UNITED STATES PATENT OFFICE

2,148,980

PHOTOGRAPHIC MATERIAL FOR COLOR **PHOTOGRAPHY**

Walter Dieterle, Dessau-Ziebigk, Germany, assignor to Agfa Ansco Corporation, Binghamton, N. Y., a corporation of New York

No Drawing. Application July 14, 1937, Serial No. 153,516. In Germany July 17, 1936

2 Claims. (Cl. 95—2)

My present invention relates to an improved photographic material for color photography.

One of its objects is to provide a photographic material for multi-color photography having sensitized silver halide emulsion layers of high sensitivity to red and low sensitivity to blue-green. Further objects will be seen from the detailed specification following hereafter.

In certain processes of subtractive multi-color 10 photography a multi-layer photographic material is used in which the lowest light-sensitive layer is sensitive only for red above 6000 A. U. (in the region of the threshold of sensitivity). This red-sensitive layer must always fulfill the fundamental condition that it is insensitive to blue-green light since the presence of blue-green sensitivity gives rise to falsification of color. In all color-photography processes in which the color of the component pictures is produced by 20 chromogenic development or the like, for example with aid of leuco bases or anti-diazotates there may be present in the photographic layer in addition to the sensitizer a dyestuff former which when the exposed silver halide emulsion is devel-25 oped combines with the oxidation product of the developer to form a sparingly soluble dyestuff distributed in the layer proportionately to the quantity of silver image. In this case a sensitizer must be selected the effect of which is not en-30 feebled by the presence of the dye component. Sensitizers are already known which have a high intensity in the red region of the spectrum but these for the most part have also very high sensitivity to green. Such dyestuffs are, for example 35 the carbocyanines which are formed from α naphthothiazole (thiazole from α-naphthylamine) by condensation with ortho-acetic acid ester. There are also sensitizers which have a wide gap in the blue-green, for example pinacy-

The present invention is based on the observation that symmetrical and unsymmetrical dial-45 kylaminobenzthiazole-trimethinecyanines, dialkylaminobenzselenazole-trimethinecyanines and dialkylaminoindolenine-trimethinecyanines suitable dyes for sensitizing silver halide emulsion layers, which should be of high red sensi-50 tivity and low blue-green sensitivity. The dyestuffs of the two first named classes may, if desired, contain alkyl-groups as substituents in the polymethine chain. The dyestuffs for sensitizing the red-sensitive layer are described in U. S. 55 Patent 2,020,636; U. S. Patent 2,066,966; U. S.

anol blue (carbocyanine from β -naphtho-quinal-

dine) but their sensitivity to red is comparatively

small.

Patent 2,086,689; French specifications Nos. 43,345 (addition to Patent No. 730,966) and 42,256 (addition to Patent No. 734,200). These dyestuffs in outstanding manner fulfil the requirement for lack of sensitivity to blue-green and very high 5 sensitivity to red. At the same time these sensitizers have the advantage that their sensitivity is not depressed by the presence of dyestuff formers.

The following examples illustrate the invention 10 but they are not intended to limit it thereto:

Example 1

To 1 kilo of a silver halide gelatin emulsion are added 8 mg. of the dyestuff para-diethylamino- 15 benzthiazole-trimethinecyanine dissolved methanol. The gap in the blue-green extends in medium exposure, about 5 times the initial sensitivity (threshold) between about 5000 and 5500 Å. U.

Example 2

20

35

To the silver halide gelatin emulsion sensitized as described in Example 1 there is further added a methanol solution of 5 grams of 1-hydroxy-2.4'dibromonaphthalene (dye former for blue-green 25 development).

Example 3

To 1 kilo of a silver halide gelatin emulsion are added 6 mg. of the dyestuff para-diethylamino- 30 benzselenazole-trimethinecyanine. The gap in the blue-green at medium exposure, about 5 times the initial sensitivity (threshold) extends from about 5000 to about 5500 Å. U.

Example 4

To the silver halide gelatin emulsion sensitized as described in Example 3 there are added 4 grams of octodecyl-1-hydroxy-2-naphthoylamine (dye former for blue-green development). 40

Example 5

To 1 kilo of a silver halide gelatin emulsion are added 5 mg. of the dyestuff para-diethylaminoindolenine-trimethinecyanine. The gap in the 45 blue-green at medium exposure, about 5 times the initial sensitivity (threshold) extends from 5000 to about 5600 Å. U.

Example 6

To 1 kilo of a silver halide gelatin emulsion are added 6 mg. of 3.3'-diethyl-6-diethylaminobenzthiazole-trimethinecyanine iodide. The emulsion has a sensibility maximum at about 6400 Å. U. and a range of sensibility from about 5200 to 55 15

40

about 7000 Å. U. and shows a gap in the bluegreen from about 4900 to about 5200 Å. U. at medium exposure.

Example 7

To 1 kilo of a silver halide gelatin emulsion are added 8 mg. of 3.3'-diethyl-5'.6-diethoxy-6-diethylaminobenzthiazole-trimethinecyanine iodide. The emulsion has a sensibility maximum at about 6500 Å. U. and a range of sensibility from about 5300 to about 7200 Å. U. and shows a gap in the blue-green between about 4900 and about 5300 Å. U. at medium exposure.

Example 8

To 1 kilo of a silver halide gelatin emulsion are added 5 mg. of 3-ethyl-6-diethylaminobenzthiazole-1'.-1'.3'-trimethyl-6'-methoxyindolenine-trimethinecyanine. The emulsion having a sensibility maximum at about 6300 Å. U. and a range of sensibility from about 5200 to about 6800 Å. U. shows a gap in the blue-green from about 4900 to about 5200 Å. U. at medium exposure.

Example 9

To 1 kilo of a silver halide gelatin emulsion are added 8 mg. of the dyestuff para-dimethylaminobenzthiazole-trimethinecyanine in a solution of methanol. The gap in the blue-green extends between about 5000 and about 5500 Å. U. at medium exposure.

Example 10

To the silver halide gelatin emulsion sensitized as described in Example 9 there are added 5 grams of 1-hydroxy-2.4'-dibromo-naphthalene (dye former for blue-green development) dissolved in methanol.

Example 11

To 1 kilo of a silver halide gelatin emulsion are added 8 mg. of para-diethylaminobenzthiazole-β-methyl-trimethine cyanine dissolved in meth-45 anol. The gap in the blue-green extends between about 5000 and about 5500 Å. U. at medium exposure.

.

.

.

Example 12

To 1 kilo of the silver halide emulsion sensitized as described in Example 11 there are added 5 grams of 1-hydroxy-2.4'-dibromo-naphthalene in a solution of methanol.

What I claim is:

1. A photographic material for color photography which comprises a red-sensitive silver halide gelatin emulsion layer containing a dye-stuff-former capable of forming a blue-green picture and a dye corresponding with the following general formula

$$\begin{array}{c|c}
R & & Z \\
\hline
R & & C-CH=CH-CH=C \\
\hline
R & & X
\end{array}$$

wherein Y and Z stands for a member of the $_{20}$ group consisting of

R stands for alkyl, X stands for an anion, U stands for a member of the group consisting of dialkylamino radical, alkyl, alkoxy and a fused-on benzene nucleus.

2. A photographic material for color photography which comprises a red-sensitive silver halide gelatin emulsion layer containing a dyestuff-former capable of forming a blue-green picture and a dye corresponding with the following general formula

wherein V and W stand for a member of the group consisting of S and Se, R and R₁ stand for alkyl, X stands for an anion, U stands for a member of the group consisting of dialkylamino radical, alkyl, alkoxy and a fused-on benzene nucleus.

.

•

WALTER DIETERLE.