, amyl and the isomers of propyl butyl and amyl. W may be H; or



or alkyl, for instance, methyl or ethyl; or alkoxyl, for instance, methoxy or ethoxy.

The benzthiazole nucleus or the benzselenazole nucleus may contain besides the amino group one or several alkyl groups, such as methyl or ethyl groups, or alkoxyl groups, such as methoxy or ethoxy groups, or both alkyl and alkoxyl groups.

The introduction of the amino group into the benzthiazole nucleus causes a displacement of the range of sensitivity of the dyes towards the region of longer waves. For instance, the introduction of one diethylamino group into the benzthiazole nucleus of an unsymmetrical trimethinecyanine corresponding with the Formula 2 effects a displacement of the maximum of sensitization of about 30$\mu\mu$ towards longer waves and when introduced into a benzselenazole nucleus one diethylamino group effects a displacement of the maximum of sensitization of about 28$\mu\mu$.

As seen there is a slight difference between the replacement of hydrogen in the benzene nucleus by a substituted amino amino group in the molecule of the thiocyanines and the selenocyanines. It is to be understood that the foregoing statement is given only by way of example. Other radicals which have already been mentioned may represent R and R'. The replacement of r and r' by different radicals is of minor efficiency for displacing the range of sensitivity. The radicals representing X are of no influence in the purpose set forth. The influence on the displacement of the sensitization maximum and on the intensity of the sensitivity can easily be determined by a few comparative experiments.

In Figs. 1 to 3 of the accompanying drawing there are shown spectrograms of emulsions sensitized in accordance with the invention.

Fig. 1 shows the spectrogram of a silver halide emulsion sensitized with 1.1'-diethyl-5-diethylamino - benzthio-benzselenocarbocyanine iodide,

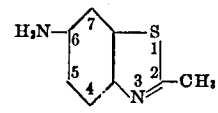
Fig. 2 shows the spectrogram of a silver halide emulsion sensitized with 1.1'-diethyl-6.5'-bis-diethylamino-benzthiocarbocyanine perchlorate, and

Fig. 3 shows the spectrogram of a silver halide emulsion sensitized with 1.1'-diethyl-6-diethylamino-5'-ethoxy-benzthiocarbocyanine perchlorate.

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 8 to 25 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. We do not wish to limit our invention exactly to the quantities just indicated, the most suitable amount will be found in each particular case by a few simple 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 may be added 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 materials in a bath in which the dye is dissolved.

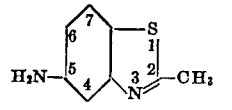
The production of the 4-, 5-, 6-, or 7-amino substituted 2-methyl-benzthiazoles serving as a starting material for preparing the dyes is described in Examples 1 to 9. Other bases than those described in these examples may be produced in an analogous manner. The method of preparing our new dyes from the bases is analogous to known methods and illustrated in Examples 10 to 20.

Example 1.—The preparation of 2-methyl-6-amino-benzo-thiazole corresponding with the formula



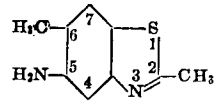
is described in U. S. Patent 1,758,385 and reference is made thereto.

Example 2.—The base 2-methyl-5-amino-benzthiazole corresponding with the formula



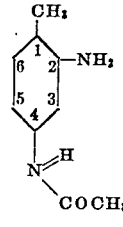
is obtained by reducing the corresponding nitro compound whose method of preparation is known (cf. Friess, Ann. 454, page 177), for instance, with iron and acetic acid. The amino compound is easily soluble in alcohol, glacial acetic acid and benzene. It can be easily recrystallized from water or benzene and forms colorless crystals which melt at about 103° C.

Example 3.—The base 2.6-dimethyl-5-amino-benzthiazole corresponding with the formula



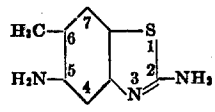
can be obtained in two ways.

According to the first way we proceed as follows: 2-amino - 4 - acetylamino-toluol corresponding with the formula

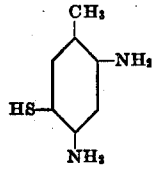


is first rhodanated with NH_4SCN and Br in its methyl-alcoholic solution in the manner described in U. S. Patent 1,787,315 and then with an aqueous ammoniacal solution. The formed

product, probably the 2.5-diamino-6-methyl-benzthiazole corresponding with the formula



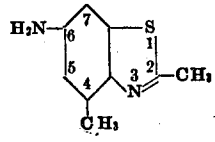
obtained from its aqueous solution in form of colorless crystals which melt at about 200° C. is split up by heating the same with an aqueous solution of caustic potassium of about 50 per cent strength in the manner described in U. S. Patent 1,788,297 in a compound corresponding with the formula



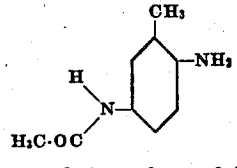
The zinc mercaptide of this compound is transformed into the 2.6-dimethyl-5-acetylamino-benzthiazole with a melting point of about 178° C. corresponding with the above formula by heating the aforesaid mercaptide with acetic anhydride.

According to the second way 3-chloro-4-acetylamino-6-nitrotoluene having a melting point of 143° C. is transformed into 2.6-dimethyl-5-nitro-benzthiazole forming compact, colorless crystals when crystallized from alcohol which melt at about 106° C. This compound yields the 2.6-dimethyl-5-amino-benzthiazole when reduced with iron and acetic acid, forming colorless crystals which melt at about 143° C. The thiazole can be easily acetylated.

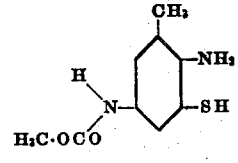
Example 4.—The base 2.4-dimethyl-6-amino-benzthiazole corresponding with the formula



is obtained as follows. Acetyl-toluylene-diamine corresponding with the formula

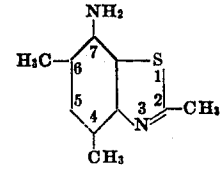


is by means of S_2Cl_2 transformed into the thiazthionium-compound in the manner described in U. S. Patent 1,637,023. When treating this compound with a solution of caustic alkali according to U. S. Patent 1,243,710 the corresponding o-amino-mercaptane corresponding with the formula

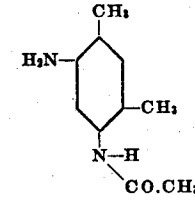


is obtained. By heating this compound with acetic anhydride it is transformed into 2.4-dimethyl-6-acetyl-amino-benzthiazole which crystallizes from its aqueous solution in form of colorless crystals melting at about 177° C. By saponification with hydrochloric acid results the 2.4-dimethyl-6-amino-benzthiazole which forms colorless crystals melting at about 118° C.

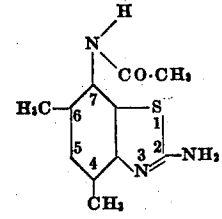
Example 5.—The base 2.4.6-trimethyl-7-amino-benz-thiazole corresponding with the formula



is obtainable as follows. Amino-acetylamino-xylidin corresponding with the formula

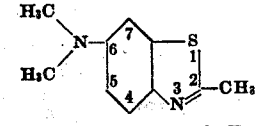


is rhodanated according to U. S. Patent 1,787,315 whereby 2-amino-4.6-dimethyl - 7 - acetylamino-benzthiazole corresponding with the formula



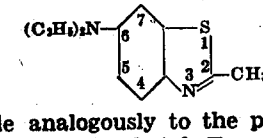
and melting at about 285° C. is obtained. By boiling this compound with a strong aqueous solution of caustic alkali according to U. S. Patent 1,788,297 it is split up to the corresponding o-amino-mercaptane, which may be separated from the reaction mixture in form of the zinc mercaptide. By heating with acetic anhydride the 2.4.6-trimethyl- 7 -acetylamino-benzthiazole is obtainable. After recrystallization from its alcoholic solution this compound forms colorless crystals melting at about 208° C. By saponification with hydrochloric acid the 2.4.6-trimethyl-7-amino-benzthiazole is obtainable in form of colorless crystals melting at about 128° C.

Example 6.—The base 2-methyl-6-dimethylamino-benzthiazole corresponding with the formula



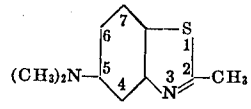
has already been described: cf. Bernthsen, Ann. 251, page 29.

Example 7.—The base 2-methyl-6-diethyl-amino-benzthiazole corresponding with the formula



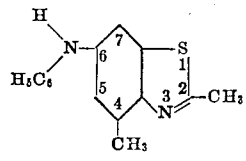
is obtainable analogously to the preparation of the dimethyl compound (cf. Example 1). The chloride forming colorless crystals is easily soluble in water and decomposes when heated to a temperature of about 160° C. under strong evolution of gas. If the base is set free from the chloride by means of an aqueous solution of caustic alkali it separates in form of a yellow oil which solidifies when cooling.

Example 8.—The base 2-methyl-5-dimethylamino-benzthiazole corresponding with the formula



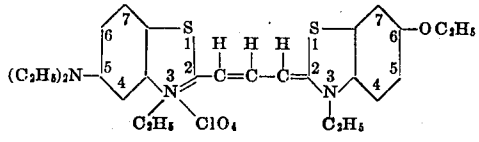
is obtainable as follows. p-bromo-dimethylaniline is nitrated in a mixture of concentrated nitric and sulfuric acid. The formed p-bromo-nitro-dimethylaniline (orange crystals) is transformed into p.p'-tetramethyl-diamino-o.o'-dinitro-diphenyl-disulfide (red crystals when crystallized from chlorobenzene) by heating it with the calculated quantity of Na_2S_2. From this compound results p-dimethyl-amino-o-amino-thiophenol by reduction with sodium sulfide in an aqueous alkaline suspension. The latter compound is transformed into 2-methyl-5-dimethylamino-benzthiazole by a treatment with acetic anhydride. The chloride forms colorless crystals which are insoluble in ether, but easily soluble in water.

Example 9.—The base 2.4-dimethyl-6-phenylamino-benzthiazole corresponding with the formula



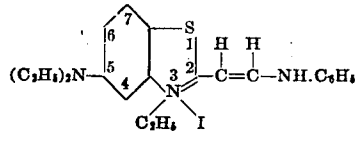
is obtainable by heating 2-amino-3-methyl-5-phenylamino-thiophenol-zinc (cf. U. S. Patent 1,566,384) with acetic anhydride. After crystallizing the compound from benzene it forms colorless crystals which melt at about 138° C. and are easily soluble in benzene, alcohol and glacial acetic acid.

Example 10.—For producing the dye [3-ethyl-5-diethylamino-benzthiazole-(2)]-[3-ethyl-6-ethoxy-benzthiazole-(2)]-trimethine-cyanine-perchlorate corresponding with the formula



we proceed as follows:

A. 9 grams of 5-diethylamino-2-methyl-benzthiazole ethyl-iodide and 6.5 grams of diphenyl-formamidine are intimately mixed; to this mixture 25 cc. of acetic anhydride are added and the whole is boiled for ¾ hour under reflux (about 140° C.). After cooling the reaction mixture ether is added drop by drop while stirring the mixture and rubbing the walls of the vessel. This procedure is continued until the formation of crystals occurs at the walls of the vessel. Now, the dye is precipitated by cooling the reaction mixture with a freezing mixture and filtered off. The intermediate product which melts in its pure state at 218 to 219° C. corresponds probably with the formula

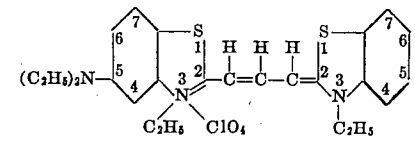


B. 4 grams of the intermediate product are boiled with 2 grams of 2-methyl-6-ethoxy-benzthiazole-ethyl-iodide and 20 cc. of pyridine for ¾ hour under reflux (about 125 to 130° C. The dye is then precipitated by addition of a few cc. of an aqueous solution of potassium iodide of 10 per cent strength and water, separated by filtration, dissolved in alcohol and precipitated from its alcoholic solution in form of its perchlorate by addition of a few cc. of an aqueous solution of sodium perchlorate of 1 per cent strength and water.

After recrystallization of the dye, its alcoholic solution shows an absorption maximum at a wave length of about 600$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 500$\mu\mu$ to about 725$\mu\mu$ with a maximum at about 625$\mu\mu$.

Example 11.—For producing the dye [3-ethyl-5-diethylamino-benzthiazole-(2)]-[3-ethyl-benzthiazole-(2)]-trimethinecyanine-perchlorate corresponding with the formula

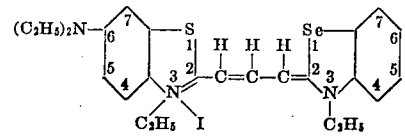


4 grams of the intermediate product obtainable from 5-diethylamino-2-methyl-benzthiazole-ethyl-iodide and diphenyl-formamidine in the manner described in Example 10 sub A, are boiled with 2 grams of 2-methyl-benzthiazole-ethyl-iodide and 20 cc. of pyridine for ¾ hour under reflux (125 to 130° C.). The reaction mixture is worked up in the manner indicated in Example 10.

The dye shows in its alcoholic solution an absorption maximum at a wave length of about 595$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 510$\mu\mu$ to about 720$\mu\mu$ with a maximum at about 635$\mu\mu$.

Example 12.—The dye [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-benzelenazole-(2)] trimethinecyanine-iodide corresponding with the formula



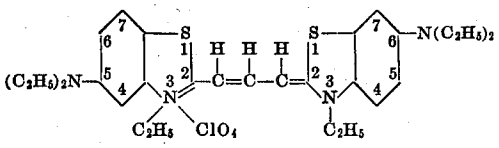
is produced in the same manner as described in the foregoing examples by starting from the corresponding materials.

The dye shows in its alcoholic solution an absorption maximum at a wave length of about 600$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver-iodide the dye imparts to it a range of sensitivity from about 510$\mu\mu$ to about 715$\mu\mu$ with a maximum at about 630$\mu\mu$.

Example 13.—The dye [3-ethyl-5-diethylamino-benzthiazole-(2)]-[3-ethyl-6-diethylamino-

benzthiazole-(2)]-trimethinecyanine-perchlorate corresponding with the formula

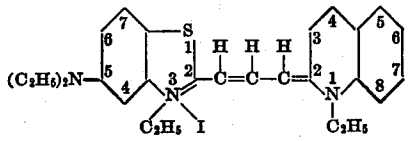


may be produced by mixing 1.5 grams of the intermediate product described in Example 10 with 2.3 grams of 6-diethylamino-2-methylbenzothiazole-ethyl-iodide and 15 cc. of pyridine, boiling this mixture for ¾ hour under reflux and working up the reaction mixture as indicated in Example 10. The dye may likewise be obtained as iodide.

The alcoholic solution of the dye has an absorption maximum at a wave length of about 625$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 510$\mu\mu$ to about 730$\mu\mu$ with a maximum at about 655$\mu\mu$.

Example 14.—For producing [3-ethyl-5-diethylamino-benzthiazole-(2)]-[1-ethyl-quinoline-(2)]-trimethinecyanine iodide corresponding with the formula

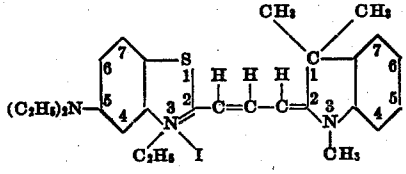


5 grams of the intermediate product obtainable from 5-diethylamino-2-methyl-benzthiazole-ethyl-iodide and diphenyl-formamidine as described in Example 10, are boiled for 2½ hours with 4 grams of quinaldine-ethyl-iodide and 15 cc. of pyridine under reflux. The dye which forms is precipitated by addition of a few cc. of an aqueous solution of potassium iodide of 10 per cent strength and water and is recrystallized from alcohol.

The alcoholic solution of the dye has an absorption maximum at a wave length of about 615$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitiveness from about 515$\mu\mu$ to about 730$\mu\mu$ with a very flat maximum at about 645$\mu\mu$.

Example 15.—For producing the dye [3-ethyl-5-diethylamino-benzthiazole-(2)]-[3-methyl-indole-(2)]-trimethinecyanine iodide corresponding with the formula



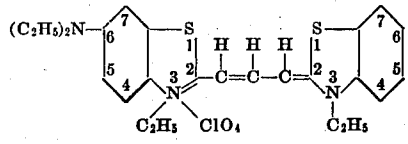
2 grams of the intermediate product obtainable from 5-diethyl-2-methyl-benzthiazole-ethyl iodide and diphenyl-formamidine are boiled for 1½ hours with 1.5 grams of trimethylindol-methyl-iodide and 10 cc. of pyridine under reflux. To this mixture while being still warm there are added a few cc. of an aqueous solution of potassium iodide and water. While cooling the reaction mixture the dye separates in form of its iodide. Eventually as by-product formed symmetrical carbo-cyanine from trimethyl-indol-ethyl iodide may be removed by fractional crystallization.

In its alcoholic solution the dye shows an absorption maximum at a wave length of about 585$\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 510$\mu\mu$ to about 700$\mu\mu$ with a maximum at about 620$\mu\mu$.

Further dyes which may be prepared according to the methods described in the foregoing examples are:

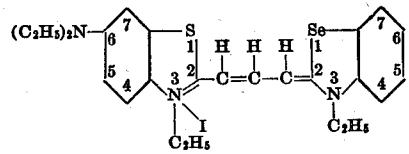
1. [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-benzthiazole-(2)]-trimethinecyanine perchlorate corresponding with the formula



Absorption maximum of the alcoholic solution: about 600$\mu\mu$.

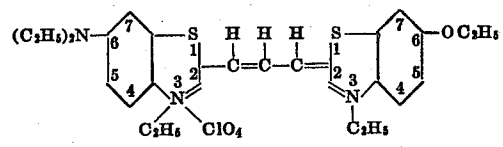
Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 500$\mu\mu$ to about 720$\mu\mu$ with a maximum at about 630$\mu\mu$.

2. [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-benzselenazole-(2)]-trimethinecyanine iodide corresponding with the formula



Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 520$\mu\mu$ to about 710$\mu\mu$, with a maximum at about 630$\mu\mu$.

3. [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-6-ethoxy-benzthiazole-(2)]-trimethinecyanine-perchlorate corresponding with the formula



Absorption maximum of the alcoholic solution: about 603 $\mu\mu$.

Incorporated in a gelatino-silver-bromide emulsion containing about 4 per cent of silver iodide the dye imparts to it a range of sensitivity from about 500$\mu\mu$ to about 730$\mu\mu$ with a maximum at about 645$\mu\mu$.

It is to be understood that our invention is not limited to the foregoing examples nor to the specific details given therein. Numerous other embodiments are possible and we contemplate as included within our invention all such modifications and equivalents as fall within the scope of the appended claims.

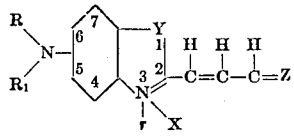
The formulae of the dyes given herein represent the molecular structure of our new dyes so far as to our actual knowledge. If, however, in future it should become evident that the formulae do not exactly correspond to the dyes this

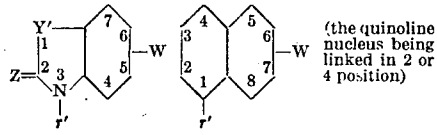
fact will not affect our invention since the dyes will be easily identified by the method of producing the same which has been fully described in the examples. The maxima of sensitivity of our dyes are all very flat and the values indicated may not be regarded too critical.

What we claim is:

1. A photographic material which comprises a silver halide emulsion containing a trimethinecyanine salt which is unsymmetrical when the salt-forming anion is disregarded and which contains an amino group in at least one of the nuclei.

2. A photographic material which comprises a silver halide emulsion containing a carbocyanine salt, which is unsymmetrical when the salt-forming anion is disregarded, corresponding with the formula

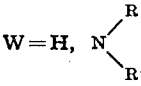




(the quinoline nucleus being linked in 2 or 4 position)

Y = S, Se

Y′ = S, Se, $C(CH_3)_2$, O

W = H, , alkyl, alkoxyl

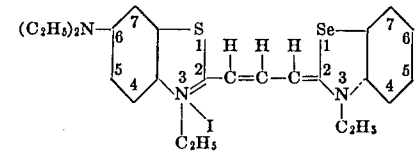
r and r′ = alkyl

R = H, alkyl, aryl, acyl,

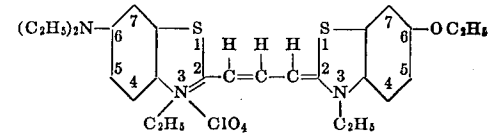
R′ = H, alkyl

X is an anion capable of precipating a carbocyanine dye.

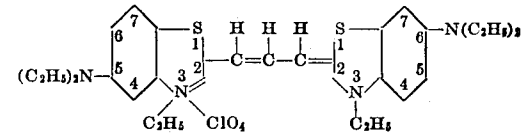
3. A photographic material which comprises a silver halide emulsion containing [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-benzseleenazole-(2)]-trimethinecyanine iodide corresponding with the formula



4. A photographic material which comprises a silver halide emulsion containing [3-ethyl-6-diethylamino-benzthiazole-(2)]-[3-ethyl-6-ethoxy-benzthiazole-(2)]-trimethinecyanine perchlorate corresponding with the formula:



5. A photographic material which comprises a silver halide emulsion containing [3-ethyl-5-diethylamino-benzthiazole-(2)]-[3-ethyl-6-diethylamino-benzthiazole-(2)]-trimethinecyanine perchlorate corresponding with the formula:



WALTER DIETERLE.
WALTER ZEH.
WERNER ZERWECK.