

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC EMULSION

No Drawing.

Application filed December 31, 1930. Serial No. 505,982.

This invention relates to a new composition of matter, and particularly to a new class of photographic sensitizing dyes, and a method for their preparation, and emulsions containing them.

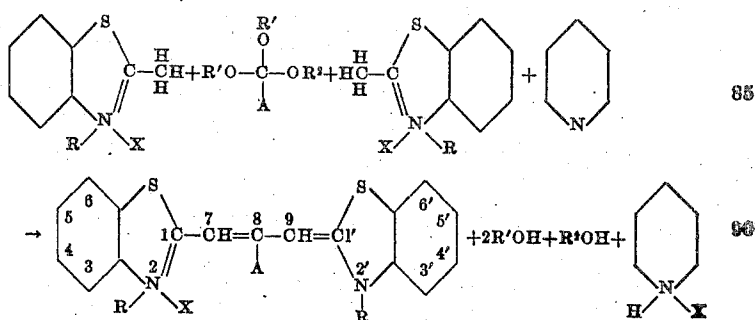
As ordinary photographic emulsions are generally indifferent to those colors of the spectrum of longer wave lengths, various types of sensitizing dyes have been suggested for incorporation in photographic emulsions, or for employing over emulsions as overcoatings so as to increase the spectral sensitiveness thereof. Many cyanine dyes have been described for this purpose containing the benzothiazole nucleus, whilst classes of these photo-sensitizing dyes containing the naphthothiazole nucleus are described in my co-pending applications of Serial Nos. 337,177, filed February 2, 1929; 435,104 and 435,105, filed March 12, 1930; and 437,017, filed March 19, 1930, whilst those containing the thiazoline nucleus are described in my co-pending application Serial No. 460,548 filed June 11, 1930, and those containing the thiazole nucleus, are described in my co-pending application Ser. No. 548,026, filed June 30, 1931.

An object of the present invention is to provide a process for the preparation of photo-sensitizing dyes of the thiocarbocyanine series containing benzothiazole nuclei

added to photographic emulsions or coated thereon as an overcoating whereby the spectral sensitivity of the photographic emulsion is increased. Other objects will hereinafter appear, such as to provide a photographic emulsion which contains or in which is incorporated or which has been treated with the herein described photo-sensitizing dyes. This silver halide emulsion may be of the gelatino silver halide type or, in fact, any type of photographic emulsion customarily employed in the art.

I have found that dyes having good photo-sensitizing properties may be prepared by the treatment of a 1-methylbenzothiazole alkyl quaternary salt with an ortho-ester of an aliphatic carboxylic acid, the acid corresponding to which contains more than two carbon atoms in the molecule. The reaction may be carried out in boiling dry pyridine. Ortho-esters of the carboxylic acids which have been found particularly suitable include such esters as trimethyl ortho-propionate, methyldiethyl ortho-n-caproate, methyldiethyl ortho-iso-caproate, and trimethyl ortho-valerate.

The reaction of a 1-methylbenzothiazole alkyl quaternary salt with one of these ortho-esters of a carboxylic acid in the presence of pyridine may be written graphically as follows:



and having alkyl substituents with more than one carbon atom in the radical attached to the central carbon atom of the three-carbon chain.

A further object of this invention is to provide such photo-sensitizing dyes as may be

In the above structures R represents an alkyl group and X an acid radical. A stands for the alkyl group to be introduced into the three-carbon chain of the thiocarbocyanine dye and OR' and OR2 represent the alkoxy groupings of the ortho-ester and these may

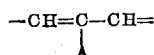
be similar or dissimilar. The dye molecule is numbered as shown, so that a compound of this type may be described as a 2:2'-dialkyl-8-alkyl-thiocarbocyanine salt.

In the actual practice it is frequently desirable to carry out the condensation with an acid radical such as the p-toluenesulfonate, which confers a comparatively high degree of solubility on the 1-methylbenzothiazole alkyl quaternary salt and on the dye. The latter is then conveniently isolated as a less soluble salt by double-decomposition in the ordinary way, such salts as ammonium or potassium bromide or iodide being employed for this purpose, usually in aqueous solution.

The $-\text{CH}=\text{CH}-$ group is called the methenyl group and therefore the chain



may be called a tri-methenyl chain, and the chain



may similarly be called a tri-methenyl chain in which the hydrogen attached to the central carbon atoms has been replaced by the group denoted by the letter A.

The nomenclature and numbering of the above classes of compounds and intermediates are in accord with present usage and also the system used in my co-pending applications given above. The numbering, of course, is arbitrary and is given for the guidance of those skilled in the art in order that there be no question as to the identity of a compound covered by my invention.

The methods for the formation of the 1-methylbenzothiazoles (used in the preparation of the photographic sensitizing dyes herein described) are given in the literature. One general method consists of the conversion of the acetyl compound of an aromatic primary amine, such as p-toluidine, into the thio-acetyl compound by the action of phosphorous pentasulfide. This thio-acetyl compound is then dissolved in aqueous caustic alkali solution and oxidized with a cold aqueous solution of alkali ferricyanide whereupon the base is produced and may be extracted with ether.

The preparation of some of the ortho-esters of the aliphatic carboxylic acids, the acids corresponding to which have more than two carbon atoms in the molecule have not, however, been described in the literature and I will give here, therefore, one method for their preparation. These ortho-esters are prepared by taking the nitrile of the corresponding acid as the starting material. The nitrile (one mol.) is dissolved in dry absolute ethyl ether together with an alcohol (1 mol.) such as methyl or ethyl alcohol, all of the reactants being as free from moisture as possible, and dry hydrochloric acid gas

(rather more than 1 mol.) is led in, using good cooling throughout the operation. The imino-ether hydrochloride separates and the whole is kept cold until crystallization appears to be complete, when the crystals are filtered off, carefully washed with dry absolute ethyl ether and dried in a vacuum over solid caustic potash until free from all excess of hydrochloric acid. The dry imino-ether hydrochloride is then decomposed at room temperature with an alcohol, taking roughly 2 cc. of the alcohol, as free from moisture as possible, for every gram of the hydrochloride. The latter dissolves more or less completely and the formation of the ortho-ester is accompanied by the separation of ammonium chloride, the formation of which may be used as an indication of the course of the reaction.

The reaction vessel is tightly stoppered and allowed to stand for several days or even several weeks until the reaction is apparently complete. The insoluble material is then filtered off and the excess alcohol is removed by distillation, filtering again if necessary. The ester is finally distilled over, using diminished pressure as a rule, and is purified by refractionation. Thus propionitrile on treatment with methyl alcohol and hydrochloric acid gas in the manner described above yields propio-imino-methyl-ether hydrochloride, and this, when subjected to the action of methyl alcohol in the manner described, yields trimethyl ortho-propionate. Mixed esters may be made by taking two different alcohols for the two separate steps of the reaction. Thus n-capronitrile may be converted into n-capro-imino-methyl-ether hydrochloride by the joint action of methyl alcohol and hydrochloric acid gas and this on further treatment with ethyl alcohol yields methyl-diethyl ortho-n-caproate as the principal product. The ortho-esters of other aliphatic carboxylic acids having more than two carbon atoms in the molecule may be prepared in a similar manner.

I will now give several examples for preparing various dyes referred to, but it will be understood that they are merely representative of a great number of reactions in which the proportions given and equivalents used may vary in accord with the particular type of dye required. My invention, therefore, will not be restricted thereby except as indicated in the appended claims.

The 1-methylbenzothiazole used in any of the described condensations may be unsubstituted in the benzene nucleus, or it may be substituted therein, as for example by a fused-on benzene nucleus, as described in my co-pending application Serial No. 435,104.

Example 1.—2:2':8 - triethylthiocarbocyanine iodide

6.1 g. (1 mol.) of 1-methylbenzothiazole

ethiodide was refluxed for one hour with 5.4 g. (2 mols., 300% excess) trimethyl ortho-propionate and 30 cc. dry pyridine. The solution was well diluted with water and let stand for several days to crystallize out. Greenish-bronze crystals were obtained, weighing 0.6 g., which were crystallized from a mixture of acetone and methyl alcohol. Dark green prisms separated showing a bronze reflex and the solution was bluish-red.

A larger yield of the material was obtained as follows: 7 g. (1 mol.) of 1-methylbenzothiazole etho-p-toluene-sulfonate was boiled under reflux for one hour with 2.7 g. (1 mol.) trimethyl ortho-propionate and 7 cc. dry pyridine. A warm solution of 10 g. potassium iodide in 50 cc. water was added and the iodide of the dye was filtered off when cold and obtained as a dull greenish-black powder weighing 3.67 g. after washing with water and with cold acetone. This was crystallized from 50 cc. methyl alcohol using an extraction apparatus and on cooling the dye crystallized out in beautiful prisms, some faces of which reflected blue light and others green light.

If in place of the 1-methylbenzothiazole etho-p-toluene-sulfonate used above, one employs 6.7 g. (1 mol.) of 1-methylbenzothiazole metho-p-toluenesulfonate (made by condensing equimolecular proportions of 1-methylbenzothiazole and methyl-p-toluenesulfonate together overnight on the steam bath and crystallizing the crude salt from methyl alcohol and drying it well) and refluxes it for an hour with 2.7 g. (1 mol.) of trimethyl ortho-propionate and 20 cc. pyridine, 2:2'-dimethyl-8-ethylthiocarbocyanine p-toluenesulfonate will be produced. The dye may be isolated as the bromide by precipitating it with an excess of an aqueous solution of ammonium bromide and weighed 2.9 g. when dry. The dye crystallizes from methyl alcohol in purplish-brown needles with a green reflex, and gives a bluish-red solution in this solvent.

Example 2.—8-ethyl-2:2'-diallylthiocarbocyanine iodide

12.7 g. (1 mol.) of 1-methylbenzothiazole alliodide (made by condensing the base with an equivalent amount of allyl iodide and purifying the product by recrystallizing it) was refluxed for forty-five minutes with 10.8 g. (2 mols.) trimethyl ortho-propionate and 40 cc. of pyridine. A solution of 10 g. of potassium iodide in 200 cc. of water was added and the mixture cooled in ice water and stirred with ether to induce crystallization. The dye was filtered off, washed alternately with water and with acetone and dried. A dull purplish-brown powder weighing 1.67 g. was obtained. The dye was obtained (free

from a less soluble by-product) as dark greenish crystals with a pale bronze reflex.

Example 3.—5:5'-dimethyl-2:2':8-triethylthiocarbocyanine iodide

4.1 g. (1 mol.) 1:5-dimethylbenzothiazole was heated overnight in an oil bath at 140–150° C. with 5.5 g. (1.1 mol.) ethyl p-toluene-sulfonate. The crude quaternary salt was then refluxed for forty-five minutes with 4.4 g. (1 mol.) triethyl ortho-propionate and 20 cc. dry pyridine. A solution of 20 g. potassium iodide in 100 cc. hot water was used to precipitate the dye as the iodide, and after the mixture had cooled, the dye was filtered off and washed, and 3.4 g. of a dark green crystalline powder was obtained on drying. The dye was crystallized from methyl alcohol, dark green crystals being obtained which gave a bluish-red solution in this solvent.

Example 4.—2:2'-dimethyl-8-n-butylthiocarbocyanine iodide

6.7 g. (1 mol.) of 1-methylbenzothiazole metho-p-toluene-sulfonate was refluxed with 6.5 g. (2 mols.) trimethyl ortho-n-valerate (obtained from n-valeronitrile) and 15 cc. dry pyridine for forty minutes. The dye was precipitated as the iodide using 10 g. of potassium iodide dissolved in 50 cc. of hot water, when a felted mass of crystals was obtained which weighed 3.1 g. after filtering, washing and drying. When recrystallized from methyl alcohol the dye formed dark purplish needles with a greenish-blue reflex. The solution of the dye in methyl alcohol was bluish-red.

Example 5.—2:2'-diethyl-8-n-butylthiocarbocyanine iodide

7.0 g. (1 mol.) 1-methylbenzothiazole etho-p-toluene-sulfonate was refluxed with 6.5 g. (2 mols.) of trimethyl ortho-n-valerate and 20 cc. dry pyridine for forty minutes. The dye was precipitated as the iodide using a solution of 20 g. potassium iodide in 100 cc. hot water, when rapid crystallization occurred. The dye weighed 3.8 g. after filtering, washing and drying, and when recrystallized from methyl alcohol formed beautiful greenish-gray crystals with a marcasite-like lustre, which gave a bluish-red solution in the solvent.

Example 6.—2:2'-dimethyl-8-n-amylthiocarbocyanine iodide

6.7 g. (1 mol.) 1-methylbenzothiazole metho-p-toluene-sulfonate was refluxed for an hour with 8.2 g. (2 mols.) of methyl-diethyl ortho-n-caproate (obtained from n-capronitrile) and 30 cc. dry pyridine. The dye was then precipitated as the iodide using a solution of 10 g. potassium iodide in 50 cc. hot water for this purpose. The product

crystallized on cooling and was filtered off, washed, and dried. Weight 3.4 g. Reddish needles with a brilliant blue reflex were obtained on recrystallizing the dye from methyl alcohol, the solution being bluish-red.

Example 7.—2:2'-diethyl-8-n-amylthiocarbocyanine iodide

7.0 g. (1 mol.) 1-methylbenzothiazole etho-
p-toluene-sulfonate was refluxed for about an
hour with 8.2 g. (2 mols.) methyldiethyl
ortho-n-caproate and 15 cc. dry pyridine.
The reaction mixture was then treated with
a solution of 10 g. potassium iodide dissolved
in 50 cc. of hot water and the whole allowed
to stand overnight. The product, when fil-
tered, washed with water followed by ace-
tone, and dried, weighed 3.5 g. The dye
crystallized from methyl alcohol in greenish-
bronze granular crystals and gave a bluish-
red solution.

*Example 8.—2:2'-dimethyl-8-isoamylthio-
carbocyanine iodide*

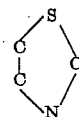
6.7 g. (1 mol.) 1-methylbenzothiazole
metho-p-toluene-sulfonate was refluxed with
8.2 g. (2 mols.) methyldiethyl ortho-isocapro-
ate (obtained from isocapronitrile) and 20
cc. pyridine for forty minutes. The dye was
precipitated as the iodide, using a solution
of 10 g. potassium iodide in 50 cc. of hot
water, and weighed 1.8 g. when filtered off,
washed, and dried. It crystallized from
methyl alcohol in compact dark bluish-grey
prisms with a green reflex, and gave a bluish-
red solution in this solvent.

By substituting various alkyl groups hav-
ing more than one carbon atom in the posi-
tion in the structural formula of the dye oc-
cupied by the letter A, and various alkyl
groups in the two positions occupied by the
letter R, many sensitizing dyes may be ob-
tained. The letter X indicates any suitable
anion such, for example, as a halide, p-tol-
uenesulfonate, alkylsulphate, nitrate, ace-
tate, perchlorate, or, in fact, any salt forming
anion that will not render the dye too spar-
ingly soluble or deleteriously affect the
photographic sensitizing properties of the
dye.

In the preparation of emulsions containing
these photographic sensitizers, it has been
found that the dye may be dissolved in
methyl alcohol and a volume of solution con-
taining from 5 to 100 milligrams of dye added
to 1000 cc. of emulsion. While it may not be
necessary to add some of the sensitizers in a
large amount, it may be necessary to add
others in amounts larger than those given
above; generally about 10 to 20 milligrams is
sufficient to obtain the maximum sensitizing
effect with a dye having good sensitizing
power. The more powerful dyes, however,
may require much less. The regulation or
adoption of the most economical proportions

will be apparent to those skilled in the art
upon observing the sensitizing power of the
particular dye for the particular emulsion to
be formed. The above examples are, there-
fore, illustrative and not to be understood as
limiting the invention in any sense, as it will
be apparent that these dyes may be incor-
porated by other methods in many of the
photographic emulsions customarily employ-
ed in the art, such for instance as by bathing
the plate or film, upon which the emulsion has
been coated, in a solution of the dye in an
appropriate solvent although this method of
incorporating the dye in the emulsion is not
preferred over that above described. Ob-
viously the claims are all intended to cover
any combination of these dyes with a photo-
graphic emulsion whereby the dye exerts a
sensitizing effect upon the emulsion.

It is apparent from a thorough considera-
tion of the above description that any thio-
carbocyanine dye prepared from a 1-methyl-
benzothiazole unsubstituted or substituted, in
which the 8 position of the dye is substituted
by an alkyl group containing more than one
carbon atom, will come within the scope of
this invention whatever may be the radicals
occupying the other substitutable positions of
the structure, together with the employment
of such dyes for photographic sensitizing
and other purposes. Furthermore, it will
also be apparent that the genus claimed here-
inafter not only includes the foregoing but
also includes any carbocyanine dye contain-
ing two of the five-membered rings.



linked together by a tri-methenyl chain, the
hydrogen attached to the central carbon atom
of which is substituted by an alkyl group
containing more than one carbon atom such
as, for example, the 8-substituted thiocarbo-
cyanines derived from mu-methylnaphtho-
thiazole described in my application Serial
No. 435,104, the 7-substituted thiazolino-
carbocyanines derived from 2-methylthiazolo-
line described in my application Serial No.
460,548 and the 7-substituted thiazolocarbo-
cyanines derived from 2-methylthiazole
described in my application Ser. No. 548,026.

In the claims, by an ortho-ester of an al-
iphatic carboxylic acid is meant an ortho-ester
of a carboxylic acid, the acid corresponding
to which contains a simple, unsubstituted
alkyl group directly attached to the carbon
atom of the carboxyl group. Examples of
such ortho-esters have already been given.

What I claim as my invention and desire
to be secured by Letters Patent of the United
States is:

1. A photographic gelatino-silver-halide
emulsion which contains a carbocyanine dye

comprising two heterocyclic rings of the structure



alkyl group contains more than one carbon atom.

12. A photographic gelatino silver halide emulsion which contains 5:5'-dimethyl-2:2'-8-triethylthiocarbocyanine iodide. 70

13. A photographic gelatino silver halide emulsion which contains 2:2'-dimethyl-8-n-butylthiocarbocyanine iodide.

14. A photographic gelatino silver halide emulsion which contains 2:2'-dimethyl-8-ethyl-thiocarbocyanine bromide. 75

15. As an article of manufacture, a supporting surface coated with a photographic gelatino-silver-halide emulsion including a 2:2'-dialkyl-8-alkylthiocarbocyanine salt in which the 8-alkyl group contains more than one carbon atom. 80

Signed at Rochester, N. Y., this 29th day of December, 1930.

LESLIE GEORGE SCOTT BROOKER. 85

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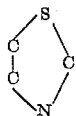
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linked together by a tri-methenyl chain, the hydrogen of the central carbon atom of which has been substituted by an alkyl radical containing more than one carbon atom.

2. A photographic gelatino-silver-halide emulsion which contains a carbocyanine dye resulting from the condensation of two molecular proportions of a compound containing a heterocyclic ring of the structure



with one molecular proportion of an ortho-ester of a monobasic aliphatic carboxylic acid having more than two carbon atoms.

3. A photographic gelatino silver halide emulsion which contains a thiocarbocyanine dye substituted in the 8 position with an alkyl radical containing more than one carbon atom.

4. A photographic gelatino silver halide emulsion which contains a thiocarbocyanine dye substituted in the 8 position with an alkyl radical containing more than one carbon atom, said dye containing two benzothiazole nuclei.

5. A photographic gelatino silver halide emulsion which contains a 2:2'-dialkyl-8-alkylthiocarbocyanine salt in which the 8-alkyl group contains more than one carbon atom.

6. A photographic gelatino silver halide emulsion which contains a 2:2'-dialkyl-8-alkylthiocarbocyanine salt in which the 8-alkyl group contains more than one carbon atom, said salt containing two benzothiazole nuclei.

7. A photographic gelatino silver halide emulsion which contains a thiocarbocyanine dye resulting from the condensation of two molecules of a 1-methylbenzothiazole alkyl quaternary salt with an ortho-ester of a monobasic aliphatic carboxylic acid having more than two carbon atoms.

8. A photographic gelatino silver halide emulsion which contains a 5:5'-dimethyl-2:2'-8-triethylthiocarbocyanine salt.

9. A photographic gelatino silver halide emulsion which contains a 2:2'-dimethyl-8-n-butylthiocarbocyanine salt.

10. A photographic gelatino silver halide emulsion which contains a 2:2'-dimethyl-8-ethyl-thiocarbocyanine salt.

11. A photographic gelatino silver halide emulsion which contains a 2:2'-dialkyl-8-alkylthiocarbocyanine halide in which the 8-

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