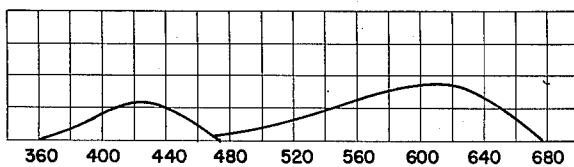
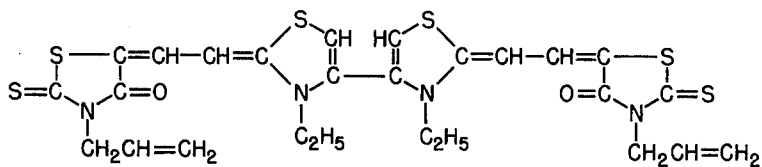


Feb. 19, 1952

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PHOTOGRAPHIC EMULSIONS CONTAINING SYMMETRICAL  
TETRANUCLEAR DYESTUFFS  
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2,586,164



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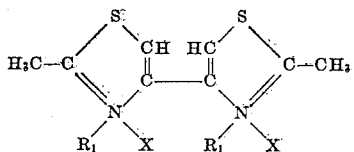
wherein R represents an alkyl group, e. g., methyl, ethyl, propyl, butyl, etc., allyl and phenyl, and R<sub>1</sub> represents an alkyl or aralkyl group, e. g., methyl, ethyl, propyl, isopropyl, butyl, etc., benzyl, phenethyl, and the like.

The process of preparing the above dyes comprises heating, preferably, under reflux conditions, with or without a tertiary base, an alcoholic solution containing one mol of a di-quaternary cyclammonium salt of 2,2'-dimethyl-4,4'-bithiazole and two mols of a rhodanine intermediate having a reactive acetanilido group linked to a monomethine chain adjacent to a keto group of such intermediate. The rhodanine intermediates are described in United States Patent No. 2,186,608.

As illustrative examples of such rhodanine intermediates, reference is made to:

5-acetanilidomethylene-3-methylrhodanine  
5-acetanilidomethylene-3-ethylrhodanine  
5-acetanilidomethylene-3-allylrhodanine  
5-acetanilidomethylene-3-propylrhodanine  
5-acetanilidomethylene-3-phenylrhodanine

The di-quaternary cyclammonium salts of 2,2'-dimethyl-4,4'-bithiazole utilized in the condensation reaction are characterized by the following general formula:



wherein R<sub>1</sub> has the same value as above and X represents an anionic acid radical, e. g., Cl, Br, I, ClO<sub>4</sub>, SO<sub>4</sub>CH<sub>3</sub>, SO<sub>4</sub>C<sub>2</sub>H<sub>5</sub>, SO<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, and the

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product was 109-111° C. After crystallizing from petroleum ether (B. P. 60-75° C.), the melting point was 117° C. and the yield of the product was 13.6 grams.

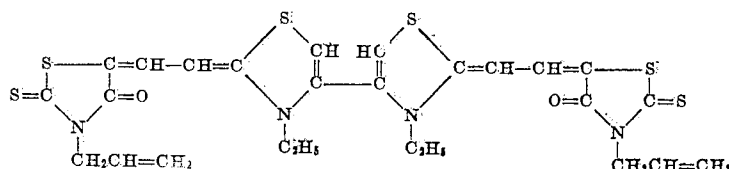
One gram of 1,4-dibromobutane-2,3 and 0.63 gram of thioacetamide were dissolved in 20 cc. of absolute methanol and warmed for 10 minutes on the steam bath. The mixture (a solid had separated) was poured into 100 cc. of water. The aqueous mixture was made acid with diluted hydrochloric acid and filtered. Upon neutralization, a brownish solid appeared in the filtrate. This solid was filtered off and recrystallized from methanol and had a melting point of 165° C.

The quaternization of the 2,2'-dimethyl-4,4'-bithiazole is effectuated by fusion with an alkylating agent, e. g., an alkyl or aralkyl halide or by heating the base with an alkylating agent, e. g., an alkyl or aralkyl halide in a sealed tube in a water bath under increased pressure in the usual manner. The alkylating agent employed may be methyl or ethyl iodide, dimethyl sulfate, methyl p-toluenesulfonate, phenethyl iodide, and the like.

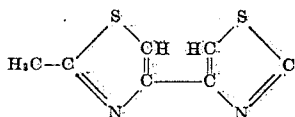
As solvent-diluents employed in the preparation of the new dyes of the present invention, the following alcohols may be employed: methyl, ethyl, propyl, isopropyl, butyl, benzyl, furfuryl alcohol and the like. Triethylamine, tributylamine and the like are representative of the tertiary bases which I may use.

The following examples describe in detail the methods of accomplishing the above objects, but it is to be understood that they are inserted merely for the purpose of illustration and are not to be construed as limiting the scope of the invention.

#### Example I



like, and are obtained by quaternizing 2,2'-dimethyl-4,4'-bithiazole characterized by the following formula:

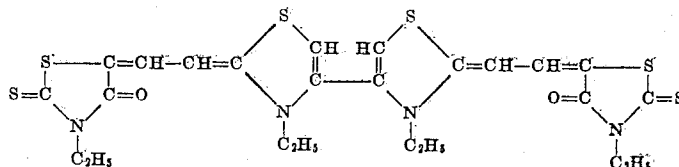


The 2,2'-dimethyl-4,4'-bithiazole is prepared in the following manner:

Eight and six-tenths grams (0.1 mol) of butanedione-2,3 (diacetyl) in 35 cc. of carbon disulfide were treated dropwise with stirring, with a solution of 10.6 cc. of bromine in 20 cc. of carbon

A mixture of 0.25 gram of 2,2'-dimethyl-4,4'-bithiazole diethiodide and 0.35 gram of 3-allyl-5-acetanilidomethylenerhodanine in 15 cc. of isopropanol containing a few drops of triethylamine was heated at reflux for 15 minutes. After cooling, the solid was filtered off and digested a few minutes with 15 cc. of isopropanol. After cooling the product was filtered by suction. The resulting dye had an absorption maximum at 545 m $\mu$  and sensitized a silver chlorobromide emulsion to 640 m $\mu$  with a maximum at 610 m $\mu$ , as illustrated in the figure of the accompanying drawing.

#### Example II

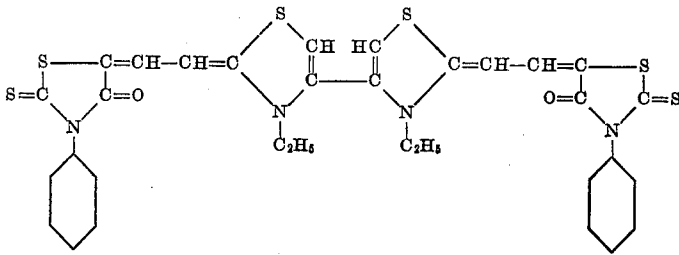


disulfide at the boiling point of the carbon disulfide. The addition was completed in 3 hours. The stirring and heating were continued another 2 hours. After cooling, the carbon disulfide was decanted from the solid which had separated. The crystals were washed with petroleum ether (P. B. 60-75° C.). The melting point of the crude

Example I was repeated with the exception that 0.33 gram of 3-ethyl-5-acetanilidomethylenerhodanine was substituted for 0.35 gram of 3-allyl-5-acetanilidomethylenerhodanine. A tetranuclear merocyanine dyestuff was obtained which has approximately the same sensitizing properties as the dyestuff of Example I.

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Example III



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illustrations, or to the specific details given therein, but is capable of variations and modifications

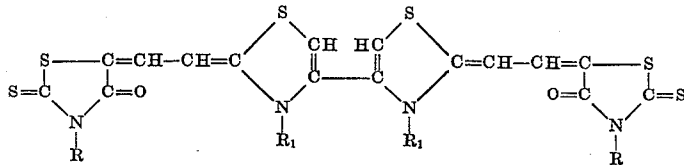
Example I was repeated with the exception that 0.4 gram of 3-phenyl-5-acetanilidomethylmerhodanine was substituted for 0.35 gram of 3-allyl-5-acetanilidomethylmerhodanine. The dyestuff obtained has approximately the same sensitizing characteristics as the dyestuff of Example I.

The diagrammatic spectrogram constituting the accompanying drawing illustrates the regions of the spectrum to which the symmetrical tetra-

15 as to the reactants, proportions, and conditions employed. Accordingly, it is intended that the invention be defined only by the accompanying claims.

I claim:

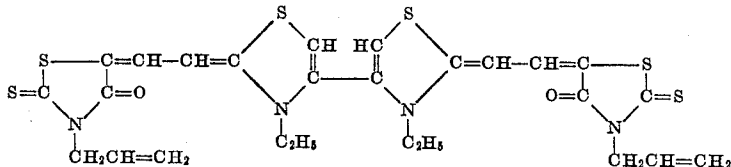
20 1. A photographic gelatino silver halide emulsion containing a symmetrical tetranuclear merocyanine dyestuff characterized by the following general formula:



nuclear merocyanine dyestuffs will sensitize a gelatino silver halide emulsion containing 4-5% of silver halide and the extent of the sensitization at various wavelengths. The single figure of the accompanying drawing illustrates the sensitizing properties of the dyes prepared in accordance with Examples I to III, respectively.

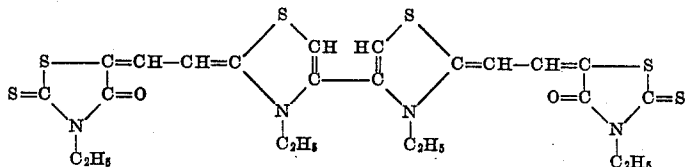
35 wherein R represents a member selected from the class consisting of alkyl, allyl, and phenyl groups, and R1 represents a member selected from the class consisting of alkyl and aralkyl groups.

2. A photographic gelatino silver halide emulsion which contains a dyestuff of the following structure:



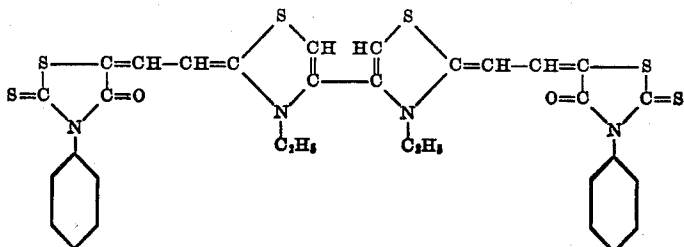
This application is a continuation-in-part of my application Serial No. 92,585, filed May 11, 1949, now abandoned, which was a division of application Serial No. 75,751, filed February 10,

3. A photographic gelatino silver halide emulsion which contains a dyestuff of the following structure:



1949, now abandoned. The sensitizing dyestuffs, per se, are claimed in copending application Serial No. 189,487, filed October 10, 1950, now Patent No. 2,553,503.

4. A photographic gelatino silver halide emulsion which contains a dyestuff of the following structure:



While there have been pointed out above certain preferred embodiments of the invention, the same is not limited to the foregoing examples,

LEE C. HENSLEY.

No references cited.