

Jan. 2, 1940.

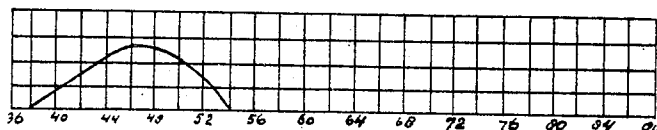
R. STEVENS

2,185,798

PHOTOGRAPHIC EMULSION

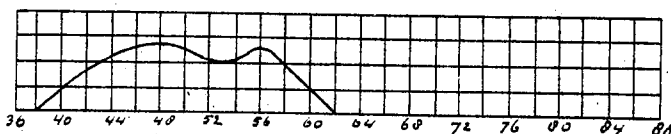
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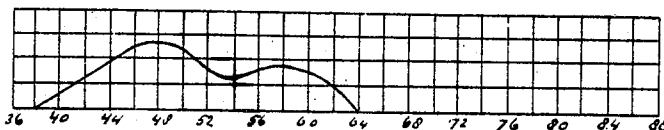
NON-SENSITIZED SILVER  
BROMIDE EMULSION

FIG. 1.



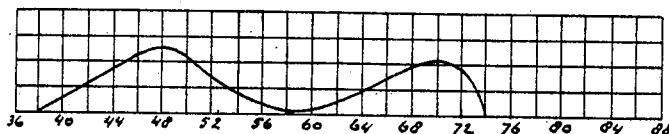
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 1.

FIG. 2.



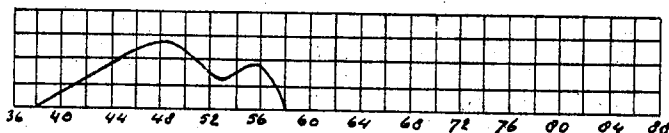
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 2.

FIG. 3.



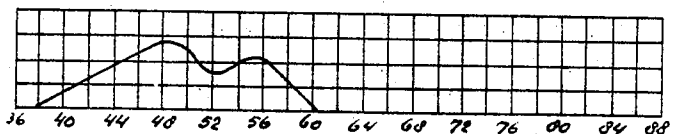
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 3.

FIG. 4.



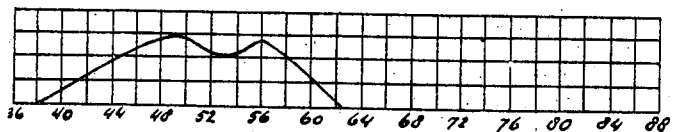
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 4.

FIG. 5.



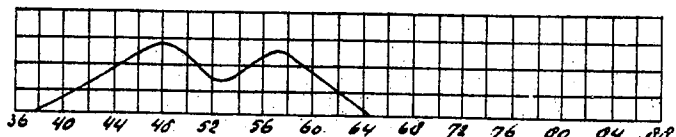
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 5.

FIG. 6.



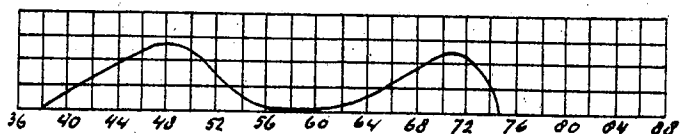
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 6.

FIG. 7.



SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 7.

FIG. 8.



SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYESTUFF OF EXAMPLE 8.

FIG. 9.

INVENTOR

RENÉ STEVENS

by *Michaelis & Michaelis*

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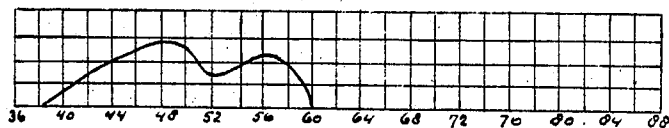
R. STEVENS

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PHOTOGRAPHIC EMULSION

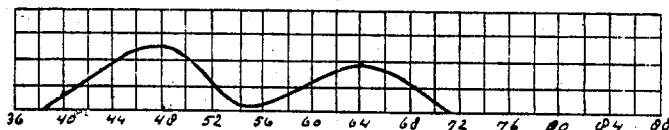
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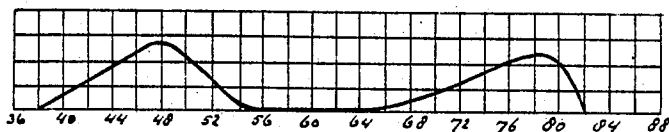
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 9.

FIG. 10.



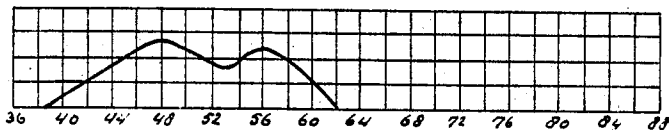
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 10.

FIG. 11.



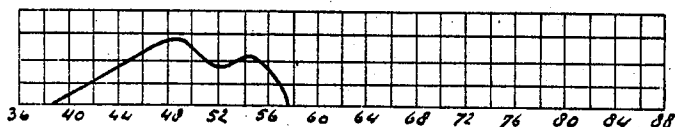
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 11.

FIG. 12.



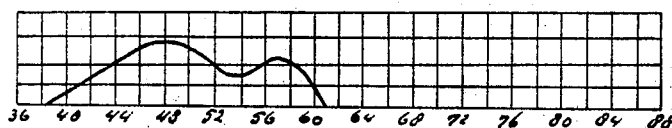
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 12.

FIG. 13.



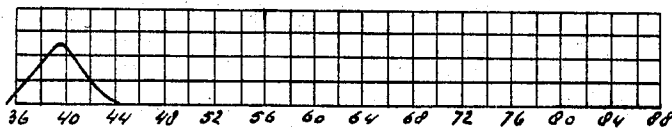
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 13.

FIG. 14.



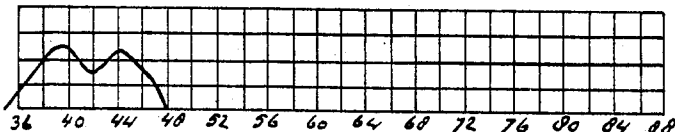
SILVER BROMIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 14.

FIG. 15.



NON-SENSITIZED SILVER  
CHLORIDE EMULSION

FIG. 16.



SILVER CHLORIDE EMULSION  
SENSITIZED WITH THE  
DYE STUFF OF EXAMPLE 15.

FIG. 17.

INVENTOR

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By *Michaëlis & Michaëlis*

ATTYS

## UNITED STATES PATENT OFFICE

2,185,798

## PHOTOGRAPHIC EMULSION

René Stevens, Antwerp, Belgium

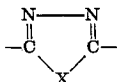
Application August 9, 1938, Serial No. 223,873  
In Austria May 9, 1935

5 Claims. (Cl. 95-7)

The present application is a continuation in part of my applications for U. S. Letters Patent Serial No. 78,408, filed May 7, 1936, and Serial No. 125,039, filed February 10, 1937.

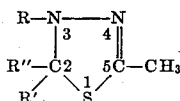
My invention relates to photographic materials and more especially to silver halide emulsions which are sensitized with a new kind of polymethenyl dyestuffs.

In a prior application for U. S. Letters Patent Serial No. 63,737, filed February 13, 1936, I have disclosed as sensitizers for photographic silver halide emulsions dyestuffs which contain at least one thiodiazole ring in which the two nitrogen atoms are in meta positions with respect to the sulfur atom, or to the oxygen or selenium atom, by which the sulfur atom may be replaced according to the formula



wherein X is S or Se or O.

In my further investigations I succeeded in synthetically producing another kind of new polymethenyl dyestuffs useful as photographic sensitizers, which offer certain advantages as compared with the thiodiazole dyestuffs. I found that such sensitizing dyestuffs may be obtained from dihydro-thicdiazole or thiodiazoline compounds provided that the thiodiazoline nucleus is substituted according to the formula



wherein R is an aryl radical and more especially phenyl or alpha mono-halogen-substituted phenyl or alpha naphthyl or beta naphthyl, while R' is H or an alkyl and R'' is an alkyl. Thus, according to my invention polymethenyl dyestuffs can be produced from 3-aryl-2-mono- or dialkyl-2:3-dihydrothiodiazoles(1:3:4), which in the 5-position carry a reactive group such as the methyl group.

The manufacture of these dihydrothiazole or thiodiazoline compounds has been partly described by Wuyts and Lacourt in "Bulletin de la Classe des Sciences de l'Académie Royale de Belgique"—5e Série, XIX, 1933—page 543. Thiodiazolines with a methyl group in the 5-position and which are substituted in the manner required according to my invention may for instance be obtained by condensation of alpha-phenyl, beta-thioacetyl-hydrozine



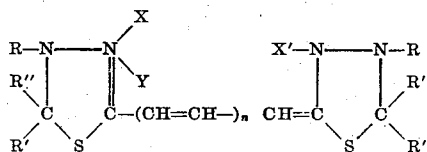
with an aldehyde or a ketone. The phenyl group of this hydrazine compound may be substituted by a halogen atom or may be replaced by naphthyl

for the production of the correspondingly substituted thiodiazolines. All these hydrazine compounds can easily be produced from phenylhydrazine or mono-halogen-phenylhydrazine or naphthylhydrazine by acting thereon with acetic anhydrid and treating the product thus obtained with  $\text{P}_2\text{S}_5$ .

For the production of my new dyestuffs I convert these substituted thiodiazoline bases in any convenient manner, for instance by means of an appropriate ester such as dimethyl sulfate or ethyl iodide or methyl iodide, into the corresponding alkyl quaternary ammonium salts. The quaternary salts thus obtained are treated in the presence of a solvent and of a cyanine-condensing agent, whereby polymethenyl dyestuffs are formed. While substances such as pyridine may be used as solvents, I found that the best yields are obtained with acetic anhydrid as solvent.

The condensing agent serves for introducing the methenyl chain into the dyestuff to be produced. Therefore the substances known to effect condensation in the production of other kinds of cyanine or carbocyanine dyestuffs may be employed in the condensation according to my invention. Such condensing agents are for instance alkyl esters of ortho acids, such as ortho formic or acetic or propionic acid, diphenylformamidine, diphenylacetamidine, beta-ethoxyacroleinacetal, glutaconaldehyde-dianilide-hydrochloride and beta-anilino-acrolein-anil.

In the manner described above symmetrical dyestuffs are obtained of the general formula

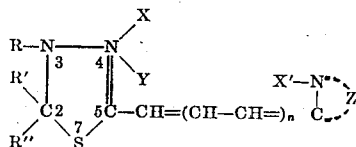


wherein the R are similar or dissimilar phenyl or alpha or beta naphthyl or mono-halogen-substituted phenyl radicals, while the R' are H or similar or dissimilar alkyl radicals, the R'' and X' being similar or dissimilar alkyl radicals, while Y is an inorganic anion, for instance  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{CH}_3\text{SO}_4^-$  or  $\text{CH}_3\text{C}_6\text{H}_4\text{HSO}_4^-$ . n is an integer and may for instance be 0, 1, 2 or 3, but it may also have a considerably higher value such as 6, for my method allows of producing dyestuffs with very long polymethenyl chains. Slightly asymmetrical dyestuffs may be produced by condensing for instance alkyl quaternary salts of 5-methyl-3-aryl-2:3-dihydrothiodiazoles with different alkyl or aryl radicals.

I can however also produce asymmetrical dyestuffs which contain a thiodiazoline nucleus by adding to the mixture of substances to be condensed, as described above, another heterocyclic nitrogen compound and more particularly a

substance selected from the group constituted by the pyridines, quinolines, quinaldines, thiazoles, thiazolines, indolenins, pyrimidines, quinazolines, thiodiazoles, furodiazoles, selenodiazoles, methyl- and ethyl-diazoles, methyl- and ethyl-furodiazoles, methyl- and ethyl-selenodiazoles.

In this manner I obtain dyestuffs of the following general formula



wherein R is again phenyl or mono-halogen-substituted phenyl or naphthyl, R' is H or alkyl, while R'', X and X' are similar or dissimilar alkyls, n is an integer, which may again be 0 or possess a high value such as 6, and Z represents the nonmetallic atoms of a heterocyclic nucleus constituted by five or six members, which nucleus may carry substituents and may form part of a condensed system of nuclei.

Styryl compounds can be obtained on principle in the same manner by employing an appropriate condensing agent, for instance paradimethyl aminobenzaldehyde.

It is an advantage of my invention that a great number of more or less different dyestuffs with more or less different sensitizing capacity and solubility properties can be obtained according to a single method of synthesis by simply varying the aldehyde or ketone with which the aryl hydrazine is condensed in the manner mentioned above. Other dyestuffs of the same class can be obtained by employing different aryl hydrazines as has been described above, or by the use of different esters for the conversion of the substituted thiodiazoline bases into the alkyl quaternary salts. In every case however it is of decisive importance that the nitrogen atom which is not linked with that carbon atom which carries the reactive methyl group, is substituted by an aryl radical and that that carbon atom, which is linked to the aryl-substituted nitrogen atom, carries at least one alkyl group. These substitutions are surprisingly the conditions which allow the condensation into polymethenyl compounds. All the variations mentioned can be effected in practice in a very simple manner and very quickly, since neither the production of the corresponding hydrazine compounds nor their conversion into the thiodiazoline bases offer great difficulties.

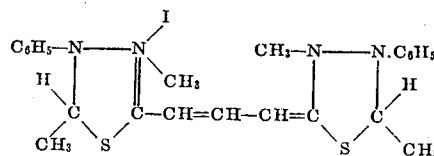
The dyestuffs to be obtained according to my invention can be incorporated in the silver halide emulsion to be sensitized, before, during or after manufacture, or the emulsion layers may be bathed in a solution of the dyestuff.

The invention may be illustrated more in detail by the following examples which show the production of the sensitizing dyestuffs:

#### Example 1

20 grams 2:5-dimethyl-3-phenyl-2:3-dihydrothiodiazole (1:3:4) methiodide, obtained by condensing in a sealed tube equi-molecular quantities of 2:5-dimethyl-3-phenyl-2:3-dihydrothiodiazole (1:3:4) and methyl iodide in a boiling water bath for 24 hours, are dissolved in 200 ccms. acetic anhydrid; 20 ccms. triethyl orthoformate are added and the whole is boiled for 20 minutes in a reflux apparatus. After cooling, the dyestuff is precipitated by the addition of

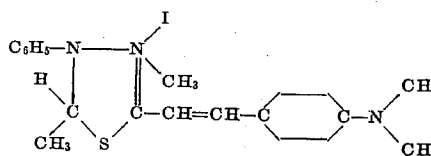
ether, washed with water and recrystallized from alcohol. The dyestuff has probably the following composition:



and sensitizes a gelatine silver halide emulsion up to about 620  $\mu$  with a maximum at 560  $\mu$ .

#### Example 2

8.4 grams of the quaternary salt used in Example 1 is dissolved in 36 ccms. absolute alcohol with 4.2 grams paradimethylaminobenzaldehyde. To the boiling solution are added 3 ccms. piperidine and boiling is continued for 5 minutes. The red dye which is formed immediately, is precipitated, after cooling, with ether, washed with water and recrystallized from a mixture of alcohol and ether. It has most probably the following structure:

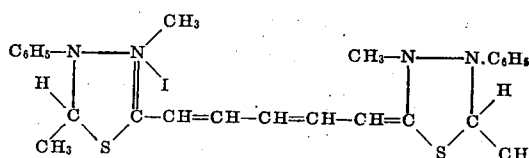


and sensitizes a photographic emulsion up to about 640  $\mu$  with a broad maximum extending from 560 to 580  $\mu$ .

#### Example 3

10 grams of the quaternary salt used in Example 1 are mixed with 5 grams  $\beta$ -anilino-acrolein anil and 2 ccms. acetic anhydrid. The addition of 2 ccms. triethylamine causes immediate formation of a blue dyestuff, which is completed by gentle heating. The dyestuff is precipitated with ether, washed with water until all green by-products are eliminated, and recrystallized from a mixture of methyl alcohol and ether.

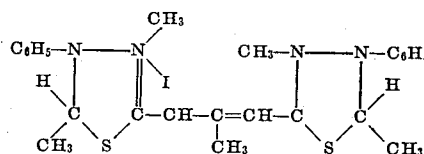
The dye most probably has the following structure:



It sensitizes a photographic gelatine silver halide emulsion between 600 and 740  $\mu$  with a maximum at 720  $\mu$ .

#### Example 4

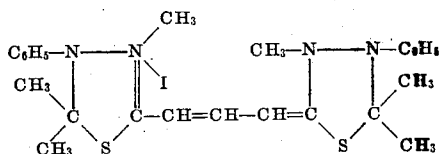
7 grams of the quaternary salt of Example 1 are boiled together with 7 ccms. triethyl orthoacetate in 30 ccms. acetic anhydrid for 3/4 of an hour. The so-formed dyestuff is precipitated with ether, washed with water and recrystallized from a mixture of methyl alcohol and ether. It has most probably the following structure:



The sensitizing action of this dyestuff in a gelatine-silver halide emulsion extends to about 580  $\mu$  with a maximum at 550  $\mu$ .

## Example 5

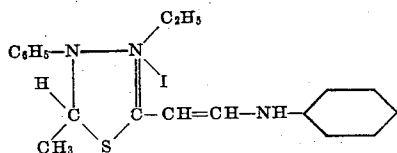
7 grams of the condensation product obtained by heating equimolecular quantities of 2:2':5-trimethyl-3-phenyl-2:3-dihydrothiodiazole (1:3:4) with methyl iodide in a sealed tube in a boiling water bath for 36 hours, are dissolved in 30 ccms. acetic anhydrid and after addition of 15 ccms. triethyl ortho-formate boiling is continued for 1 hour. The so-formed dyestuff is precipitated with ether, washed with water and recrystallized from methyl alcohol. It has most probably the following structure:



and sensitizes a gelatine silver halide emulsion up to  $600\mu$  with a maximum approximately at  $550\mu$ .

## Example 6

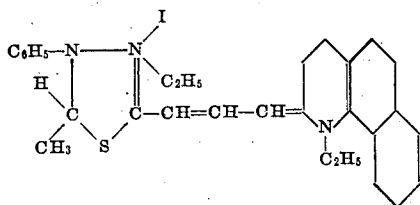
7.9 grams 2:5-dimethyl-3-phenyl-2:3-dihydrothiodiazole (1:3:4) ethiodide are melted with 4.7 grams diphenyl-formamidine at a temperature of  $115^{\circ}\text{C}$ . for about one hour. The product thus obtained has most probably the following structure:



and is useful as an intermediate product for the manufacture of symmetrical and asymmetrical carbocyanines by condensation with various heterocyclic quaternary ammonium salts. A symmetrical dyestuff, having the same characteristics as the dyestuff of Example 1, may for instance be obtained by condensing in the presence of acetic anhydrid an equimolecular quantity of the intermediate product and of 2:5-dimethyl-3-phenyl-2:3-dihydrothiodiazole (1:3:4) ethiodide.

By using the quaternary salt of another heterocyclic nucleus, asymmetrical carbocyanines are obtained.

By boiling together for 10 minutes a mixture of 3 grams of the above-mentioned intermediate product with 1.9 grams  $\alpha$ -naphthylquinoline ethiodide in the presence of 20 ccms. acetic anhydrid, a red dyestuff is formed, having most probably the following composition:

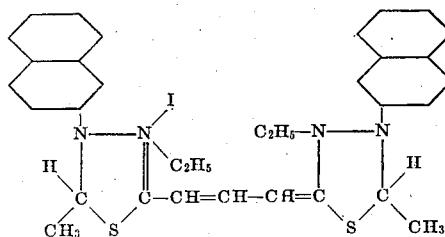


The dyestuff is precipitated with ether, washed with water and recrystallized from a mixture of methyl alcohol and ether. When incorporated in a photographic emulsion, it extends the sensitivity to the longer wave lengths with a maximum near  $550\mu$ .

## Example 7

10 grams 2:5-dimethyl-3-beta-naphthyl-2:3-

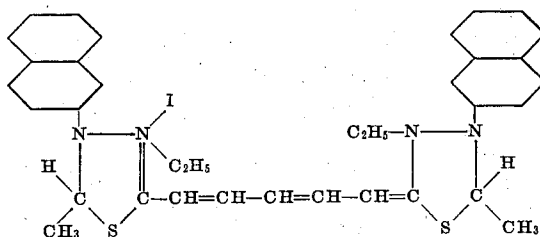
dihydrothiodiazole (1:3:4) are treated with 3.8 ccms. ethyl iodide on the boiling water bath during 14 hours to be converted into the corresponding alkyl quaternary salt. The solid mass thus formed is washed first with a small quantity of ethyl ether and subsequently with acetone. 5 grams of the quaternary salt thus obtained are boiled with 50 ccms. acetic anhydrid and 5.5 ccms. orthoethylformate during 3 hours. A precipitate is produced by an addition of ether and is thoroughly washed first with ether, subsequently with water and finally with a small quantity of acetone. The product obtained is extracted by means of methyl alcohol and from the solution thus obtained the pure dyestuff is precipitated by an addition of ether. This dyestuff has probably the following formula:



and sensitizes a silver halide emulsion up to about  $640\mu$  with a maximum at  $560\mu$ .

## Example 8

2.1 grams of 2:5-dimethyl-3-beta-naphthyl-1-2:3-dihydrothiodiazole (1:3:4) ethiodide are mixed with 0.6 grams of beta-anilino-acrolein-anil-hydrochloride. 3 ccms. triethylamine are added to this mixture and the whole is moderately heated on the water bath until it has assumed a beautiful blue color. Ether is now added to form a precipitate which is washed with water and thereupon partly dissolved in alcohol. The dyestuff is precipitated from this alcoholic liquor by an addition of ether and has probably the following formula:

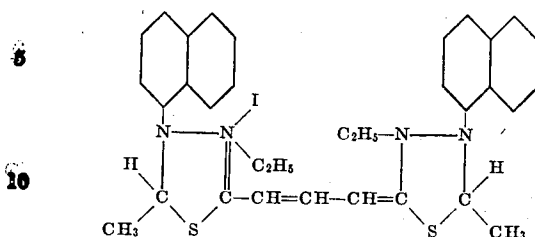


It sensitizes a silver halide emulsion up to about  $740\mu$  with a maximum at  $720\mu$ .

## Example 9

10 grams 2:5-dimethyl-3-alpha-naphthyl-2:3-dihydrothiodiazole (1:3:4) are heated with 3.8 ccms. ethyl iodide on the boiling water bath during 14 hours. The solid product thus obtained is washed first with a small quantity of ether and subsequently with acetone. 5 grams of the quaternary salt thus obtained are mixed with 50 ccms. acetic anhydrid and 5.5 ccms. ortho-ethyl-formate and the mixture is boiled during 3 hours. A precipitate is produced by the addition of ether and is thoroughly washed first with ether, subsequently with water and finally with a small quantity of acetone. The washed product is extracted with methyl alcohol and from the solution thus obtained the pure dyestuff is precipi-

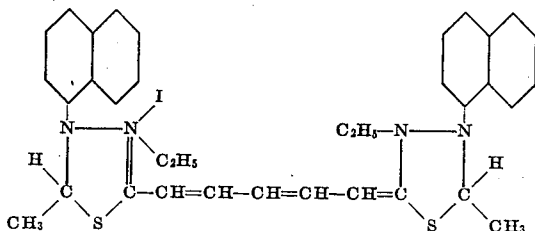
tated by an addition of ether. The dyestuff has probably the following formula:



and sensitizes a silver halide emulsion up to about 600 $\mu$  with a maximum at 560 $\mu$ .

#### Example 10

2.1 grams 2:5-dimethyl-3-alpha-naphthyl-2:3-dihydrothiadiazole (1:3:4)-ethiodide are mixed with 0.6 grams alpha-aniline-acrolein-anil-hydrochloride and with 3.5 ccms. acetic anhydrid. 3 ccms. triethylamine are added to the mixture and the whole is moderately heated on the water bath until it has assumed a beautiful blue color. Ether is now added to produce a precipitate which is washed with water and thereupon extracted with alcohol. The dyestuff is obtained from the solution thus produced by an addition of ether. It probably possesses the following formula:



It sensitizes a silver halide emulsion up to about 700 $\mu$  with a maximum at 650 $\mu$ .

Naphthyl-thiadiazolines such as are used as starting materials in Examples 7 to 10, can be obtained in a similar manner as the corresponding phenyl-thiadiazolines. In order to prepare the alpha-naphthyl compounds, one may start from alpha-naphthyl-hydrazines, which are treated according to the method of Freund-Schuftan ("Berichte der Deutschen Chemischen Gesellschaft", vol. 24, page 4183) with an excess of acetic anhydrid, yielding needles of N'-acetyl-N-alpha-naphthyl-hydrazine with a melting point of 142-143° C. This compound is thereafter boiled during half an hour with P<sub>2</sub>S<sub>5</sub> in benzene, whereby N'-thioacetyl-N-alpha-naphthyl-hydrazine is formed which can be extracted from the benzene solution by means of NaOH and can be precipitated from the solution thus obtained with HCl. The thio-compound, when re-crystallized from water, melts at 120° C. Condensation of the thio-compound with aldehydes or ketones results in the formation of the corresponding alpha-naphthyl-thiadiazolines.

N'-thio-acetyl-N-alpha-naphthyl-hydrazine may for instance be condensed with acetic aldehyde according to the method of Wuyts, whereby 2:5-dimethyl-3-alpha-naphthyl-2:3-dihydrothiadiazole (1:3:4), melting at 61° C., is obtained. Condensation with acetone results in the formation of 2:2':5-trimethyl-3-alpha-naphthyl-2:3-dihydrothiadiazole (1:3:4), melting at 125° C. Condensation with formaldehyde results in the formation of an oil composed of 5-methyl-3-alpha-naphthyl-2:3-dihydrothiadiazole (1:3:4). The beta-naphthyl compounds, for instance

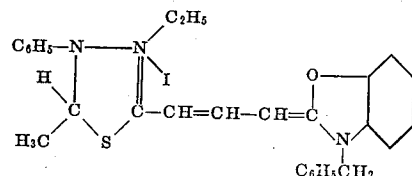
2:5-dimethyl-3-beta-naphthyl-2:3-dihydrothiadiazole (1:3:4), melting at 125-126° C., or 5-methyl-3-beta-naphthyl-2:3-dihydrothiadiazole (1:3:4), melting at 133-135° C., can be synthesized in an analogous manner.

#### Example 11

3 grams 2:5-dimethyl-3-phenyl-2:3-dihydrothiadiazole (1:3:4)-ethiodide and 1.2 grams glutacone-dialdehyde-dianil hydrochloride and 2 ccms. triethylamine are boiled 20 minutes in 15 ccms. alcohol. While the solution is allowed to cool, a blue dyestuff crystallizes out, which is washed with water and re-crystallized from alcohol. This dyestuff is a symmetrical heptacarbocyanine with  $n=3$ . It sensitizes a silver bromide gelatine emulsion from 660 $\mu$  to 820 $\mu$  with a maximum at about 780 $\mu$ .

#### Example 12

Equimolecular quantities of ethyl iodide and 2:5-dimethyl-3-phenyl-2:3-dihydrothiadiazole (1:3:4) are heated in a boiling water bath during 36 hours; 4.5 grams of the quaternary salt thus obtained are condensed with an equimolecular quantity, amounting to 2.7 grams, of diphenylformamidine by heating the mixture 30 minutes in an oil bath to 120° C. The condensation product is washed with water and re-crystallized from alcohol. Equimolecular quantities, viz. 1 gram of the condensation product and 0.7 gram benzoxazole-benzylbromide are boiled in 5 ccms. pyridine during 20 minutes. The dyestuff thus formed is precipitated with ether, washed with water and re-crystallized from alcohol. It has most probably the following structure:



The alcoholic solution of this dyestuff absorbs up to about 590 $\mu$ . The dyestuff sensitizes a silver halide emulsion up to about 620 $\mu$  with a maximum at 560 $\mu$ .

#### Example 13

2:5-dimethyl-3-alpha-naphthyl-2:3-dihydrothiadiazole (1:3:4)-ethiodide is condensed with benzoxazole-benzylbromide in the same manner as described with reference to Example 12. The product is an asymmetrical carbocyanine dyestuff which absorbs up to about 538 $\mu$ , while sensitizing up to about 565 $\mu$  with a maximum at 530 $\mu$ .

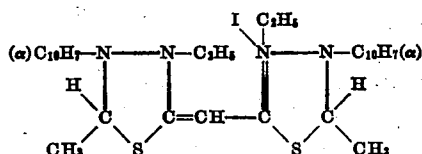
#### Example 14

An asymmetrical carbocyanine which absorbs up to about 568 $\mu$ , while sensitizing up to about 600 $\mu$  with a maximum at 560 $\mu$ , can be obtained from 2:5-dimethyl-3-beta-naphthyl-2:3-dihydrothiadiazole (1:3:4)-ethiodide and benzoxazole-benzylbromide in the manner described with reference to Example 12.

#### Example 15

2.4 grams 2:5-dimethyl-3-alpha-naphthyl and 2:3-dihydrothiadiazole (1:3:4) are heated in a water bath under increased pressure with 1.5 ccms. ethyl chloride during 20 hours. 2.3 grams of the quaternary salt thus obtained are dissolved in 36 ccms. acetic anhydrid. 3 ccms. amyl nitrite are added to this solution at 50° C. The

temperature of 50° C. is maintained during 2 hours, whereupon a dyestuff compound can be precipitated with ether. This compound is thereafter dissolved in alcohol and the ethiodide of the dyestuff is precipitated from the alcoholic solution by means of a saturated solution of potassium iodide. The dyestuff is washed with water and re-crystallized from alcohol. Most probably it has the following structure:



The alcoholic solution of this dyestuff absorbs up to about 440 $\mu$ . A silver halide emulsion is sensitized by the dyestuff up to about 470 $\mu$  with a maximum at 440 $\mu$ .

The drawings affixed to this specification and forming part thereof show sensitizing curves of some non-sensitized emulsions and of emulsions sensitized with the dyestuffs described in the above examples.

In the drawings,

Fig. 1 is the sensitizing curve of a non-sensitized silver-bromide emulsion as usually employed for photographic materials.

Figs. 2-15 are corresponding curves of an emulsion of the same kind, but sensitized by an addition of the dyestuffs of the above Examples 1 to 14, respectively, while

Fig. 16 is the corresponding curve of a non-sensitized silver-chloride emulsion and

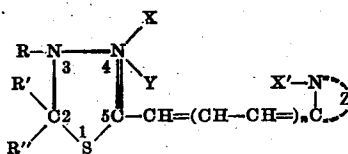
Fig. 17 the curve of the same emulsion sensitized with the dyestuff of Example 15.

The correctness of the formulae, used in this specification and the claims affixed to it, for defining the new substances depends on the correctness of the assumptions nowadays adopted by the experts in the field of cyanine and related dyestuffs. Therefore although these formulae may be subject to corrections or changes in correspondence with the scientific development of chemistry, they clearly designate to the expert, who knows the present state of the art, the nature of the substances thus defined.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

I claim:

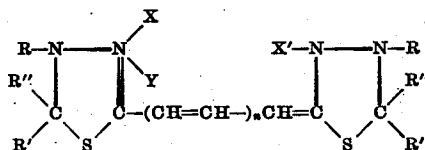
1. As a photographic material, a silver halide emulsion with an addition of a dyestuff of the general formula



wherein R is a member of the group constituted by phenyl, the naphthyls and the mono-halogen-substituted phenyls, while R' is a member of the group constituted by H and the alkyls, R'', X and X' are alkyls, Y is an anion and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five- and six-membered heterocyclic nuclei; n being a member of the group constituted by the integers including 0.

2. As a photographic material, a silver halide emulsion with an addition of a dyestuff as defined in claim 1, wherein the nucleus, which is completed by the atoms represented by Z, forms part of a condensed system of nuclei.

3. As a photographic material, a silver halide emulsion with an addition of a dyestuff of the general formula



wherein the R are members of the group constituted by phenyl, the naphthyls and the mono-halogen-substituted phenyls, while the R' are members of the group constituted by H and the alkyls, R'', X and X' are alkyls and Y is an inorganic anion; n being a member of the group constituted by the integers including 0.

4. As a photographic material, a silver halide emulsion with an addition of a dyestuff as defined in claim 1, wherein the polymethenyl chain carries a substituent.

5. As a photographic material, a silver halide emulsion with an addition of a dyestuff as defined in claim 3, wherein the polymethenyl chain carries a substituent.

RENÉ STEVENS.