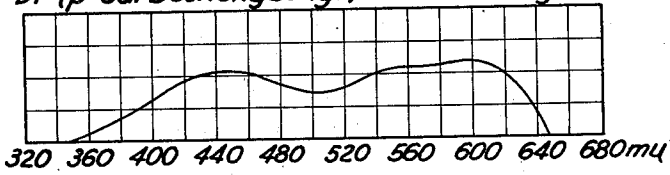
Feb. 11, 1941. L. G. S. BROOKER ET AL 2,231,658

PHOTOGRAPHIC EMULSION

Filed Dec. 16, 1937

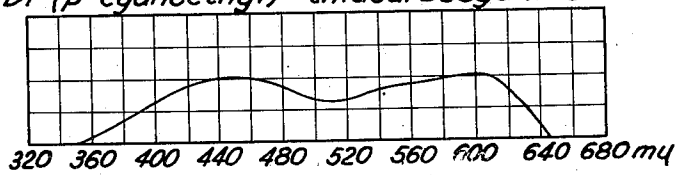
2,2'-Di-(β-carbethoxyethyl)-thiacarbocyanine Iodide.

FIG. 1



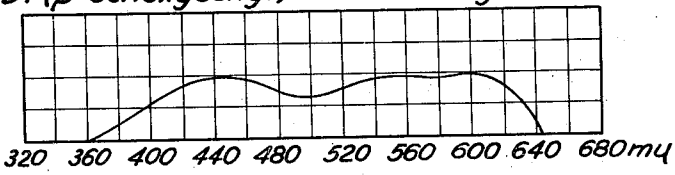
2,2'-Di-(β-cyanoethyl)-thiacarbocyanine Iodide.

FIG. 2



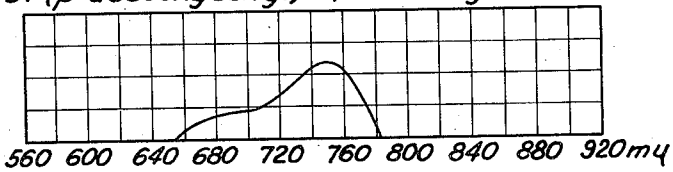
2,2'-Di-(β-ethoxyethyl)-thiacarbocyanine Iodide.

FIG. 3



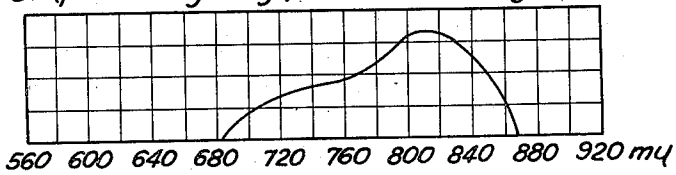
1,1'-Di-(β-acetoxyethyl)-4,4'-carbocyanine Iodide.

FIG. 4



2,2'-Di-(β-acetoxyethyl)-thiatricarbocyanine Iodide.

FIG. 5



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UNITED STATES PATENT OFFICE

2,231,658

PHOTOGRAPHIC EMULSION

Leslie G. S. Brooker and Lloyd A. Smith, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application December 16, 1937, Serial No. 180,214

14 Claims. (Cl. 95—7)

This invention relates to new dyes and to photographic emulsions containing the same.

This application is a continuation-in-part of our co-pending application Serial No. 133,524, filed March 29, 1937.

A number of cyanine dyes are known and some of these have been found to sensitize photographic emulsions in a number of different useful manners. We have now found that cyanine dyes of the sensitizing types, in which at least one of the alkyl groups on the cyanine nitrogen atoms is an oxygen-containing alkyl group which is devoid of aryl group substituents or a cyanogen-containing alkyl group which is devoid of aryl group substituents or a halogen-containing alkyl group which is devoid of aryl group substituents are very useful sensitizers from various standpoints. Our new sensitizers are particularly useful in sensitizing photographic emulsions to light of longer wavelengths, i. e. to light of the red, far-red and infra-red regions of the spectrum.

Accordingly, it is among the objects of our invention to provide new photographic emulsions sensitized with new cyanine dyes, particularly photographic emulsions sensitized to the red, far-red and infra-red with new cyanine dyes. A further object is to provide a process for sensitizing photographic emulsions, particularly to the red, far-red and infra-red. A still further object is to provide a photographic element comprising an emulsion sensitized with our new dyes. A still further object is to provide new cyanine dyes and intermediates therefor. A still further object is to provide a process for preparing our new cyanine dyes and the intermediates therefor. The mode of accomplishing these objects and other more specific objects will become apparent upon a complete perusal of the following specification and claims.

The oxygen-containing alkyl groups contemplated in our invention include, for example, hydroxyalkyl, alkoxyalkyl, acyloxyalkyl, carbalkoxyalkyl, acylalkyl, hydroxyalkoxyalkyl and alkoxy-alkoxyalkyl groups which are devoid of aryl substituents. The cyanogen-containing alkyl groups contemplated in our invention include, for example, cyanalkyl groups which are devoid of aryl substituents. The halogen-containing alkyl groups contemplated in our invention include, for example, chloralkyl, bromalkyl, iodalkyl and fluoralkyl groups which are devoid of aryl substituents. The reasons for the specific effects of the oxygen, cyanogen or halogen in the alkyl groups are not at present known.

Our new dyes can be prepared from cyclammonium quaternary salts which salts can be prepared as hereinafter set forth. Cyclammonium alkoxyalkyl quaternary salts can be prepared, for example, by reacting a heterocyclic nitrogen base with an alkoxyalkyl ester. We have found that the alkoxyalkyl toluenesulfonates are advantageously employed. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, though they are not essential. The alkoxyalkyl toluenesulfonate quaternary salts can be converted into the less soluble quaternary salts e. g. the alkoxyalkyl halides and perchlorates, by treating solutions of the toluenesulfonate quaternary salts with solutions of soluble halides or perchlorates as hereinafter set forth.

While our method of obtaining alkoxyalkyl quaternary salts is subject to variation, particularly as respects the nature and quantity of heterocyclic nitrogen base employed, the nature and quantity of alkoxyalkyl ester employed, the temperatures employed, the time of reaction employed, the nature and quantity of diluent employed, if any, and the method of isolation and purification of the quaternary salts and the method of converting the toluenesulfonate quaternary salts to the other quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 1.—*1-methylbenzothiazole-β-ethoxyethiodide*

7.5 (1 mol.) of 1-methylbenzothiazole and 12.2 g. of β-ethoxyethyl-p-toluenesulfonate were heated together in an oil bath at about 100° C. for about one week. 8.0 g. of the crude reaction product was dissolved in 8.0 cc. of water, and treated with 5 g. of potassium iodide dissolved in sufficient water to give a 50% (by weight) solution. The alkoxyalkiodide separated out. Upon recrystallization from methyl alcohol it was obtained as colorless crystals melting at 185° to 195° C.

EXAMPLE 2.—*Quinaldine-β-ethoxyethiodide*

7.2 g. (1 mol.) of quinaldine and 12.2 g. of β-ethoxyethyl-p-toluenesulfonate were heated together for about seven days at about 100° C. The crude reaction product was dissolved in methyl alcohol and the resulting solution treated with diethylether to precipitate the quaternary salt. 2.6 g. of the precipitated product was dissolved in 20 cc. of methyl alcohol, and treated with 2 g. of potassium iodide dissolved in sufficient water to form a 50% (by weight) solution. The alkoxyalkiodide was obtained as reddish crystals obtained by carefully concentrating the solution. The crystals were not further purified.

EXAMPLE 3.—*Lepidine-β-ethoxyethiodide*

7.2 (1 mol.) of lepidine and 12.2 g. (1 mol.) of β-ethoxyethyl-p-toluenesulfonate were heated together for about five days at about 100° C. The crude reaction product was dissolved in about 50 cc. of water and treated with 11.5 g. of potassium iodide dissolved in sufficient water to form an 88% (by weight) solution in water. The alkoxyalkiodide separated from the solution. It was recrystallized from methyl alcohol and obtained as yellow crystals melting at 129° to 131° C. with decomposition.

In a manner similar to that illustrated in the above examples, 1-methylbenzoselenazole, μ-methylnaphthothiazoles, μ-methylnaphthoxazoles, 1-methylbenzoxazoles, 4-phenyl-2-methylthiazole, 2-methyl-5,6-benzoquinolines, 4-phenyl-2-methyloxazole, 2-methylthiazoline, 1-methylmercaptobenzothiazole, 1-phenylmercaptobenzothiazole for example can be converted into alkoxyalkyl quaternary salts.

The alkoxyalkyl-p-toluenesulfonates employed in the above examples can be prepared by a method similar to that described by Földi in Berichte der deutschen chemischen Gesellschaft, vol. 53, page 1836 (1920), for preparing esters of benzene sulfonic acid. The following example is illustrative:

EXAMPLE 4.—*β-Ethoxyethyl-p-toluenesulfonate*

22.5 g. (1 mol.) of ethylene glycol monoethyl ether and 47.5 g. (1 mol.) of p-toluenesulfonyl chloride were mixed by stirring together. The mixture was chilled in an ice-salt bath. A 20% (by weight) aqueous solution of sodium hydroxide was added to the mixture dropwise and the temperature of the mixture was held below 10° C. Sufficient sodium hydroxide was added to make the mixture alkaline. After alkalinity was reached, the mixture was stirred for a further fifteen minutes. 48 cc. (1.12 mol.) of sodium hydroxide solution were added. 300 cc. of water were then added to the mixture. The oily layer was taken up in benzene. The benzene extract was dried over anhydrous potassium carbonate, the benzene distilled away and the residue distilled in vacuo. β-Ethoxyethyl-p-toluenesulfonate was obtained as a practically colorless liquid boiling at 157° to 158° C. at 2 mm. Instead of employing alcohols such as β-ethoxyethyl alcohol, alcohols such as diethylene glycol monomethyl ether or diethylene glycol monoethyl ether can be employed.

Cyclammonium acyloxyalkyl quaternary salts can be prepared, for example, by reacting a heterocyclic nitrogen base with an acyloxyalkyl ester. We have found that acyloxyalkyl halides, particularly bromides, are advantageously employed. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, though they are not essential. The acyloxyalkyl bromide quaternary salts can be converted into the less soluble quaternary salts, e. g. the acyloxyalkyl iodides or perchlorates, by treating solutions of the quaternary salts with solutions of soluble halides or perchlorates as hereinafter described.

While our method of obtaining acyloxyalkyl quaternary salts is subject to variation particularly as respects the nature and quantity of heterocyclic nitrogen bases employed, the nature and quantity of acyloxyalkyl ester employed, the temperatures employed, the time of reaction employed, the nature and quantity of diluent employed, if any, and the method of isolation and purification of the quaternary salts and the method of converting the bromide quaternary salts into other quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 5.—*1-methylbenzothiazole-β-acetoxyethiodide*

14.9 g. (1 mol.) of 1-methylbenzothiazole and 16.7 g. (1 mol.) of β-bromethyl acetate were heated together at about 100° C. for about one week. The crude reaction product was dissolved in about 15 cc. of water and the resulting solution treated with 14 g. (1 mol. plus 50% excess) of potassium iodide dissolved in a small amount of water. The acyloxyalkyl iodide separated out. It was twice recrystallized from methyl alcohol decolorizing the alcoholic solution with activated charcoal. It was obtained as nearly colorless crystals melting at 200° to 201° C.

EXAMPLE 6.—*Lepidine-β-acetoxyethiodide*

28.6 g. (1 mol.) of lepidine and 33.4 g. (1 mol.) of β-bromethyl acetate were heated at about 100° C. for about four hours. The crude reaction product was dissolved in about 40 cc. of hot water and the resulting solution treated with 39 g. (1 mol. plus 50% excess) of potassium iodide dissolved in a small amount of water. The acyloxyalkyl iodide separated. It was twice recrystallized from methyl alcohol and obtained as yellow crystals melting at 177° to 178° C.

In a manner similar to that illustrated in the above two examples, acyloxyalkyl quaternary salts of quinaldines, α- and γ-picolines, 1-methylbenzoxazole, 1-methylbenzoselenazole, μ-methylnaphthothiazoles, μ-methylnaphthoxazoles, 2-methyl-4-phenylthiazoles, 2-methyl-4-phenylselenazole, 2-methyl-4-phenyloxazole, 2-halogenoquinolines, 4-chloro-1-methylbenzothiazole, 2,4-dimethylthiazole, 1-methylmercaptobenzothiazole, 1-methylmercaptobenzoxazole and 1-phenylmercaptobenzothiazole, for example, can be prepared.

Cyclammonium acylalkyl quaternary salts can be prepared, for example, by reacting a heterocyclic nitrogen base with a halogenoketone. We have found that chloroketones are advantageously employed. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, though they are ordinarily not to be preferred. The acylalkyl chlorides can be converted into the less soluble quaternary salts, e. g. the acylalkyl iodides or perchlorates, as hereinafter set forth.

While our method of obtaining acylalkyl quaternary salts is subject to variation, particularly as respects the nature and quantity of heterocyclic nitrogen base employed, the nature and quantity of halogenoketone employed, the temperatures employed, the time of reaction employed, the nature and quantity of diluent employed, if any, the method of converting the acylalkyl chlorides to other quaternary salts and the methods of isolation and purification of the quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 7.—*1-methylbenzothiazole acetonyl iodide*

14.9 g. (1 mol.) of 1-methylbenzothiazole and

9.2 g. (1 mol.) of chloracetone were heated on a steam bath at about 100° C. for about four days. The resulting solid dark mass of crystals was dissolved in methyl alcohol and converted directly to the iodide by treating the methyl alcohol solution with a concentrated aqueous solution containing 18 g. of potassium iodide. The acylalkyl iodide separated from the solution as grayish crystals. The crude crystals were twice recrystallized from methyl alcohol and obtained as colorless crystals melting at 180° to 184° C. with decomposition.

EXAMPLE 8.—*Lepidine acetonyl iodide*

7.2 g. (1 mol.) of lepidine and 4.6 g. (1 mol.) of chloracetone were heated on the steam bath at about 100° C. for about five hours. The reaction mixture set to a solid dark mass. The mass was dissolved in about 30 cc. of methyl alcohol and converted directly to the iodide by treating the methyl alcoholic solution with a concentrated aqueous solution containing 9 g. of potassium iodide. The acylalkyl iodide was obtained as yellowish crystals. The yellowish crystals were twice recrystallized from methyl alcohol (decolorizing the methyl alcoholic solution with activated charcoal) and obtained as yellowish crystals melting at 218° to 219° C. with decomposition.

In a manner similar to that illustrated in the above two examples acylalkyl quaternary salts of quinaldines, α- and γ-picolines, 1-methylbenzoxazole, 1-methylbenzoselenazole, μ - methyl - naphthoxazoles, μ-methylnaphthothiazoles, 2-methyl-4-phenylthiazole, 2-methyl - 4 - phenylselenazole, 2-methyl-4-phenyloxazole, 2-halogenoquinolines, 4-chloro-1-methylbenzothiazole, 2,4-dimethylthiazole, 1-methylmercaptobenzothiazole and 1-phenylmercaptobenzothiazole for example can be prepared.

Cyclammonium carbalkoxyalkyl quaternary salts can be prepared for example by reacting a heterocyclic nitrogen base with an ester of a halogenated fatty acid. We have found that bromesters are advantageously employed. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, though they are not essential. The carbalkoxyalkyl quaternary bromides can be converted into the less soluble quaternary salts, e. g. the iodides and perchlorates, by treating solutions of the bromides with solutions of soluble iodides or perchlorates as hereinafter set forth.

While our method of obtaining carbalkoxyalkyl quaternary salts is subject to variation, particularly as respects the nature and quantity of heterocyclic nitrogen base employed, the nature and quantity of bromester employed, the temperatures employed, the time of reaction employed, the nature and quantity of diluent employed, if any, and the method of isolation and purification of the quaternary bromides and the method of converting the bromides to other quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 9.—*1-methylbenzothiazole β-carbethoxyethiodide*

14.9 g. (1 mol.) of 1-methylbenzothiazole ethiodide and 18.1 g. (1 mol.) of ethyl-β-bromopropionate were heated in about 25 cc. of dry chloroform at the refluxing temperature for about one week. Diethyl ether was added to the cooled reaction mixture to precipitate the quaternary bromide. The crude quaternary bromide was dissolved in 20 cc. of hot water and converted to the iodide by treating the hot aqueous solution with a concentrated aqueous solution containing 17.5 g. of potassium iodide. The crude iodide was slightly pink in color. It was twice recrystallized from methyl alcohol and obtained as nearly colorless crystals melting at 131° to 133° C. with decomposition.

EXAMPLE 10.—*1-methylbenzothiazole carbethoxymethiodide*

14.9 g. (1 mol.) of 1-methylbenzothiazole and 16.7 g. (1 mol.) of ethyl bromacetate were heated together at about 100° C. for about 22 hours. The cooled reaction mixture (a nearly solid mass of crystals) was dissolved in about 25 cc. of methyl alcohol and converted to the quaternary iodide by treating the methyl alcoholic solution with a concentrated aqueous solution of potassium iodide (30 g. dissolved in 25 cc. of hot water). The iodide separated and was recrystallized from methyl alcohol. It was obtained as colorless crystals melting at 178° to 180° C. with decomposition.

EXAMPLE 11.—*Quinaldine carbethoxymethiodide*

28.6 g. (1 mol.) of quinaldine and 33.4 g. (1 mol.) of ethyl bromacetate were allowed to stand together at room temperature for about 24 hours. The reaction mixture set to a crystalline mass. The mass was dissolved in about 25 cc. of hot water and converted to the iodide by treating the solution with a concentrated aqueous solution containing 21 g. of potassium iodide. The quaternary iodide separated as a light red crystalline powder. It was twice recrystallized from methyl alcohol and obtained as light reddish crystals melting at 192° to 194° C. with decomposition.

EXAMPLE 12.—*Lepidine carbethoxymethiodide*

14.9 g. (1 mol.) of lepidine and 16.7 g. (1 mol.) of ethyl bromacetate were heated in about 25 cc. of dry chloroform for about 3 days at the refluxing temperature of the chloroform. The quaternary bromide separated out. It was filtered off and dissolved in about 100 cc. of hot water and converted to the iodide by treating the aqueous solution with a concentrated aqueous solution containing 17 g. of potassium iodide. The quaternary iodide separated as yellow crystals. It was twice recrystallized from methyl alcohol and obtained as faintly yellow crystals melting at 163° to 164° C. with decomposition.

In a manner similar to that illustrated in the above four examples, carbalkoxy quaternary salts of α- and γ-picolines, 1-methylbenzoxazole, 1-methylbenzoselenazole, α-methylnaphthoxazoles, μ - methylnaphthiazoles, 2-methyl-4-phenylthiazole, 2-methyl-4-phenylselenazole, 2-methyl-4-phenyloxazole, 2-halogenoquinolines, 4-chloro-1-methylbenzothiazole, 2,4 - dimethylthiazoles, 1-methylmercaptobenzothiazole, 1-phenylmercaptobenzothiazole for example can be prepared.

Cyclammonium carboxyalkyl quaternary salts can be prepared for example by reacting a heterocyclic nitrogen base with a halogenated fatty acid. We have found that bromoacids are advantageously employed. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, though they are not essential. The carboxyalkyl quaternary bromides can be converted into the less soluble quaternary salts, e. g. the iodides and perchlorates, by treating solutions of the bromides with solutions of soluble iodides or perchlorates as

hereinbefore set forth for carbalkoxy quaternary salts.

While our method of obtaining carbalkoxy quaternary salts is subject to variation, particularly as respects the nature and quantity of heterocyclic nitrogen base employed, the nature and quantity of bromoacid employed, the temperatures employed, the time of reaction employed, the nature and quantity of diluent employed, if any, and the method of isolation and purification of the quaternary bromides and the method of converting the bromides to other quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. The examples are not intended to limit our invention.

EXAMPLE 13.—*1-methylbenzothiazole carboxymethobromide*

22.4 g. (1 mol.) of 1-methylbenzothiazole and 20.9 g. (1 mol.) of bromoacetic acid were heated together at about 100° C. for about 8 hours. The resulting hard dark mass was dissolved in about 150 cc. of methyl alcohol. The resulting solution was treated with diethyl ether to precipitate the quaternary bromide. The quaternary bromide was twice recrystallized from methyl alcohol and obtained as colorless crystals melting at 224° to 226° C. with decomposition.

EXAMPLE 14.—*Lepidine carboxymethobromide*

21.5 g. (1 mol.) of lepidine and 20.4 g. (1 mol.) of bromoacetic acid were well mixed and allowed to stand at from 20° to 25° C. for about 18 hours. The resulting solid mass was dissolved in water and the quaternary bromide precipitated by addition of acetone to the aqueous solution. The quaternary bromide was twice recrystallized from methyl alcohol and obtained as colorless crystals melting at 159° to 161° C. with decomposition.

In a manner similar to that illustrated in the above two examples carboxyalkyl quaternary salts of α- and γ-picolines, quinaldine, 1-methylbenzoxazole, 1-methylbenzoselenazole, μ-methylnaphthotiazoles, μ-methylnaphthoxazoles, 2-methyl-4-phenylthiazole, 2-methyl-4-phenyloxazole, 2-methyl-4-phenylselenazole, 2,4-dimethylthiazole, 2-halogenoquinolines, 4-chloro-1-methylbenzothiazole, 1-methylmercaptobenzothiazole, and 1-phenylmercaptobenzothiazole for example can be prepared.

Cyclammonium halogenated alkyl quaternary salts can be prepared for example by reacting a heterocyclic nitrogen base with toluenesulfonate esters of halogenated alcohols. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, although they are not essential. The halogenated alkyl quaternary toluenesulfonates can be converted in less soluble quaternary salts, e. g. the bromides, iodides or perchlorates, by treating solutions of the bromides with solutions of soluble bromides, iodides or perchlorates as hereinafter set forth.

While our method of obtaining halogenated alkyl quaternary salts is subject to variation, particularly as respects the nature and quantity of heterocyclic nitrogen bases employed, the nature and quantity of toluenesulfonate ester employed, the time of reaction employed, the temperatures employed, the nature and quantity of diluent employed, if any, the method of converting the toluenesulfonate quaternary salts to other quaternary salts and the methods of isolation and purification of the quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 15.—*1-methylbenzothiazole β-chloroethiodide*

14.3 g. (1 mol.) of 1-methylbenzothiazole and 23.4 g. (1 mol.) of β-chloroethyl-p-toluenesulfonate were mixed and heated together at about 100° C. for about 10 days. The reaction product was dissolved in water and converted to the quaternary iodide by treating the aqueous solution with a concentrated aqueous solution of potassium iodide containing 25 g. of potassium iodide. The quaternary iodide separated and was recrystallized from methyl alcohol, decolorizing the methyl alcoholic solution with activated charcoal. It was thus obtained as crystals having a greenish yellow tint and melting at 188° to 190° C.

EXAMPLE 16.—*Lepidine β-chloroethiodide*

7.15 g. (1 mol.) of lepidine and 11.7 g. (1 mol.) of β-chloroethyl-p-toluenesulfonate were mixed and heated together at about 100° C. for 3 days. The reaction product was dissolved in water and converted directly to the quaternary iodide by treating the aqueous solution with a concentrated aqueous solution of potassium iodide containing 12.5 g. of potassium iodide. The quaternary iodide separated. It was twice recrystallized from methyl alcohol and obtained as yellowish crystals melting at 184° to 186° C. with decomposition.

In a manner similar to that illustrated in the above two examples halogenated alkyl quaternary salts of α- and γ-picolines, quinaldine, 1-methylbenzoxazole, 1-methylbenzoselenazole, μ-methylnaphthothiazoles, μ-methylnaphthoxazoles, 2-methyl-4-phenylthiazole, 2-methyl-4-phenyloxazole, 2-methyl-4-phenylselenazole, 2,4-dimethylthiazole, 2-halogenoquinolines, 4-chloro-1-methylbenzothiazole, 1-methylmercaptobenzothiazole, and 1-phenylmercaptobenzothiazole for example can be prepared.

β-Chloroethyl-p-toluenesulfonate can be prepared according to the method of Clemo and Perkin, Journal of the Chemical Society (London) vol. 121, page 642 (1922).

Cyclammonium alkyl quaternary salts containing a cyanogen group on the alkyl group can be prepared for example by reacting a heterocyclic nitrogen base with a toluenesulfonate ester of a cyanoalcohol. Heat accelerates the formation of the quaternary salts. Diluents can be employed in the reaction mixture, although they are not essential. The cyanoalkyl quaternary toluenesulfonates can be converted into the less soluble quaternary salts, e. g. the bromides, iodides or perchlorates, by treating solutions of the toluenesulfonates with solutions of soluble bromides, iodides or perchlorates as hereinafter set forth.

While our method of obtaining cyanoalkyl quaternary salts is subject to variation, particularly as respects the nature and quantity of the heterocyclic nitrogen base employed, the nature and quantity of the toluenesulfonate ester employed, the temperatures employed if any, the method of converting the toluenesulfonate quaternary salts to other quaternary salts and the methods of isolation and purification of the quaternary salts, the following examples will serve to illustrate the mode of obtaining our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 17.—*1-methylbenzothiazole β-cyanoethiodide*

3.75 g. (1 mol.) of 1-methylbenzothiazole and 5.63 g. (1 mol) of β-cyanoethyl-p-toluenesulfonate were mixed and heated together at about 100° C. for about 8 days. The reaction mass was dissolved in about 10 cc. of methyl alcohol and converted directly to the quaternary iodide by treating the alcoholic solution with a concentrated aqueous solution of potassium iodide containing 4.15 g. of potassium iodide. The quaternary iodide separated. It was recrystallized from methyl alcohol and obtained as glittering colorless crystals having a greenish cast and melting at 251° to 253° C. with decomposition.

EXAMPLE 18.—*Lepidine β-cyanoethiodide*

3.6 g. (1 mol.) of lepidine and 5.63 g. (1 mol.) of β-cyanoethyl-p-toluenesulfonate were heated together on the steam bath for about 6 days. The reaction mass was dissolved in about 10 cc. of methyl alcohol and the methyl alcoholic solution treated with a concentrated aqueous solution of potassium iodide containing 5.8 g. of potassium iodide. The quaternary iodide separated. It was recrystallized from methyl alcohol, decolorizing the solution with activated charcoal. The product consisted of colorless crystals contaminated with some yellowish crystals.

In a manner similar to that illustrated in the above two examples cyanoalkyl quaternary salts of α- and γ-picolines, quinaldine, 1-methylbenzoxazole, 1-methylbenzoselenazole, μ-methylnaphtothiazoles, μ-methylnaphthoxazoles, 2-methyl-4-phenylthiazole, 2-methyl-4-phenyloxazole, 2-methyl-4-phenylselenazole, 2,4-dimethylthiazole, 2-halogenoquinolines, 4-chloromethylbenzothiazole, 1-methylmercaptobenzothiazole and 1-phenylmercaptobenzothiazole for example can be prepared.

β-cyanoethyl toluenesulfonates can be prepared as described by Clemo and Walton in the Journal of the Chemical Society (1928), page 723.

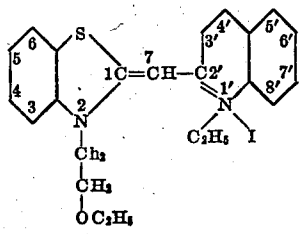
In the foregoing seventeen examples of the preparation of quaternary salts, 1-methylbenzothiazole, quinaldine and lepidine have been used as illustrations because many of the most useful sensitizing cyanine dyes contain such nuclei. In these three heterocyclic nitrogen bases as well as in the other heterocyclic nitrogen bases, particularly those containing a benzene nucleus, various groups can be substituted, particularly in the benzene nuclei, for example groups such as dialkylamino, alkyl, alkoxy, halogen and acylamino.

Having set forth the manner of obtaining the intermediate necessary to the preparation of our new dyes, a number of examples of the preparation of various cyanine dyes of the sensitizing types from such intermediates are hereinafter set forth.

Our new intermediates can be employed in preparing simple cyanine dyes, i. e. cyanine dyes containing a single methenyl group between two heterocyclic nuclei, such as simple thiacyanines, simple oxacyanines, simple 4,4'-cyanines, simple selenacyanines, simple oxathiacyanines, simple 2,2'-pyridocyanines, simple dibenzothiacyanines, 4,4'-cyanines, pseudocyanines, such as thia-2'-cyanines, thiazolo-2'-cyanines, oxa-2'-cyanines, oxazolo-2'-cyanines, 2,2'-cyanines and benzothia-2'-cyanines for example, and isocyanines, such as thia-4'-cyanines, selena-4'-cyanines and 2,4'-cyanines for example. The following examples are illustrative of the manner of obtaining simple cyanine dyes from our new quaternary salts. These examples are not intended to limit our invention.

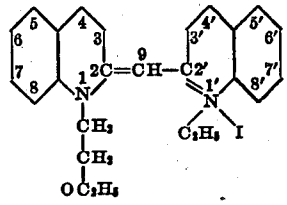
EXAMPLE 19.—*2-(β-ethoxyethyl)-1'-ethylthia-2'-cyanine*

1.0 g. (1 mol.) of 1-methylbenzothiazole β-ethoxyethiodide and 1.03 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in about 10 cc. of absolute ethyl alcohol containing 0.73 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye separated upon cooling the reaction mixture. The crude dye was recrystallized from methyl alcohol and obtained as minute orange-red crystals which melted at 221° to 223° C. with decomposition. The dye has the following formula:



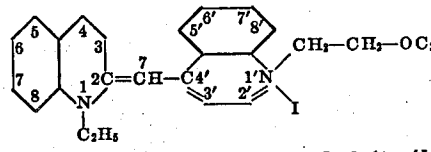
EXAMPLE 20.—*1-(β-ethoxyethyl)-1'-ethyl-2,2'-cyanine iodide*

0.97 g. (1 mol.) of quinaldine β-ethoxyethiodide and 1.03 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in about 10 cc. of absolute ethyl alcohol containing 0.73 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye separated from the chilled reaction mixture. It was recrystallized from methyl alcohol and obtained as red crystals having a bluish reflex and melting at 139° to 141° C. with decomposition. The dye has the following formula:



EXAMPLE 21.—*1-(β-ethoxyethyl)-1'-ethyl-2,4'-cyanine iodide*

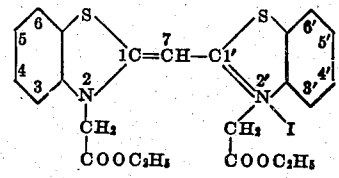
1.72 g. (1 mol.) lepidine β-ethoxyethiodide and 2.06 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in about 10 cc. of absolute ethyl alcohol containing 1.46 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The cooled reaction mixture was diluted with diethyl ether to precipitate the dye. The crude dye was recrystallized from methyl alcohol and obtained as brassy green needles melting at 101° to 106° C. with decomposition. A methyl alcoholic solution of the dye was bluish red. The formula of the dye is:



EXAMPLE 22.—*1-carbethoxymethyl-1'-ethylthia-2'-cyanine iodide*

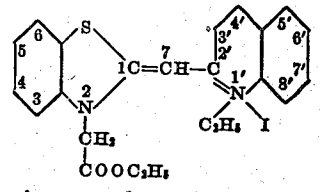
2.73 g. (1 mol.) of 1-methylbenzothiazole carbethoxymethiodide and 3.1 g. (1 mol.) of 2-iodo-

quinoline ethiodide were heated in about 25 cc. of absolute ethyl alcohol containing 2.2 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye separated from the cooled reaction mixture. The crude dye was extracted with hot methyl alcohol. The extract yielded long orange-yellow crystals upon cooling. These long orange-yellow crystals gave a yellow methyl alcoholic solution and melted at 246° to 247° C. with decomposition. This dye was not the 2'-cyanine but rather 2,2'-dicarbethoxymethylthia-2'-cyanine iodide having the following formula:



The thia-2'-cyanine is obtained by treating the reaction mixture, after removing the separated dye, with diethyl ether. The dye which separated was obtained, after recrystallization from methyl alcohol, as orange crystals having a greenish reflex.

The thia-2'-cyanine is more advantageously obtained by heating together 3.63 g. (1 mol.) of 1-methylbenzothiazole carbethoxymethiodide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide in 20 cc. of absolute ethyl alcohol containing 2.76 g. (2 mol.) of potassium carbonate at the refluxing temperature for about twenty minutes. The dye separated from the chilled reaction mixture. It was recrystallized from methyl alcohol and obtained as orange crystals having a greenish reflex and melting at 209° to 210° C. with decomposition. The dye has the following formula:



No thiacyanine was formed using potassium or sodium carbonate.

EXAMPLE 23.—*1-carbethoxymethyl-1'-ethyl-2,2'-cyanine iodide*

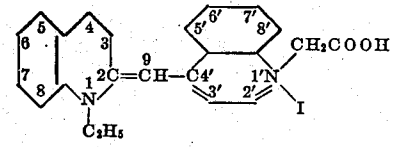
1.8 g. (1 mol.) of quinaldine carbethoxy methiodide and 2.06 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in about 10 cc. of ethyl alcohol containing 1.5 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about five minutes. The reaction mixture was diluted with water to precipitate the dye. After recrystallization from acetone, the dye was obtained as garnet rosettes having a grayish-green reflex and melting at 142° to 145° C. with decomposition.

EXAMPLE 24. — *1-carbethoxymethyl-1-ethyl-2,4'-cyanine iodide*

3.57 g. (1 mol.) of lepidine carbethoxymethiodide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide were heated together in about 15 cc. of absolute ethyl alcohol containing 2.9 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. Diethyl ether was added to the cooled reaction mixture to precipitate the dye. The crude dye was recrystallized from methyl alcohol and obtained as dark crystals having green and blue reflexes. The dye gave a bluish-red methyl alcoholic solution and melted at 215° to 216° C. with decomposition.

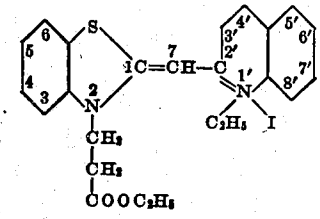
EXAMPLE 25. — *1'-carboxymethyl-1-ethyl-2,4'-cyanine iodide*

2.82 g. (1 mol.) of lepidine carboxymethobromide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in 25 cc. of absolute ethyl alcohol containing 2.9 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye was precipitated from the cooled reaction mixture by adding diethyl ether to the cooled reaction mixture. The crude dye was recrystallized from a methyl alcohol and water mixture (equal volumes) and obtained as garnet crystals having a green reflex and giving a bluish-red methyl alcohol solution. The dye melted at 208° to 210° C. with decomposition and has the following formula:



EXAMPLE 26.—*1-β-carbethoxyethyl-1'-ethylthia-2'-cyanine iodide*

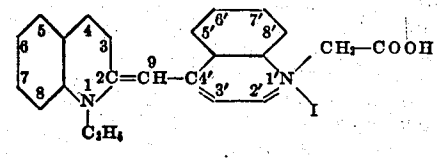
2.2 g. (1 mol.) of 1-methylbenzothiazole β-carbethoxyethiodide and 2.74 g. (1 mol.) of 2-iodoquinoline ethiodide were heated in about 15 cc. of absolute ethyl alcohol containing 2.0 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about three minutes. The dye separated from the cooled reaction mixture. The dye was recrystallized from methyl alcohol and obtained as brownish-red crystals giving an orange solution in methyl alcohol and melting at 186° to 188° C. with decomposition. It has the following formula:



The dye is more advantageously prepared employing an alkali metal carbonate as condensing agent instead of triethylamine.

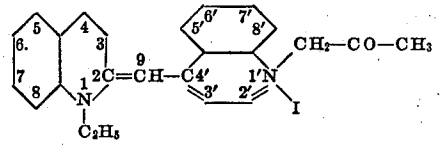
EXAMPLE 27.—*1'-carboxymethyl-1-ethyl-2',4'-cyanine iodide*

2.82 g. (1 mol.) of lepidine carboxymethobromide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide were heated together in 25 cc. of absolute ethyl alcohol containing 2.9 cc. (2 mol.) of triethylamine at the refluxing temperature for about twenty minutes. Diethyl ether was added to the cooled reaction mixture to precipitate the dye. It was recrystallized from a mixture of equal volumes of methyl alcohol and water and obtained as garnet crystals having a green reflex and giving a bluish-red solution in methyl alcohol. The dye melted at 208° to 210° C. with decomposition. It has the following formula:



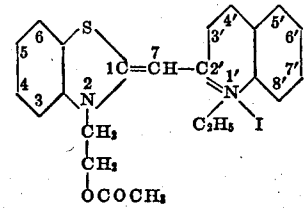
EXAMPLE 28.—*1 - acetonyl - 1 - ethyl-2,4'-cyanine iodide*

3.27 g. (1 mol.) of lepidine acetonyl iodide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide were heated together in 25 cc. of absolute ethyl alcohol containing 2.9 cc. of triethylamine at the refluxing temperature for about twenty minutes. The dye separated from the cooled reaction mixture upon the addition of diethyl ether thereto. The dye was recrystallized from methyl alcohol and obtained as beautiful green crystals having a bronze reflex and giving a bluish-red methyl alcohol solution. The dye melted at 233° to 235° C. with decomposition. It has the following formula:



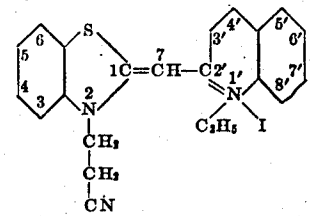
EXAMPLE 29.—*2 - (β-acetoxyethyl) - 1' - ethylthia-2'-cyanine iodide*

3.63 g. (1 mol.) of 1-methylbenzothiazole β-acetoxyethiodide and 4.1 g. (1 mol.) of 2-iodoquinoline ethiodide were heated together in 25 cc. of absolute ethyl alcohol containing 2.65 g. (2.5 mol.) of anhydrous sodium carbonate at the refluxing temperature for about twenty minutes. The dye separated from the cooled reaction mixture. After recrystallization from methyl alcohol, the dye was obtained as a reddish powder which gave an orange methyl alcoholic solution. The dye melted at 268° to 269° C. with decomposition. It has the following formula:



EXAMPLE 30.—*2-(β-cyanoethyl) -1'-ethylthia-2'-cyanine iodide*

1.65 g. (1 mol.) of 1-methylbenzothiazole β-cyanoethiodide and 2.06 g. (1 mol.) of 2-iodoquinoline ethiodide were heated together in 15 cc. of absolute ethyl alcohol containing 1.5 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye separated from the cooled reaction mixture. After recrystallization from methyl alcohol, it was obtained in the form of reddish-brown crystals with a golden reflex and giving an orange methyl alcoholic solution. The dye melted at 263° to 265° C. with decomposition. The dye has the following formula:



EXAMPLE 31.—*2-(β-chloroethyl) -1'-ethylthia-2'-cyanine iodide*

1.7 g. (1 mol.) of 1-methylbenzothiazole β-chloroethiodide and 2.06 g. (1. mol.) of 2-iodoquinoline ethiodide were heated together in 20 cc. absolute ethyl alcohol containing 1.5 cc. (2.1 mol.) of triethylamine at the refluxing temperature for about twenty minutes. The dye separated from the reaction mixture upon chilling. On recrystallization from methyl alcohol, the dye was obtained as brick colored glittering crystals which gave an orange methyl alcoholic solution. It melted at 258° to 261° C. with decomposition.

In the above examples of the preparation of simple cyanines, ethyl alcohol has been employed exclusively as a diluent in the reaction mixture because the reactions proceed well at the refluxing temperature of the alcohol, i. e. from 70° to 80° C. Other diluents can be employed, e. g. methyl alcohol or n-propyl alcohol. The reactions can be carried out without a diluent, although it is difficult to isolate the dyes under such conditions.

In the above examples of the preparation of 2'-cyanine, i. e. pseudocyanine, dyes, the basic condensing agent employed in a large number of the cases has been triethylamine. Strong tertiary organic bases, that is, tertiary organic bases whose aqueous solutions have dissociation constants substantially greater than that of an aqueous solution of pyridine, are particularly suitable, e. g. N-methylpiperidine, triethanolamine, tributylamine, and triethylamine. Other basic condensing agents can be employed. As shown above in the examples, alkali metal carbonates are particularly efficacious.

2'-cyanine dyes can also be prepared by treating oxygen-, halogen- or cyanogen-containing-alkyl quaternary salts of 2-phenylmercaptoquinoline with cyclammonium quaternary salts containing a reactive methyl group, such as 1-methylbenzothiazole, quinaldine, α-picoline, 2-methyl-4-phenylthiazole or 2-methyl-4-phenyloxazole for example, according to the processes given in the above examples.

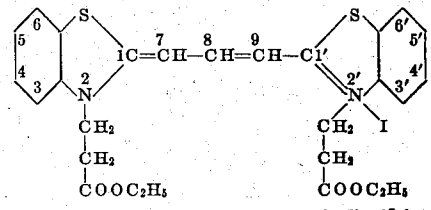
Simple thiacyanines can be prepared by treating oxygen-, halogen- or cyanogen-containing-alkyl quaternary salts of 1-methylmercaptobenzothiazole with 1-methylbenzothiazole quaternary salts according to the process of the above examples. Simple oxa- and selenacyanines can be similarly prepared.

Our new intermediates can be employed to prepare carbocyanine dyes, i. e. cyanine dyes containing a trimethenyl chain between two heterocyclic nuclei, such as 2,2'-carbocyanines, 2,4'-carbocyanines, 4,4'-carbocyanines, thia-2'-carbocyanines, oxa-2'-carbocyanines, thiazolo-2'-carbocyanines, selenazolo-2'-carbocyanines, thia-4'-carbocyanines, selena-4'-carbocyanines, oxa-4'-carbocyanines, thiacarbocyanines, dibenzothiacarbocyanines, oxa-thiacarbocyanines, dibenzoxacarbocyanines, oxabenzothiacarbocyanines, benzoxathiacarbocyanines, thiazolocarbocyanines, thiathiazolocarbocyanines and the like. The following examples are illustrative of the manner of obtaining our new carbocyanine dyes from our new quaternary salts. These examples are not intended to limit our invention.

EXAMPLE 32.—*2,2' - di-(β-carbethoxyethyl) -thiacarbocyanine iodide*

3.77 g. (2 mol.) of 1-methylbenzothiazole β-carbethoxy-ethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine for about forty-five minutes at the refluxing temperature. The dye separated from the chilled reaction mixture. The dye was recrystallized from methyl alcohol and obtained as dark crystals having a metallic reflex and giving

a bluish-red methyl alcoholic solution. The dye melted at 207° to 208° C. with decomposition. It has the following formula:



EXAMPLE 33.—*2,2'-di-(β-cyanoethyl)-thiacarbocyanine iodide*

3.3 g. (2 mol.) of 1-methylbenzothiazole β-cyanoethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 40 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye separated from the cooled reaction mixture. It was recrystallized from methyl alcohol and obtained as fine grayish crystals having a bronze reflex and giving a bluish-red methyl alcoholic solution. It melted at 274° to 277° C. with decomposition.

EXAMPLE 34.—*2,2'-di-(β-chloroethyl)-thiacarbocyanine iodide*

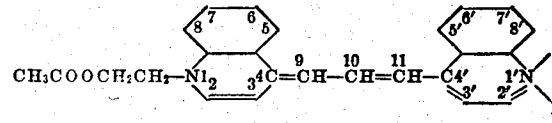
3.4 g. (2 mol.) of 1-methylbenzothiazole β-chloroethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye separated upon chilling the reaction mixture. It was recrystallized from methyl alcohol and obtained as dark brownish crystals which gave a bluish-red methyl alcoholic solution. The dye melted at 327° to 329° C. with decomposition.

EXAMPLE 35.—*2,2' - di-(β-acetoxyethyl)-thiacarbocyanine iodide*

3.63 g. (2 mol.) of 1-methylbenzothiazole β-acetoxyethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye separated from the cooled reaction mixture. It was recrystallized from methyl alcohol and obtained as dark crystals having a greenish reflex and giving a bluish-red methyl alcoholic solution. The dye melted at 256° to 258° C. with decomposition.

EXAMPLE 36.—*1,1'-di-(β-acetoxyethyl)-4,4'-carbocyanine iodide*

7.14 g. (2 mol.) of lepidine β-acetoxyethiodide and 4.95 cc. (3 mol.) of ethyl orthoformate were heated together in 35 cc. of pyridine at the refluxing temperature for about four hours. The dye was precipitated from the cooled reaction mixture by the addition of diethyl ether thereto. The dye was recrystallized from methyl alcohol and obtained as green crystals having a brassy green reflex and giving a blue methyl alcoholic solution. The dye melted at 224° to 225° C. with decomposition. It has the following formula:



EXAMPLE 37.—*2,2'-diacetonylthiacarbocyanine iodide*

3.33 g. (1 mol.) of 1-methylbenzothiazole acetonyl iodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye was precipitated from the reaction mixture by the addition of diethyl ether thereto. The dye was recrystallized from methyl alcohol and obtained as fine green needles having a blue reflex, and giving a bluish-red methyl alcoholic solution. The dye melted at 249° C. to 250° C. with decomposition.

EXAMPLE 38.—*2,2' - di-(carboxymethyl)-thiacarbocyanine bromide*

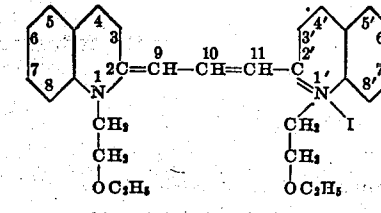
5.76 g. (2 mol.) of 1-methylbenzothiazole carboxymethobromide and 4.95 cc. (3 mol.) of ethylorthoformate were heated together in 50 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye separated from the cooled reaction mixture. It was suspended in 400 cc. of methyl alcohol and treated with 0.4 g. of guanidine carbonate. The guanidine salt was formed as a purplish crystalline powder giving a bluish-red methyl alcoholic solution and melting at 221° to 222° C.

EXAMPLE 39.—*2,2'-dicarbethoxymethylthiacarbocyanine iodide*

3.63 g. (2 mol.) of 1-methylbenzothiazole carbethoxymethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine at the refluxing temperature for about twenty-five minutes. The dye separated upon chilling the reaction mixture. The dye was recrystallized from methyl alcohol and obtained as beautiful crystals having a greenish metallic reflex and giving a bluish-red methyl alcoholic solution. The dye melted at 218° to 219° C. with decomposition.

EXAMPLE 40.—*1,1'-dicarbethoxymethyl-2,2'-carbocyanine iodide*

3.57 g. (2 mol.) of quinaldine carbethoxymethiodide and 2.5 cc. of ethyl orthoformate were heated together in 25 cc of pyridine at the refluxing temperature for about three minutes. The dye was precipitated by adding diethyl ether to the cooled reaction mixture. After recrystallization from methyl alcohol, the dye was obtained as minute green needles with a metallic reflex giving a blue methyl alcoholic solution. The dye melted at 240° to 241° C. with decomposition. The dye has the following formula:



EXAMPLE 41.—*1,1'-dicarbethoxymethyl-4,4'-carbocyanine iodide*

7.14 g. (2 mol.) of lepidine carbethoxymethiodide and 4.95 cc. (3 mol.) of ethyl orthoformate were heated together in 25 cc. of pyridine at the refluxing temperature for about four hours. The dye separated from the cooled reaction mixture. Upon recrystallization from methyl alcohol, it was obtained as a greenish-bronze felted mat of crystals which gave a blue methyl alcoholic solution. The dye melted at 189° to 191° C.

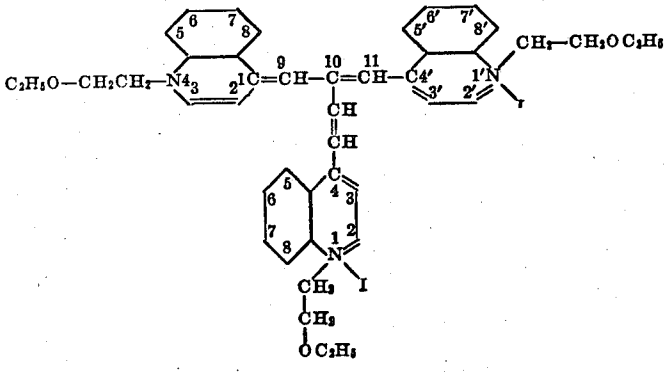
EXAMPLE 42.—*2,2'-di-(β-ethoxyethyl)-thiacarbocyanine iodide*

2.0 g. (2 mol.) of 1-methylbenzothiazole β-ethoxyetho-p-toluenesulfonate and 1.25 cc. (3 mol.) of ethyl orthoformate were heated together in 10 cc. of pyridine at the refluxing temperature for about forty-five minutes. The dye was precipitated as the dye-iodide by adding a concentrated aqueous solution of 1.0 g. of potassium iodide to the hot reaction mixture. The dye was recrystallized from methyl alcohol and obtained as greenish crystals having a bronze reflex and giving a bluish-red methyl alcoholic solution. The dye melted at 212° to 214° C. with decomposition.

1,1' - di - (β - ethoxyethyl) - 2,2' - carbocyanine iodide was prepared in a similar manner from 1.94 g. of quinaldine β-ethoxy-etho-p-toluenesulfonate and 1.25 cc. of ethyl ortho formate. After recrystallization from methyl alcohol, the dye was obtained as minute greenish needles which gave a blue methyl alcoholic solution and melted at 274° to 276° C. with decomposition.

EXAMPLE 43.—*1,1'-di-(β-ethoxyethyl)-10-[β-(4-quinolyl-1-β-ethoxyethiodide)-vinyl]-4,4'-carbocyanine iodide*

3.43 g. (2 mol.) of lepidine β-ethoxyethiodide and 2.5 cc. (3 mol.) of ethyl orthoformate were heated together in 15 cc. of acetic anhydride containing 0.45 g. (1.05 mol.) of anhydrous sodium acetate at the refluxing temperature for about one-half hour. The dye separated from the reaction mixture upon chilling. After recrystallization from methyl alcohol, it was obtained as beautiful bronze crystals which gave a green methyl alcoholic solution. The dye melted at 227° to 230° C. with decomposition. The dye has the following formula:

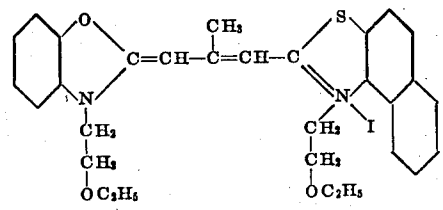


In the above examples, the pyridine functions as both a basic condensing agent and as a diluent. Pyridine is a particularly efficacious condensing agent. Other diluents can be added to the reaction mixture. The reactions are advantageously carried out at about the refluxing temperature of pyridine. In a manner similar to that illustrated in the above examples, dibenzothiacarbocyanines, oxacarbocyanines, selenacarbocyanines, thiazolo-carbocyanines and thiazolinocarbocyanines containing oxygen-containing-alkyl, halogen-containing-alkyl or cyanogen-containing-alkyl groups can be prepared. In the above examples, instead of employing ethyl orthoformate, other esters of orthoformic acid can be used. Likewise, ethyl orthoacetate, ethyl orthopropionate and ethyl orthobenzoate can be employed in the above examples instead of ethyl orthoformate. Using these latter esters, carbocyanine dyes containing a substituent, such as methyl, ethyl or phenyl, at the central carbon atom of the trimethenyl chain can be prepared.

Example 43 shows the preparation of a neocyanine. Similarly other neocyanines can be prepared.

Unsymmetrical carbocyanine dyes containing oxygenated, halogenated or cyanogenated alkyl groups can be prepared by first condensing a cyclammonium oxygenated, halogenated or cyanogenated alkyl quaternary salt containing a reactive methyl group in the alpha or gamma position, i. e. one of the so-called reactive positions, advantageously a quaternary iodide, with diphenyl-formamidine, advantageously in the presence of an organic acid anhydride, such as acetic anhydride. The resulting condensation product can then be condensed with a different cyclammonium oxygenated, halogenated or cyanogenated alkyl quaternary salt containing a reactive methyl group, again advantageously a quaternary iodide, in the presence of a basic condensing agent, advantageously a strong organic base, such as triethylamine or piperidine for example. In such a manner 2,2'-di(β-ethoxyethyl)-oxathiacarbocyanine iodide can be prepared for example.

Unsymmetrical carbocyanine dyes containing at least one oxygenated, halogenated or cyanogenated alkyl group on the cyanine nitrogen atoms and having an alkyl group, particularly one of the ordinary alkyl groups, such as methyl or ethyl, on the central carbon atom of the trimethenyl chain can be prepared as illustrated for the dye having the following formula:



To prepare this dye, 2-methyl-β-naphthothiazole β-ethoxyethiodide is reacted with acetyl chloride in the presence of pyridine to give 2-acetylmethy-

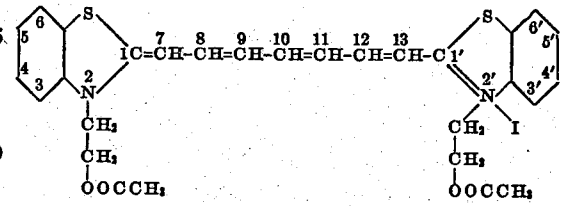
lene-1-(β-ethoxyethyl)-β-naphthothiazoline. The naphthothiazoline is then condensed with 1-methylbenzoxazole β-ethoxyethiodide in the presence of a water-binding agent, such as acetic or propionic anhydride.

Dicarbocyanine dyes containing oxygenated, halogenated or cyanogenated alkyl groups on at least one of the cyanine nitrogen atoms can be prepared by first condensing one of our new cyclammonium quaternary salts containing a reactive methyl group, advantageously a quaternary iodide, with β-anilinoacrolein and hydrochloride, in the presence of anhydrous sodium acetate and acetic anhydride. The condensation product can then be condensed with the same or a different cyclammonium quaternary salt, advantageously a quaternary iodide, containing a reactive methyl group, in the presence of a basic condensing agent, advantageously, a strong organic base, such as triethylamine. In such a manner 2,2'-di-(β-ethoxyethyl)-thiadicarbocyanine can be prepared.

Tricarbocyanine dyes can be prepared from our new cyclammonium quaternary salts containing a reactive methyl group as illustrated in the following examples. These examples are not intended to limit our invention.

EXAMPLE 44.—*2,2'-di-(β-acetoxyethyl)-thiatricarbocyanine iodide*

3.36 g. (2 mol.) of 1-methylbenzothiazole β-acetoxyethiodide and 1.43 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride were dispersed in 50 cc. of absolute ethyl alcohol. To the dispersion was added 1.0 cc. (2 mol.) of piperidine and the whole was allowed to stand in an ice-box for twenty-four hours. The dye separated from the reaction mixture. It was recrystallized from methyl alcohol and obtained as beautiful glittering emerald green crystals which gave a blue methyl alcoholic solution and melted at 203° to 205° C. with decomposition. The dye has the following formula:



EXAMPLE 45.—*2,2'-di-(β-ethoxyethyl)-thiatricarbocyanine iodide*

3.5 g. (2 mol.) of 1-methylbenzothiazole β-ethoxyethiodide and 1.43 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride were dispersed in absolute ethyl alcohol containing 1.0 cc. (2 mol.) of piperidine. The mixture was allowed to stand at about 10° C. for about eighteen hours. The dye which separated was recrystallized from methyl alcohol. It was obtained as minute needles having a greenish-bronze reflex and giving a blue methyl alcoholic solution. The dye melted at 188° to 190° C. with decomposition.

2,2'-di-(β-carbethoxyethyl)-thia-tricarbocyanine iodide was prepared in a similar manner from 1-methylbenzothiazole β-carbethoxyethiodide. The β-carbethoxyethyl dye was obtained as beautiful green crystals which gave a blue methyl alcoholic solution and melted at 142° to 145° C. with decomposition.

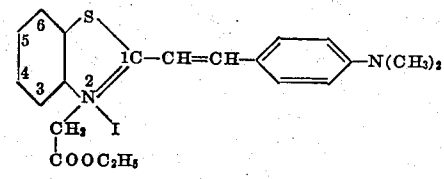
In a manner similar to that illustrated in the above two examples, 2,2'-, selena-, dibenzothia-, thiazolino-, 4,4'- and thiazolotricarbocyanine dyes can be prepared. Instead of piperidine in the above two examples, other strong organic bases can be employed for example triethylamine, tributylamine or diethylamine.

Our new cyclammonium quaternary salts can be employed to prepare tetra- and pentacarbocyanine dyes. Our new cyclammonium quaternary salts containing a reactive methyl group, such as 1-methylbenzothiazole β-ethoxyethiodide or 2-methylnaphthothiazole β-ethoxyetho-p-toluenesulfonate for example, can be condensed with 4-acyloxy-$\Delta^{3,5}$-heptadiene-1,7-dial ditetrahydroquinolide perchlorate or 4-acyloxy-$\Delta^{3,5,7}$-monotriene-1,9-dial ditetrahydroquinolide perchlorate, in the presence of pyridine or piperidine or a mixture of the two, to give tetra- and pentacarbocyanines respectively.

Our new cyclammonium quaternary salts containing a reactive methyl group can be condensed with aldehydes, such as dialkylaminobenzaldehydes, dialkylaminocinnamaldehydes or the like to give dyes. The following examples are illustrative, but are not intended to limit our invention.

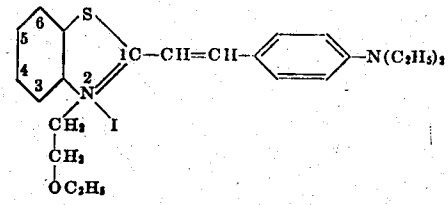
EXAMPLE 46.—*1-(p-dimethylaminostyryl)-benzothiazole carbethoxymethiodide*

3.63 g. (1 mol.) of 1-methylbenzothiazole carbethoxymethiodide and 1.5 g. (1 mol.) of p-dimethylaminobenzaldehyde were heated together in 25 cc. of absolute ethyl alcohol containing four drops of piperidine catalyst at the refluxing temperature for about four hours. The dye separated from the cooled reaction mixture. It was recrystallized from methyl alcohol and obtained as minute dark crystals having a blue reflex and giving a bluish-red methyl alcoholic solution. The dye melted at 218° to 220° C. with decomposition. It has the following formula:



EXAMPLE 47.—*1-(p-diethylaminostyryl)-benzothiazole β-ethoxyethiodide*

1.0 g. (1 mol.) of 1-methylbenzothiazole β-ethoxyetho-p-toluenesulfonate and 0.44 g. (1 mol.) of p-diethylaminobenzaldehyde were heated together in 10 cc. of absolute ethyl alcohol containing four drops of piperidine at the refluxing temperature for about three hours. 1.0 g. of potassium iodide dissolved in enough water to make a 50% solution (by weight) was then added to the hot reaction mixture. The styryl-iodide separated from the reaction mixture. It was recrystallized from methyl alcohol and obtained as dark crystals having a steely reflex and giving a bluish-red methyl alcoholic solution. It melted at 227° to 229° C. with decomposition and has the following formula:



In the above two examples the piperidine acts as a catalyst. In a manner similar to that in the

above two examples the others of our new cyclammmonium quaternary salts containing a reactive methyl group can be condensed with dialkylaminobenzaldehydes and dialkylaminocinnamaldehydes.

Our new dyes sensitize photographic emulsions in a novel and useful manner. Our invention is particularly directed to the customarily employed silver halide emulsions especially the silver chloride and silver bromide emulsions, which may contain other salts which may be light sensitive. Our invention is further particularly directed to the customarily employed gelatin emulsions. However, the gelatin can be replaced with any other carrier which has substantially no deleterious effect on the light-sensitive materials, e. g. a cellulose derivative or a resin.

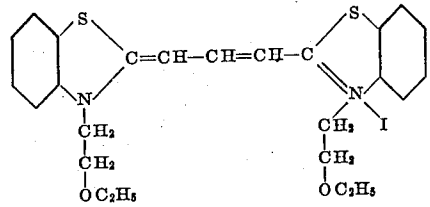
In the preparation of photographic emulsions sensitized with our new dyes, it is only necessary to thoroughly disperse a small amount of our dyes in an ordinary photographic emulsion. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art upon making the ordinary tests and observations customarily employed in the art of emulsion making. To prepare a gelatino-silver-halide emulsion, the following procedure is satisfactory: A quantity of the dye is dissolved in a suitable solvent, for example methyl alcohol or acetone, advantageously the former, and a volume of this solution (which may be diluted with water if desired) containing from 5 to 100 mg. of dye is slowly added to about 1000 cc. of an ordinary flowable gelatino-silver-halide emulsion. The dye is thoroughly incorporated. With the more powerful of our new sensitizing dyes, 10 to 20 mg. of dye per 1000 cc. of emulsion will suffice to produce maximum sensitizing effects with the ordinary gelatino-silver-halide emulsions. In the case of our new tricarbocyanine dyes, about one mg. or less of dye per liter of emulsion is advantageously employed.

The above statements are only illustrative and are not to be understood as limiting our invention in any sense as it will be apparent that these dyes can be incorporated by other methods in many of the photographic emulsions customarily employed in the art, such for instance as by bathing a plate or film, upon which an emulsion has been coated, in a solution of the dye in an appropriate solvent although such a method is ordinarily not to be preferred. The claims are intended to cover any combination of our new dyes with a photographic emulsion whereby the dyes exert a sensitizing effect upon the emulsion as well as a photographic element comprising a support, ordinarily transparent, upon which the light-sensitive emulsion is coated or spread and permitted to set and dry.

The accompanying drawing is by way of illustration and is offered primarily to show the range of sensitivity of representative members of our longer chain dyes. Each figure of the drawing is a diagrammatic reproduction of a spectrogram showing the sensitivity of an ordinary gelatino silver bromide emulsion containing one of our new dyes. In Fig. 1, the curve represents the sensitivity of an ordinary gelatino silver bromide emulsion containing 2,2'-di-(β-carbethoxyethyl)-thiacarbocyanine iodide. In Fig. 2, the curve represents the sensitivity of an ordinary gelatino silver bromide emulsion containing 2,2'-di-(β-cyanoethyl)-thiacarbocyanine iodide. In Fig. 3, the curve represents the sensitivity of an ordinary gelatino silver bromide emulsion containing 2,2'-di-(β-ethoxyethyl)-thiacarbocyanine iodide. In Fig. 4, the curve represents the sensitivity of an ordinary gelatino silver bromide emulsion containing 1,1'-di-(β-acetoxyethyl)-4,4'-carbocyanine iodide. In Fig. 5, the curve represents the sensitivity of an ordinary gelatino silver bromide emulsion containing 2,2'-di-(β-acetoxyethyl)-thiatricarbocyanine iodide.

Still further examples of our new emulsions could be given, but the foregoing will serve to teach those skilled in the art the principles of sensitizing emulsions with our new dyes. The illustrations have been confined to dyes of the longer chain types since it is this group of our dyes which is of the greatest utility in sensitizing emulsions.

In the specification and claims, by the term "cyanine nitrogen atoms" we mean the two nitrogen atoms essential to the cyanine dye chromophor, i. e. the two nitrogen atoms, the one tervalent and the other quinquevalent, which are linked together by a conjugated carbon chain. For example, in a dye such as 2,2'-di-(β-ethoxyethyl)-thiacarbocyanine iodide, which is formulated as follows:



there are two nitrogen atoms (the cyanine nitrogen atoms) linked together by a conjugated chain.

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

1. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing carbocyanine dye containing an alkyl group attached to each of the two nitrogen atoms, at least one of said alkyl groups being a β-ethoxyethyl group.

2. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing thiacarbocyanine dye containing an alkyl group attached to each of the two nitrogen atoms, at least one of said alkyl groups being a β-ethoxyethyl group.

3. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing 4,4'-carbocyanine dye containing an alkyl group attached to each of the two nitrogen atoms, at least one of said alkyl groups being a β-acetoxyethyl group.

4. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing thiatricarbocyanine dye containing an alkyl group attached to each of the two nitrogen atoms, at least one of said alkyl groups being a β-acetoxyethyl group.

5. A photographic gelatino-silver-halide emulsion sensitized with 2,2'-di-(β-ethoxyethyl)-thiacarbocyanine iodide.

6. A photographic gelatino-silver-halide emulsion sensitized with 1,1'-di-(β-acetoxyethyl)-4,4'-carbocyanine iodide.

7. A photographic gelatino-silver-halide emulsion sensitized with a 2,2'-di-(β-acetoxyethyl)-thiatricarbocyanine iodide.

8. A photographic silver halide emulsion sensitized with a sensitizing cyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl

groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

9. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing cyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxylalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

10. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing carbocyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

11. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing thiacarbocyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

12. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing 4,4'-carbocyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

13. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing tricarbocyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

14. A photographic gelatino-silver-halide emulsion sensitized with a sensitizing thiatricarbocyanine dye containing an alkyl group attached to each of the two cyanine nitrogen atoms, at least one of said alkyl groups being an alkyl group selected from the group consisting of alkoxyalkyl groups, acyloxyalkyl groups, carbalkoxyalkyl groups, carboxyalkyl groups and acylalkyl groups which are devoid of aryl group substituents.

LESLIE G. S. BROOKER.
LLOYD A. SMITH.