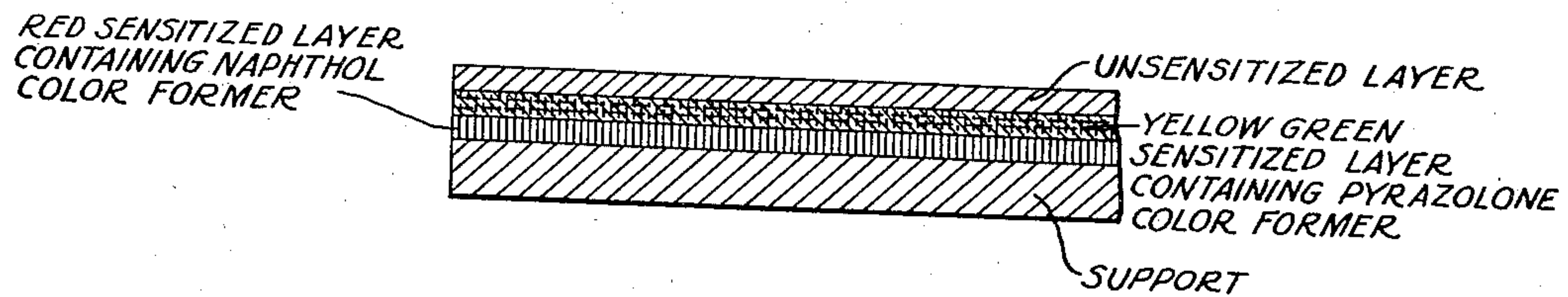


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W. DIETERLE  
COLOR PHOTOGRAPHY  
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2,148,979



*Inventor*  
WALTER DIETERLE

By *Hutz and Joslin*

*Attorneys.*

## UNITED STATES PATENT OFFICE

2,148,979

## COLOR PHOTOGRAPHY

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

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In Germany May 29, 1936

4 Claims. (Cl. 95—2)

The present invention relates to color photography and more particularly to the sensitizing of multi-layer material for color development.

One of its objects is to provide a durable silver halide emulsion layer containing color formers and highly sensitive to red and to yellow green.

A further object is to provide a layer the sensitivity of which is sufficient both for the negative and the reversal process.

Further objects will be apparent from the detailed specification following hereafter.

The present invention is based on the observation that for sensitizing multi-layer silver halide emulsions suitable for color photography not all sensitizers used for ordinary black and white photography are operative. This is due to the fact that the sensitivity of a great many sensitizers is considerably depressed by the color-forming component contained in the layer.

Reference is made to the accompanying self-explanatory drawing which shows the photographic element according to the present invention.

The invention consists in sensitizing to red a layer containing a color former for the blue-green picture by addition of a sensitizer from the class of the dialkylaminothio-, dialkylamino-seleno- and dialkylaminoindocarbocyanines, and sensitizing to yellow-green a layer containing a color former for the purple picture by addition of a dyestuff from the class of the symmetrical  $\beta,\beta'$ -naphthoxocarbocyanines or unsymmetrical carbocyanines which contain a thiazoline ring or an azole, benzoxazole-, benzthiazole- or benz-selenazole-ring with further radicals in the benzene ring. The substituents may be alkyl, halogen, benzoylamino or hydroaromatic groups (for example cyclohexyl); moreover, instead of one or both benzene rings, naphthalene rings and their tetra-hydrogenated derivatives may be connected in the three possible positions with the ring containing nitrogen. The dyestuffs used for sensitizing the red-sensitive layer are described in U. S. patent application Ser. No. 591,389 filed February 8, 1932, and also in the German specification No. 606,699; in U. S. Patent 2,020,636, U. S. Patents 2,066,966/67/68 and in French specifications Nos. 42,245 (addition to 730,966) and 42,256 (addition to 734,200). For sensitizing the yellow-green sensitive layer there may be used, for example  $\beta,\beta'$ -naphthoxocarbocyanine and its substitution products in which the middle carbon atom of the polymethine chain carries a methyl- or ethyl-group as indicated in U. S. Patent No. 2,072,908; also the  $\beta,\beta'$ -naphthoxotetra-

hydronaphtho-thiomesomethylcarbocyanine is suitable.

By the invention there are obtained durable silver halide emulsion layers containing color formers and highly sensitive to red and to yellow-green color. For practical purposes the combination disclosed herein is the first combination of layers the sensitivity of which is sufficient for negative processes or reversal processes. Obviously the invention is also applicable for producing single layers carrying color formers which serve for making component color pictures. In addition to the color formers and sensitizers, the layers may also contain other usual additions to emulsions, for example stabilizers.

The following examples when taken with the accompanying self-explanatory drawing disclosing a section of a film according to the present invention illustrate the invention without limiting it to the specific details mentioned therein.

1. To 1 kilo of silver halide emulsion containing about 10 per cent of gelatin and 6 per cent of silver halide are added 6 milligrams of the dyestuff para-diethylaminobenzthiocarbocyanine iodide and 5 grams of 1-hydroxy-2,4-dibromonaphthalene dissolved in methanol.

Maximum sensitivity: 6500 Angstrom units; strong gap in the green.

2. To 1 kilo of silver halide emulsion are added 5 milligrams of the dyestuff para-dimethylaminobenzselenocarbocyanine iodide and 4 grams of octodecyl-1-hydroxy-2-naphthoamine.

Maximum sensitivity: about 6600 A. U.

3. To 1 kilo of silver halide emulsion containing about 10 per cent of gelatin and 6 per cent of silver halide are added 4 milligrams of the dyestuff 6,6'-diethylamino-1,3,3,1'-3,3'-hexamethylindocarbocyanine iodide and 5 grams of 1-hydroxy-2,4-dibromonaphthalene in the form of a solution in methanol.

Maximum sensitivity: about 6900 A. U.

4. To 1 kilo of a silver halide emulsion which contains as color former for the purple picture 10 grams of 1-(meta-stearylaminophenyl)-3-methyl-5-pyrazolone are added 30 milligrams of 1,1'-diethylmesoethyl- $\beta,\beta'$ -naphthoxocarbocyanine bromide.

Maximum sensitivity: 5650 A. U.

5. To 1 kilo of silver halide emulsion containing as color former for the purple picture 4 grams of 1-(meta-oleylaminophenyl)-3-methyl-5-pyrazolone are added 8 milligrams of 1,1'-diethylmesomethyltetrahydro-naphthothio- $\beta,\beta'$ -naphthoxocarbocyanine iodide.

Maximum sensitivity: 5600 A. U.



6. To 1 kilo of silver halide emulsion which contains as color former for the purple picture 4 grams of 1-(meta-oleylaminophenyl)-3-methyl-5-pyrazolone are added 16 milligrams of 1.1'-diethyl- $\beta$ -naphthothiothiazoline-carbocyanine iodide.

Maximum sensitivity: 5550 A. U.

7. To 1 kilo of silver halide emulsion are added 6 milligrams of para-diethylaminobenzthio- $\beta$ , $\beta'$ -naphthoxo-carbocyanine-ethyl iodide and 4 grams of octodecyl-1-hydroxy-2-naphthoylamine.

Maximum sensitivity: 6100 A. U.

8. To 1 kilo of silver halide emulsion are added 6 milligrams of paradiethylaminobenzthio-5',6'-diethoxy-carbocyanine-ethyl iodide and 4 grams of octodecyl-1-hydroxy-2-naphthoylamine.

Maximum sensitivity: 6500 A. U.

9. To 1 kilo of silver halide emulsion which contains a color-former for the purple picture 10 grams of 1-stearyl-aminophenyl-3-methyl-5-pyrazolone are added 15 milligrams of 1-1'-diethylmesomethyl-(tetrahydro- $\beta$ -naphthothio)- $\beta$ -naphthoxocarbo-cyanine iodide.

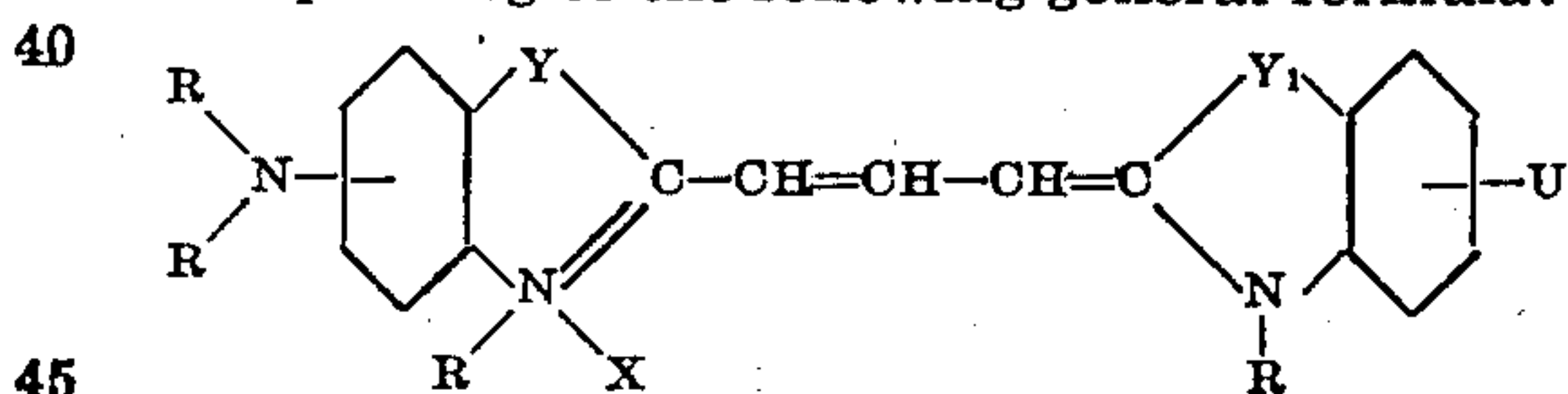
Maximum sensitivity: 5650 A. U.

10. To 1 kilo of silver halide emulsion are added 8 milligrams of 1.1'-diethyl-para-diethylaminobenzthio-meta-phenyloxocarbo-cyanine iodide and 4 grams of octodecyl-1-hydroxy-2-naphthoylamine.

Maximum sensitivity: 6000 A. U.

What I claim is:

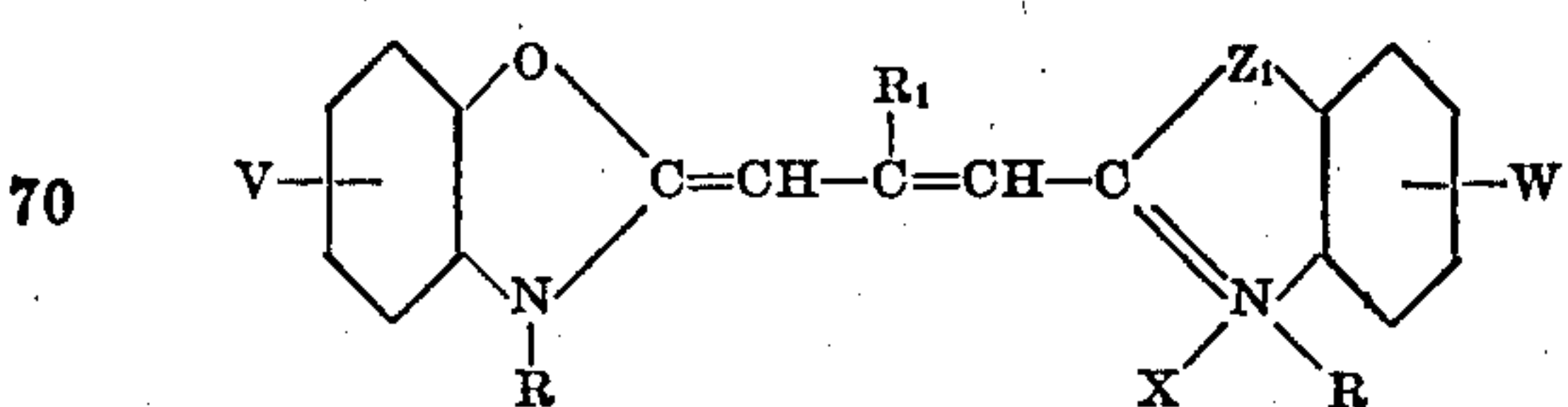
1. A multi-layer material for color photography comprising a support, a red-sensitive silver halide emulsion layer containing a color-former for the blue-green picture and capable of forming a dye-stuff selected from the group consisting of quinoneimine-, azomethine- and azo-dyestuffs, said layer containing further a sensitizing dye corresponding to the following general formula:



wherein Y and Y<sub>1</sub> stand for a member of the group consisting of



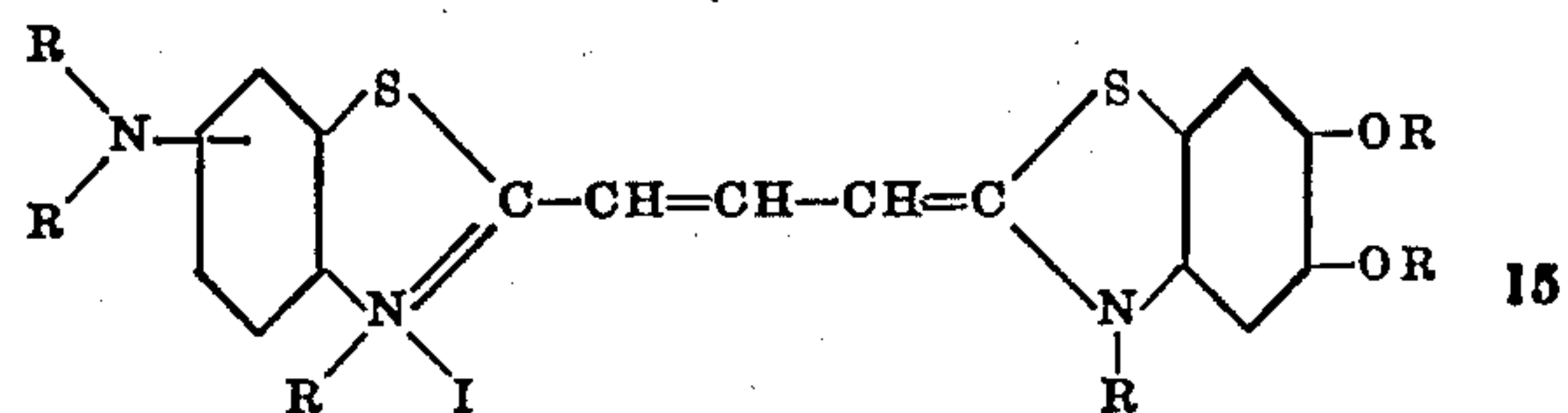
and R stands for alkyl, X stands for an anion, U stands for a member of the group consisting of the dialkylamino radical, alkyl, alkoxy, a fused-on benzene nucleus, a tetrahydrogenated benzene nucleus; and a yellow-green sensitive silver halide emulsion layer containing a color former for the purple picture and capable of forming a dyestuff selected from the group consisting of quinoneimine-, azomethine-, and azo-dyestuffs, said layer containing further a sensitizing dye being a member of the group consisting of  $\beta$ , $\beta'$ -naphthoxocarbo-cyanines, unsymmetrical carbocyanines containing one thiazoline nucleus and dyes corresponding with the following general formula:



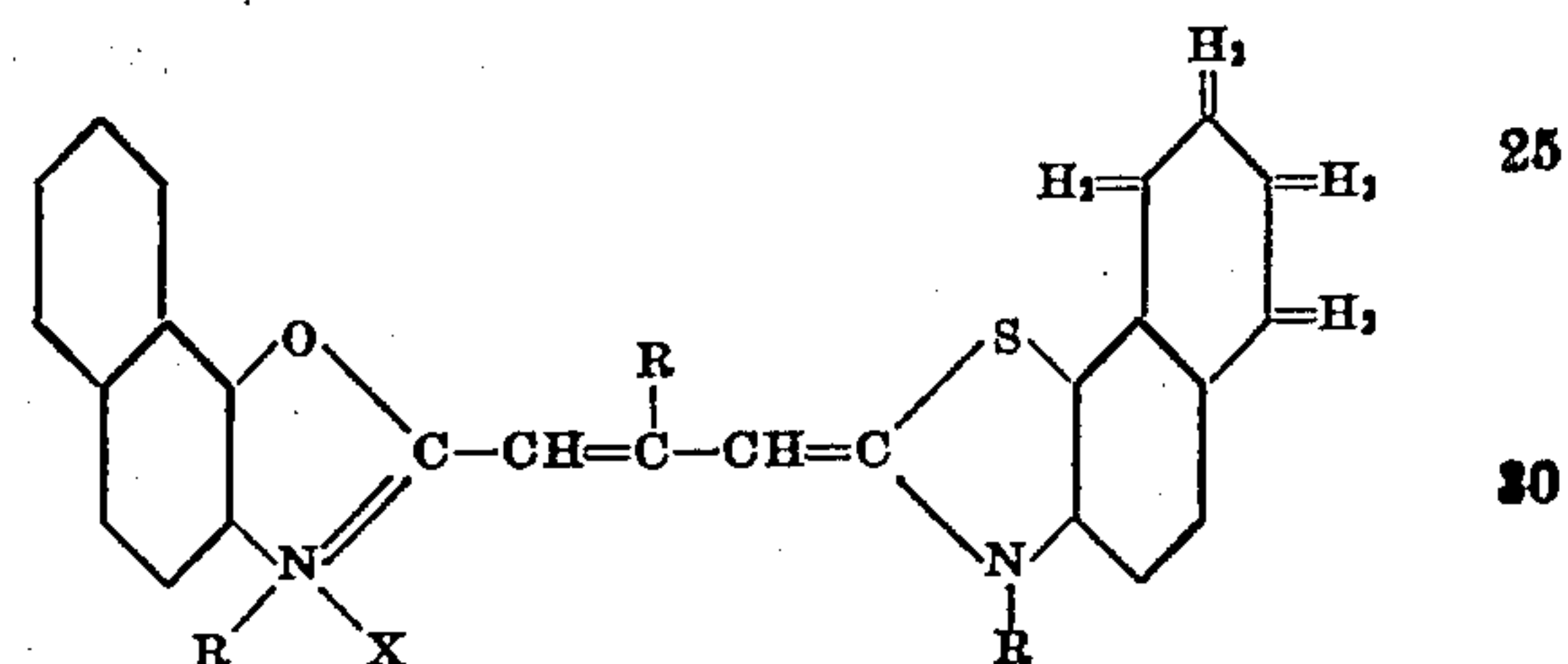
V and W being a member of the group consisting of alkyl, alkoxy, a fused-on benzene nucleus, a

tetrahydrogenated benzene nucleus, the benzoyl-amino radical and a hydroaromatic radical, X being an anion, Z<sub>1</sub> being a member of the group consisting of O, S, Se and R<sub>1</sub> being a member of the group consisting of H and alkyl.

2. A multi-layer material for color photography which comprises a support, a red-sensitive silver halide emulsion layer containing as a color-former octodecyl-1-hydroxy-2-naphthoylamine and a dye corresponding to the following formula

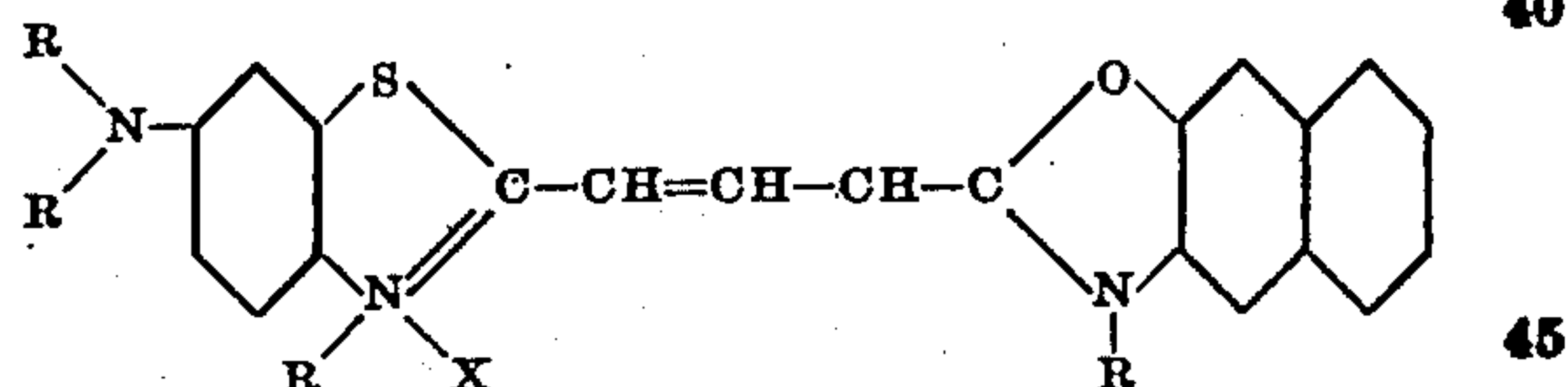


R being alkyl, X being an anion, a yellow-green sensitive silver halide emulsion layer containing as a color-former 1-(stearylaminophenyl)-3-methyl-pyrazolone and a dye corresponding to the following formula

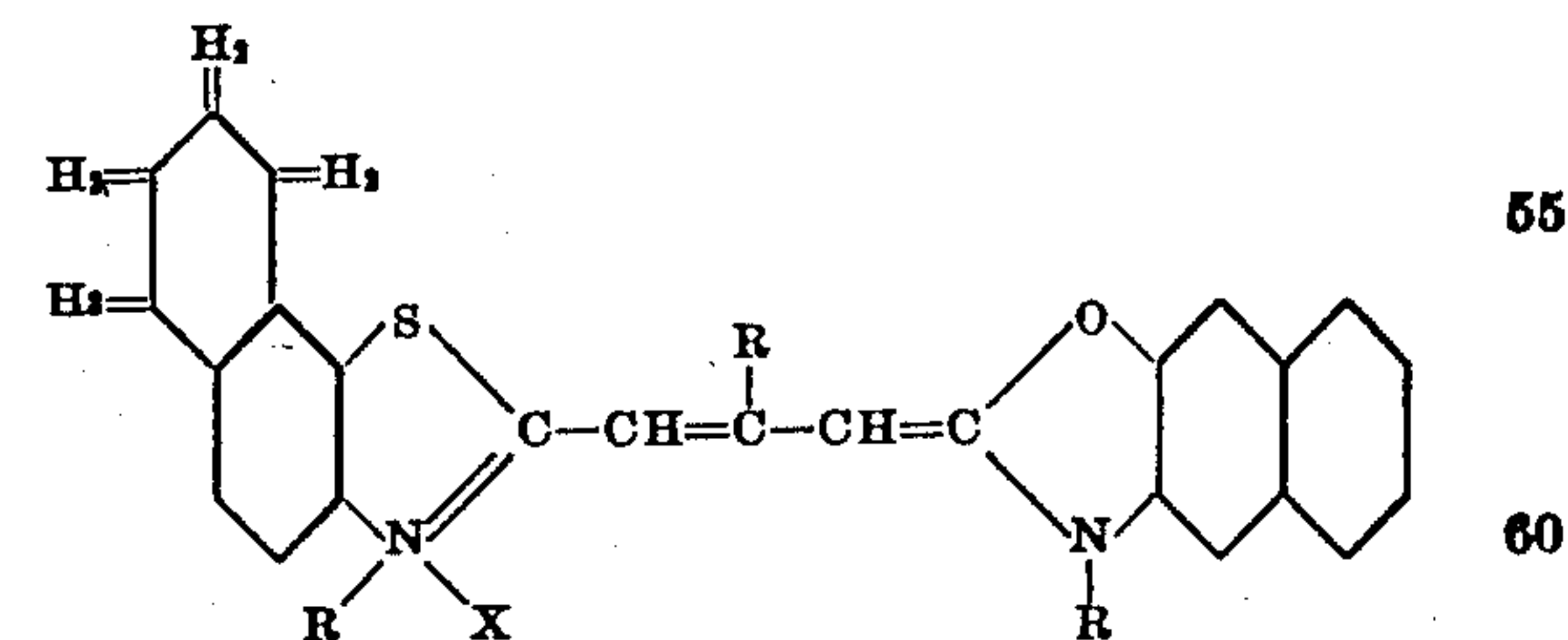


R being alkyl, X being an anion.

3. A multi-layer material for color photography which comprises a support, a red-sensitive silver halide emulsion layer containing as a color-former octodecyl-1-hydroxy-2-naphthoylamine and a dye corresponding to the following formula

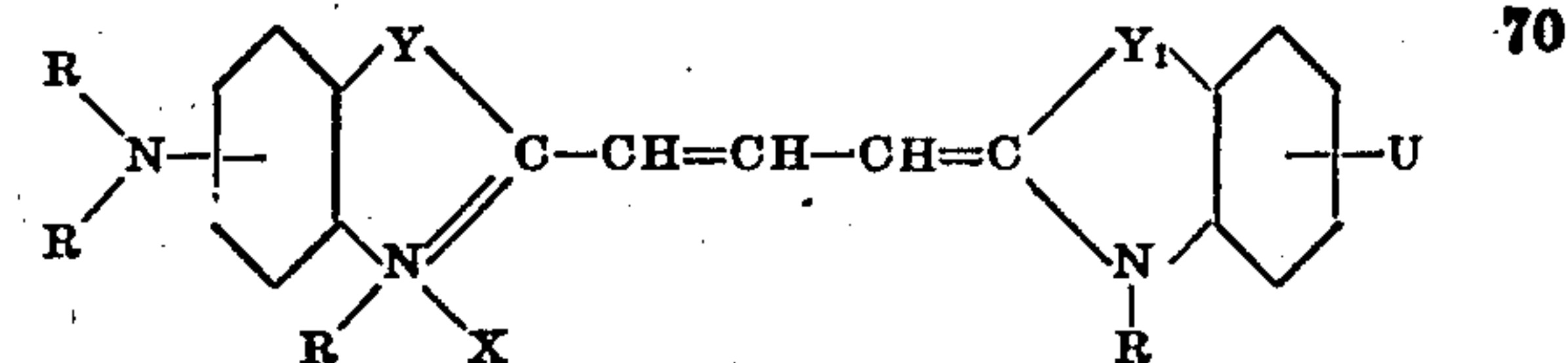


R being alkyl, X being an anion, and a yellow-green sensitive silver halide emulsion layer containing as a color-former 1-(m-oleoyl-aminophenyl)-3-methyl-5-pyrazolone and a dye corresponding to the following formula

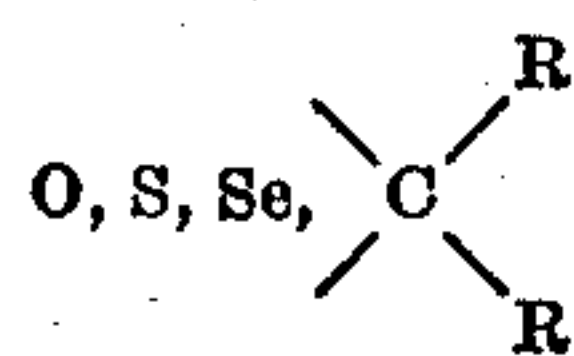


wherein R stands for alkyl and X stands for an anion.

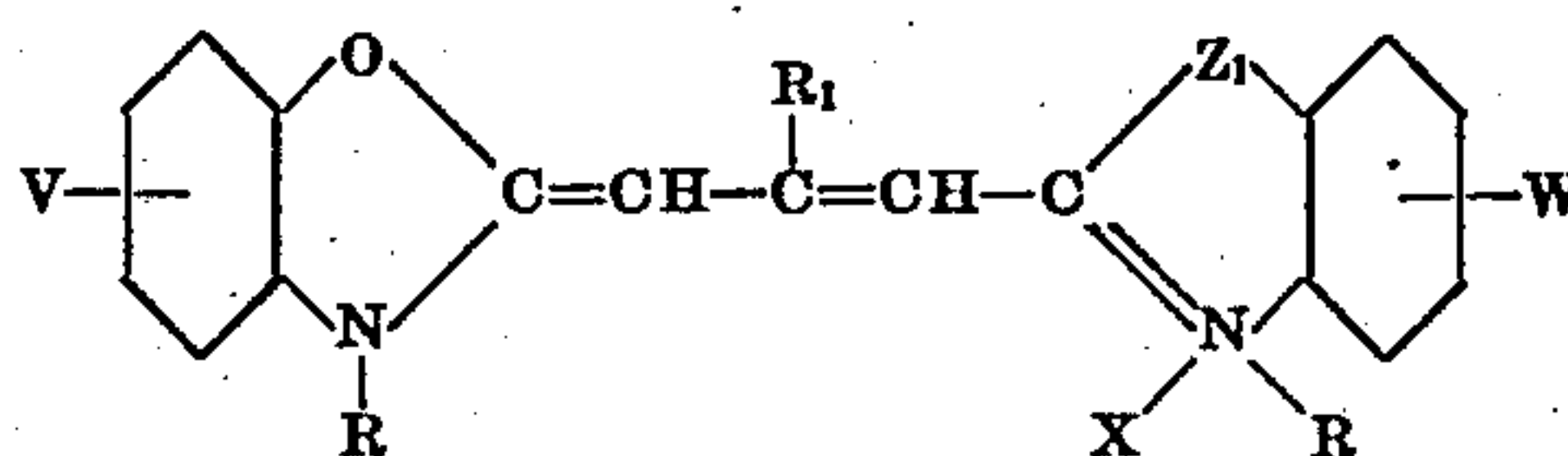
4. A multi-layer material for color photography comprising a support, a red-sensitive silver halide emulsion layer containing a naphthol color-former and a dye corresponding to the following general formula:



wherein Y and Y<sub>1</sub> stand for a member of the group consisting of



azoline nucleus and dyes corresponding to the following general formula



and R stands for alkyl, X stands for an anion, U stands for a member of the group consisting of the dialkylamino radical, alkyl, alkoxy, a fused-on benzene nucleus, a tetrahydrogenated benzene nucleus; and a yellow-green sensitive silver halide emulsion layer, containing a pyrazolone color-former and a dye being a member of the group consisting of  $\beta,\beta'$ -naphthoxocarbocyanines, unsymmetrical carbocyanines containing one thi-

V and W being a member of the group consisting of alkyl, alkoxy, a fused-on benzene nucleus, a tetrahydrogenated benzene nucleus, the benzoylamino radical and a hydroaromatic radical, X being an anion, Z<sub>1</sub> being a member of the group consisting of O, S, and Se, and R<sub>1</sub> being a member of the group consisting of H and alkyl.

WALTER DIETERLE.