Sept. 12, 1950 A. W. ANISH 2,521,959

OPTICALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSION

Original Filed March 10, 1944

1,1'-Diethyl-6,6'-dicumyloxacarbocyanine iodide

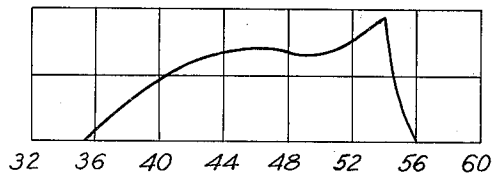


Fig. 1

1,1'-Diethyl-6,6'-ditert-butyloxacarbocyanine iodide

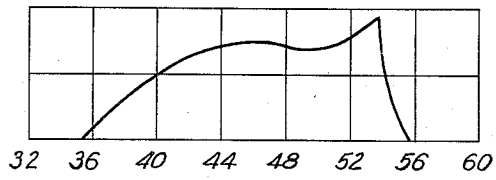


Fig. 2

1,1'-Diethyl-6,6'-diisoamyloxacarbocyanine perchlorate

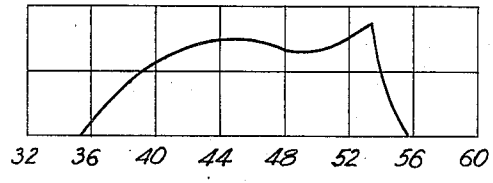


Fig. 3

INVENTOR.
Alfred W. Anish

BY

Henry B. Fellog
ATTORNEYS

Patented Sept. 12, 1950

2,521,959

UNITED STATES PATENT OFFICE

2,521,959

OPTICALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

Alfred W. Anish, Vestal, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

Original application March 10, 1944, Serial No. 525,935, now Patent No. 2,441,342, dated May 11, 1948. Divided and this application August 8, 1947, Serial No. 767,582

4 Claims. (Cl. 95—7)

1

This invention relates to photographic gelatino silver-halide emulsions, and particularly to photographic emulsions sensitized by means of benzoxazole trimethine dye salts having a substitution in the 5-position of the benzene nucleus consisting of a branched chain alkyl and a branched alkyl radical containing an aryl group.

Sensitizing dye salts of the benzoxazole trimethine series, which are substituted in the benzene nucleus by a straight chain alkyl, alkoxy, dialkylamino and hydroxy group are the subjects of several patents. In all of these dyes, however, the substitution in the benzene nucleus causes a shift in the region of sensitivity toward the longer wavelength region of the spectrum, and also causes a corresponding shift in the limits to which the dye sensitizes. In other words, the entire range of added spectral sensitivity is shifted toward the longer wavelength region by any simple straight chain alkyl substitution on the benzene ring.

In view of the foregoing facts, the problem was to provide a benzoxazole, which when condensed with a cyanine dye intermediate, would yield a oxacarbocyanine dye characterized not only by a spectral sensitivity shift toward the longer wavelength region of the spectrum, but also characterized by a steep cut-off in the spectral curve for use in silver-halide emulsions for color photography, wherein the sensitizing dye would cause a sharp decline in sensitivity maximum near the upper limit of the sensitization, and at the same time would have a more selective response to green light. This sharp cut-off is highly desirable in multi-color photography where each of the silver-halide emulsions sensitized to the primary colors, viz., blue, green, and red, should be sensitized with a dye giving a minimum overlap of sensitization in the composite layer so as to produce clearer and truer pictures.

An object of the present invention is to provide photographic silver-halide emulsions with benzoxazole trimethine cyanine dyes substituted in the 5-position by a branched chain alkyl and branched chain alkyl radical having an aryl group.

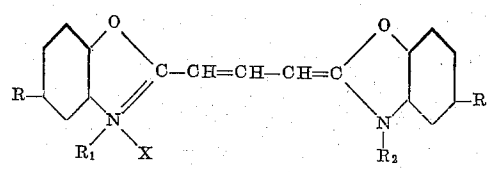
A further object is to provide such dyes which are characterized by a steep cut-off in the spectral curve and a more selective response to green light.

2

Other objects and advantages of this invention will become apparent by reference to the following specification in which the preferred details and embodiments are described.

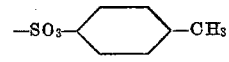
This invention is based on the discovery that such dyes can be prepared by condensing 2-methylbenzoxazole quaternary ammonium salt, substituted in the 5-position by a branched chain alkyl or a branched chain alkyl radical having a aryl group, with ethyl orthoformate. Such dyes not only cause a shift in the spectral region to longer wave lengths but also give rise to an unexpected higher sensitivity maximum than the corresponding dyes containing straight chain alkyl or dialkyl groups with a very sharp cut-off near the upper limit of sensitization. Paraphrasing this, an oxacarbocyanine dye, having a butyl group attached to the benzene ring, has a flat sensitivity maximum at a shorter wave length reading, whereas a similar dye, having a tertiary butyl group attached to the benzene ring, has a sharp sensitivity maximum. The net effect of a straight chain alkyl substitution is to cause a gradual decline from sensitivity maximum to the limits of sensitization, and the net effect in the case of a branched chain alkyl is to cause a sharp decline in sensitivity maximum to the limits of sensitization. The latter phenomenon is commonly referred to as a sharp sensitivity "cut-off."

The sensitizing dyestuffs suitable for the purpose of the present invention are characterized by the following general formula:



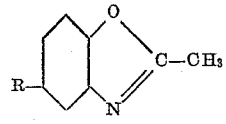
wherein R represents a branched chain alkyl radical or a branched chain alkyl radical containing an aryl group such as, for example, isobutyl, cumyl, isoamyl, tertiary amyl, tertiary hexyl, isopropyl, diisobutyl, 2-, or 3-, methylbutyl groups, R_1 and R_2 represent an alkyl or aralkyl group, e. g., methyl, ethyl, propyl, butyl, benzyl, methylbenzyl, ethylbenzyl, propylbenzyl,

and the like, and X represents an anion such as, for example, Cl, Br, I, SO_4CH_3, ClO_4,



—SCN or any other acid radical forming an alkyl or aralkyl ester.

The benzoxazole intermediates used in the preparation of the aforesaid dyestuffs are represented by the following structural formula:



wherein R is of the same value as above. These intermediates and their salts are prepared according to the methods set forth in my copending application Serial No. 525,936, filed March 10, 1944, now United States Patent 2,429,178, issued October 4, 1947. The corresponding 2 - (β - acetanilidovinyl) benzoxazole derivatives are prepared according to the methods set forth in my copending application Serial No. 525,937, filed March 21, 1947, now United States Patent 2,429,179, issued October 14, 1947.

In preparing the sensitizing dyes utilized in accordance with the present invention, the foregoing intermediate, in the form of a quaternary ammonium salt, is condensed with ethyl orthoformate under reflux conditions in the presence of a basic (acid binding) condensing agent such as pyridine, ethylmethylpyridine, trimethylpyridine, quinoline, and the like. The dye salt thus obtained may be, if desired, converted into a different salt by treating it in solution with an aqueous solution of a salt containing the desired anion such as, for example, potassium bromide or iodide.

The diagrammatic spectograms constituting the accompanying drawing, illustrate the regions of the spectrum to which the various dyes, utilized in the present invention, will sensitize a gelatino silver-halide emulsion containing about .4–.5% of silver-iodide and the extent of the sensitization at various wavelengths.

The figures of this drawing and the specific type of dyes, the sensitizing properties of which they illustrate, are as follows:

Figure 1 shows the sensitivity and the steep cut-off in the spectral curve of the emulsion containing the dye of Example I.

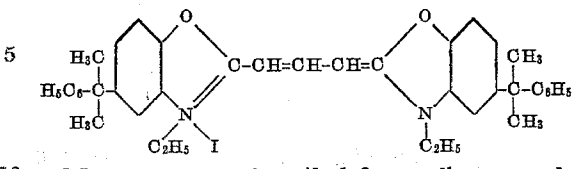
Figure 2 shows the sensitivity and the steep cut-off in the spectral curve of the emulsion containing the dye of Example II.

Figure 3 shows the sensitivity and the steep cut-off in the spectral curve of the emulsion containing the dye of Example III.

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

Example I

1,1'-diethyl-6,6'-dicumyloxacarbocyanine iodide

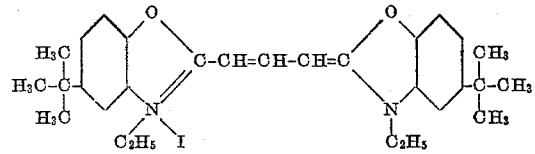


2.5 grams of 2-methyl-6-cumylbenzoxazole ethyl p-toluenesulfonate, 1.5 grams of ethyl orthoformate, and 10.0 cc. of pyridine were refluxed for 3 hours. The reaction mixture was then cooled and poured into 50 cc. of water containing 1 gram of potassium iodide and allowed to stand. The dye crystals, which precipitated, were filtered and washed with water, and finally recrystallized from ethyl alcohol. Brilliant yellow, flat, prism-shaped dye crystals are obtained which melt at 270° C.

Incorporated in a gelatino silver bromide emulsion containing about .4–.5% of silver iodide, the dye sensitizes from about 490 mμ to about 560 mμ with a maximum at about 540 mμ, and with a sharp cut-off as shown in Figure 1.

Example II

1,1'-diethyl-6,6'-ditert.-butyloxacarbocyanine iodide

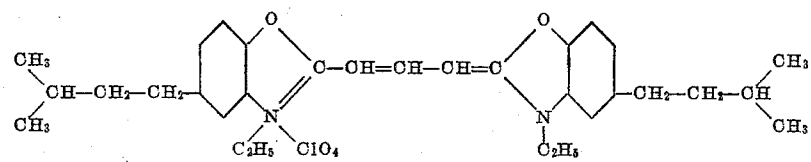


2.4 grams each of 2-methyl-6-tert.-butyl-benzoxazole ethyl p-toluenesulfonate and ethyl orthoformate were condensed by refluxing in 10.0 cc. of pyridine for 2½ hours. The cooled reaction mixture was poured into water containing three grams of potassium iodide and allowed to stand. The water was decanted, the residue was washed with water followed by ethyl ether and then crystallized twice from ethanol. Red rhombic crystals are obtained, which melt at 257° C.

Incorporated in a gelatino silver bromide emulsion containing about .4–.5% of silver iodide, the dye sensitizes from about 490 mμ to about 560 mμ with a maximum at about 535 mμ, and with a sharp cut-off as shown in Figure 2.

Example III

1,1'-diethyl-6,6'-diisoamyloxacarbocyanine perchlorate



2.0 grams of 2-methyl-6-isoamylbenzoxazole ethyl p-toluenesulfonate and 2.0 grams of ethyl orthoformate in 10.0 cc. of pyridine were heated under reflux for 2½ hours. The cooled reaction mixture was diluted with water and on standing separated as on oil. After repeated washings with water, the oil was dissolved in alcohol and 10% of sodium perchlorate solution added. The dye crystals were separated and recrystallized from ethyl alcohol. Red, blue reflex (rhombic) crystals are obtained, which melt at 225° C.

Incorporated in a gelatino silver bromide emulsion containing about .4–.5% of silver iodide, the dye sensitizes from about 490 mμ to about 560 mμ

with a maximum at about 535 mμ, and with a sharp cut-off as shown in Figure 3.

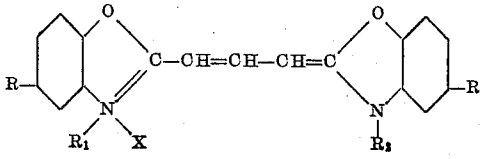
In the preparation of emulsions containing the foregoing dyes, the dyestuff may be dissolved in methyl or ethyl alcohol and a solution thereof containing from 5 to 50 milligrams of the dyestuff added to a liter of emulsion. While in general practice it may not be necessary to add the dyestuff in the amounts larger than those above given, generally, for satisfactory results, amounts usually ranging from 5 to 25 milligrams are sufficient to obtain a maximum sensitizing effect. However, I do not wish to limit my invention to the quantities indicated as the most suitable amount will, in each case, be found by a few comparative experiments. The dyestuffs may be added to the emulsion in the form of a solution. Suitable solvents as previously indicated are the alcohols, for instance, methyl or ethyl alcohol, which may be anhydrous or diluted with a small volume of water. In actual practice the dyestuffs are applied to the emulsion during any stage of its production, however, they are preferably added to the finished emulsion before being cast.

This application is a division of my copending application Serial No. 525,935, filed March 10, 1944, now United States Patent 2,441,342, issued May 11, 1948.

While there have been pointed out above certain preferred embodiments of the invention, the same is not limited to the foregoing examples, illustrations, or to the specific details given therein, but is capable of variations and modifications as to the reactants, proportions and conditions employed. Accordingly, it is intended that the invention be defined only by the accompanying claims.

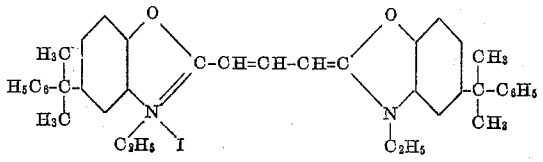
I claim:

1. A photographic gelatino-silver-halide emulsion which contains a compound selected from the group consisting of compounds of the general formula:

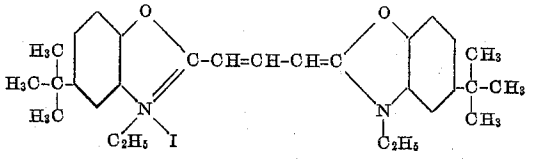


wherein R represents a member selected from the class consisting of a branched chain alkyl radical and branched chain alkyl radical containing an aryl group, R_1 and R_2 represent a member selected from the class consisting of alkyl, and aralkyl groups, and X represents an anion.

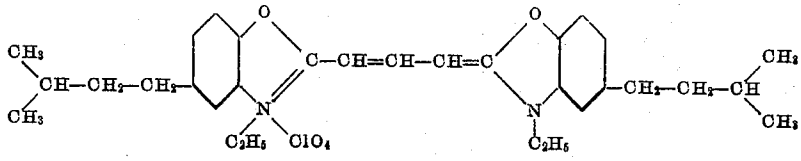
2. A photographic gelatino-silver-halide emulsion which contains a dye of the following structure:



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



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



ALFRED W. ANISH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,173,486	Schneider	Sept. 19, 1939
2,230,257	Middleton et al.	Feb. 4, 1941
2,233,509	Brooker et al.	Mar. 4, 1941
2,323,504	Wilson	July 6, 1943
2,354,524	Kumetat et al.	July 25, 1944