

July 7, 1953

J. J. JENNEN ET AL

2,644,754

SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

Filed Aug. 4, 1947

2 Sheets-Sheet 1

FIG. 1

A = 3,3'-DIETHYL-2,2'-CYANINE IODIDE.  
B = 1-PHENYL-3-METHYL-5-HYDROXYPYRAZOLYL-ALPHA'-  
METHYL-TRIMETHINE-1-PHENYL-3-METHYL-5-  
PYRAZOLONE-P-P'-DI-AMMONIUM SULPHONATE.  
C = A MIXTURE OF THESE TWO DYES.

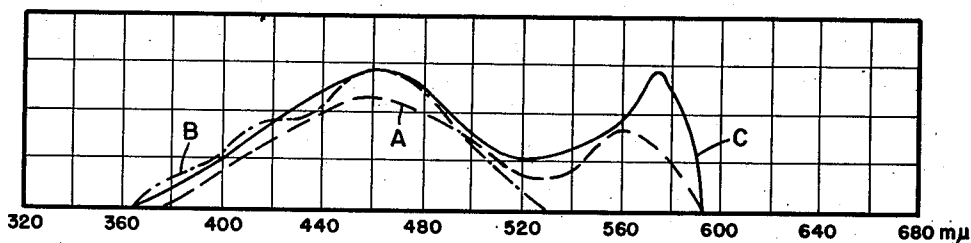
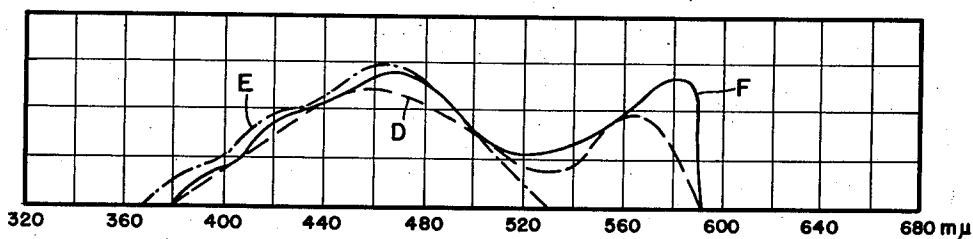


FIG. 2

D = 3,3'-DIETHYL-2,2'-CYANINE IODIDE.  
E = 1-PHENYL-3-METHYL-5-HYDROXYPYRAZOLYL-ALPHA'-  
BETA-BUTYLENETRIMETHINE-1-PHENYL-3-METHYL-  
5-PYRAZOLONE-P-P'-DI-AMMONIUM SULPHONATE.  
F = A MIXTURE OF THESE TWO DYES.



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FIG. 3

G = 3,3'-9-TRIETHYL-6,7,6',7'-DIBENZOXO-CARBOCYANINE IODIDE.  
H = 1-PHENYL-3-METHYL-5-HYDROXYPYRAZOLYL-ALPHA'-METHYL-TRIMETHINE-1-PHENYL-3-METHYL-5-PYRAZOLONE-P-P'-DI-AMMONIUM SULPHONATE.  
I = A MIXTURE OF THESE TWO DYES.

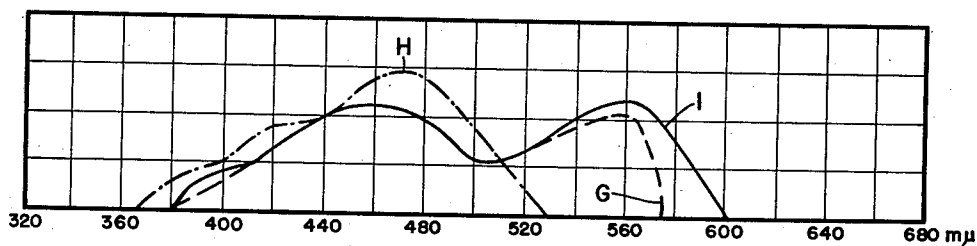
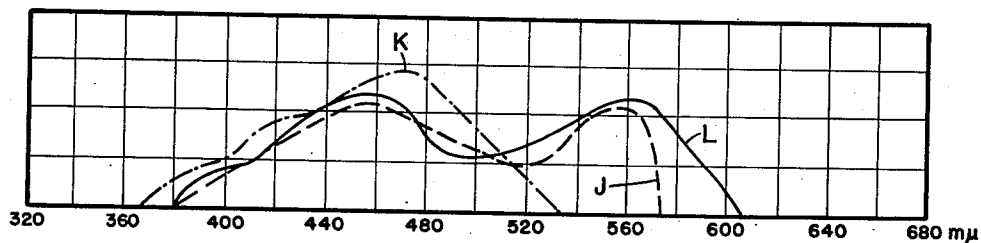


FIG. 4

J = 3,3'-9-TRIETHYL-6,7,6',7'-DIBENZOXO-CARBOCYANINE IODIDE.  
K = 1-PHENYL-3-METHYL-5-HYDROXYPYRAZOLYL-ALPHA'-BETA-BUTYLENETRIMETHINE-1-PHENYL-3-METHYL-5-PYRAZOLONE-P-P'-DI-AMMONIUM SULPHONATE.  
L = A MIXTURE OF THESE TWO DYES.



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# UNITED STATES PATENT OFFICE

2,644,754

## SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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Application August 4, 1947, Serial No. 766,098  
In Germany May 22, 1941

Section 1, Public Law 690, August 8, 1946  
Patent expires May 22, 1961

4 Claims. (Cl. 95-7)

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This invention relates to a process for sensitizing photographic silver halide emulsions by means of dyestuff combinations. In the present case, the expression "combination" does not mean a chemical combination but an association in a larger sense, i. e., a union in action.

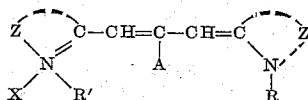
As generally known, the effect of a sensitizer is not in proportion to the quantity added to the emulsion; it passes through a certain maximum by raised concentration.

A combination of sensitizers usually does not produce a larger effect; it often causes but a smaller effect than a single sensitizer when the latter is used in a concentration equal to the sum of the concentrations of the mixed dyestuffs.

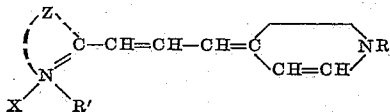
It is also known to obtain a high supersensitizing effect from certain sensitizer combinations. Such a supersensitizing effect does not imply an increase of the sensitivity of an emulsion all over the spectrum but an increase of the sensitizing maximum resulting from the addition of a second or even third chemical compound.

The number of supersensitizing associations is proportionally small in comparison with the number of possible combinations. So it appears from the U. S. Patent No. 2,066,963 that the combination of 1-1'-diethyl-seleno-2'-cyanine-iodide with 2-2'-diethyl-5-5'-tetraethyl-diamino-thiocarbocyanine-iodide produces good panchromatic sensitizing which is due to the fact that the green gap in the sensitizing curve of the carbocyanine is quite filled by a strong increase of the maximum of the pseudocyanine in the green part which strong increase is effected by the carbocyanine. In the same sense, an increase of the sensitizing effect of 2'-cyanines and 2-2'-carbocyanines, it is known, can be achieved by addition of other sensitizing dyestuffs.

Known added dyestuffs are mesosubstituted carbocyanines of the following general formula:

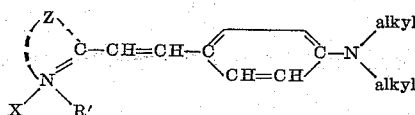


wherein Z is non-metallic atoms required to complete a heterocyclic ring, or thio and seleno-4'-carbocyanines:



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or carbocyanines bases without X and R', or styryls:



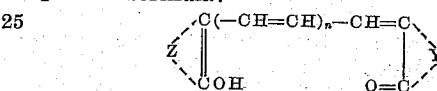
wherein the two CN groups are coupled by a pentamethine chain being partly closed by a side bridge, or styryl bases.

It is an object of our invention to provide a new process for the manufacture of photographic silver halide emulsions.

Another object of the present invention is to provide new photographic silver halide emulsions.

Further objects will appear from the following description.

We have found that the process of sensitization by means of dyestuff combinations can be applied most successfully by using two or more dyestuffs at least one of which corresponds to the following general formula:



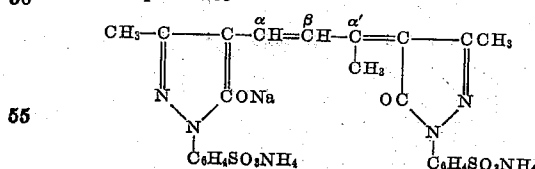
wherein Z and Y are non-metallic atoms required to complete a heterocyclic or an isocyclic ring which may have a fused-on arylene group, and n is 1 or 2.

The hydrogen of the open chain may be replaced by hydrocarbon groups, halogen or carbon-containing bridges.

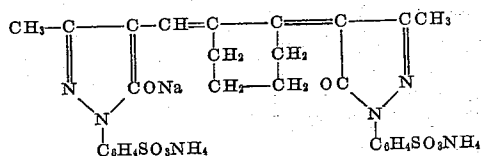
The compounds to be used in accordance with our invention, since being easily soluble, mostly even water-soluble, can, from a technical point of view, easily be handled, i. e., without the use of any organic solvents. For this very reason, they are also unstable in photographic baths so that after bathing colorless photographic layers are obtained.

Some examples of usable supersensitizing dyestuffs according to our invention are given hereinafter:

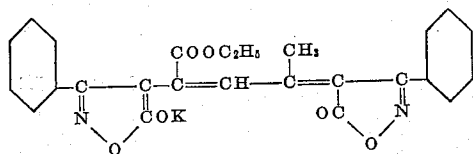
(1) 1-phenyl-3-methyl-5-hydroxypyrazolyl-alpha'-methyl-trimethine-1-phenyl-3-methyl-5-pyrazolone-p-p'-di-ammonium sulphonate



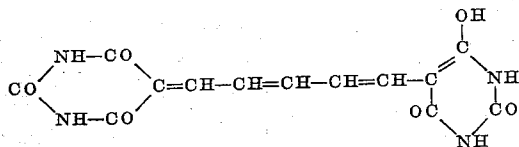
(2) 1-phenyl-3-methyl-5-hydroxypyrazolyl-alpha'-beta'-butylene-trimethine-1-phenyl-3-methyl-5-pyrazolone-p-p'-di-ammonium sulphate



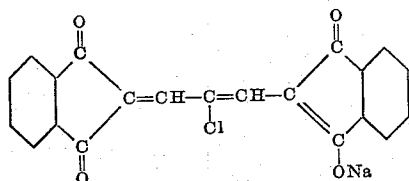
(3) 5-hydroxy-3-phenylisoxazolyl-alpha'-carbethoxy-alpha'-methyltrimethine-3-phenylisoxazolone-5



(4) barbituryl-pentamethine-hydroxyuracil

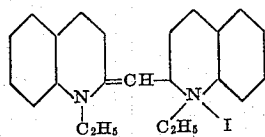


(5) (1-oxy-3-oxyhydrindyl-2)-beta-chlorotrimethine-indandione.

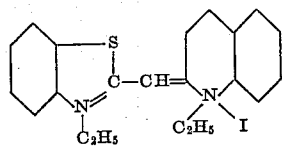


By means of the above dyestuffs, the sensitivity of pseudocyanines and alpha-alpha'-carbocyanines is increased. Examples of pseudocyanines are as follows:

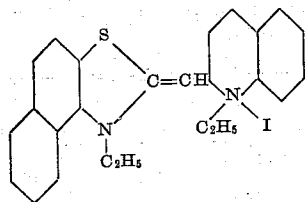
(6) 3,3'-diethyl-2,2'-cyanine iodide



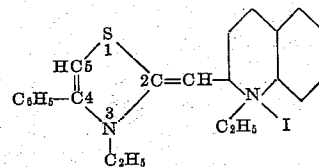
(7) 3,1'-diethyl-thia-2'-cyanine iodide



(8) 3,1-diethyl-4,5-benzthia-2'-cyanine iodide

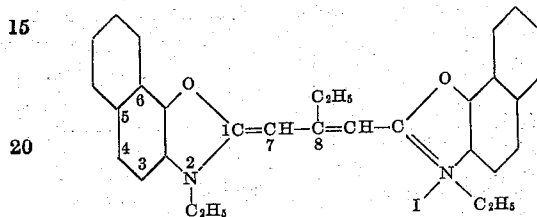


(9) 3,1'-diethyl-4-phenyl-thiazolo-2'-cyanine iodide.

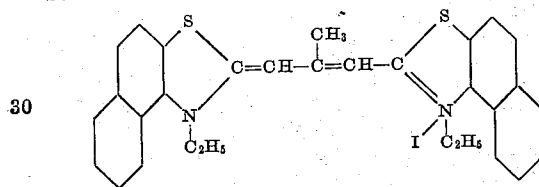


The following are examples of usable 2,2'-carbocyanines:

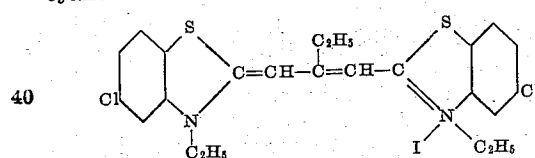
(10) 3,3'-9-triethyl-6,7,6',7'-dibenzoxo-carbocyanine iodide



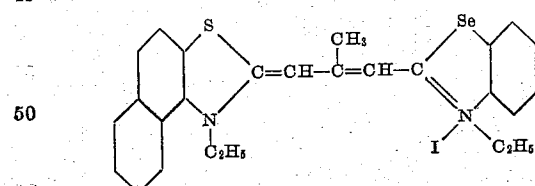
(11) 9-methyl-3,3'-diethyl-4,5,4',5'-dibenzthiacarbocyanine iodide



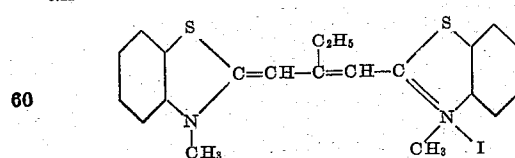
(12) 3,3',9-triethyl-5,5'-dichloro-thiacarbocyanine iodide



(13) 9-methyl-3,3'-diethyl-4,5-benzthia-seleno-carbocyanine iodide



(14) 3,3'-dimethyl-9-ethyl-thiacarbocyanine iodide.



The specification is accompanied by drawings in which the supersensitizing effects of our new associations are shown.

In Fig. 1, the curve A represents the sensitivity of an emulsion containing 3,3'-diethyl-2,2'-cyanine iodide. The curve B represents the sensitivity of the same emulsion containing 1-phenyl-3-methyl-5-hydroxypyrazolyl-alpha'-methyltrimethine-1-phenyl-3-methyl-5-pyrazolone-p-p'-di-ammonium sulphate. The curve C represents the sensitivity of the same emulsion containing 3,3'-diethyl-2,2'-cyanine

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iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - methyl - trimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate.

In Fig. 2, the curve D represents the sensitivity of an emulsion containing 3,3'-diethyl-2,2'-cyanine iodide. The curve E represents the sensitivity of the same emulsion containing 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - beta - butylenetrimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate. The curve F represents the sensitivity of an emulsion containing 3,3'-diethyl-2,2'-cyanine iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - beta - butylenetrimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate.

In Fig. 3, the curve G represents the sensitivity of an emulsion containing 3,3'-9-triethyl-6,7,6',7'-dibenzoxocarbocyanine iodide. The curve H represents the sensitivity of the same emulsion containing 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - methyl - trimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate. The curve I represents the sensitivity of the same emulsion containing 3,3'-9-triethyl-6,7,6',7'-dibenzoxocarbocyanine iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - methyl - trimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate.

In Fig. 4, the curve J represents the sensitivity of an emulsion containing 3,3'-9-triethyl-6,7,6',7'-dibenzoxocarbocyanine iodide. The curve K represents the sensitivity of the same emulsion containing 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - beta - butylenetrimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate. The curve L represents the sensitivity of the same emulsion containing 3,3'-9-triethyl-6,7,6',7'-dibenzoxocarbocyanine iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - beta - butylenetrimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate.

This invention may be applied to ordinary silver halide gelatine emulsions. However, the dyestuff combinations of our invention may also be used in emulsions wherein instead of gelatine another binder is employed, as, e. g., resinous substances or cellulose derivatives, this without a noxious influence upon the light-sensitive substance.

As far as the supersensitizing dyestuffs are concerned, the dyestuff listed as Example 2 is mentioned in the British Patents Nos. 414,664 and 506,998. 2 - (3' - hydroxythionaphthyl - 2' - allylene) - 3 - oxo - 2 - 3 - dihydrothionaphthene is mentioned in *Chemisches Zentralblatt* 1940, II 1577.

The dyestuff of Example 2 the preparation of which has not been described yet may be obtained by condensation of phenylmethylpyrazolone-p-ammonium sulphonate with sodium-oxymethylene-cyclohexanone in methyl alcohol as disclosed in the co-pending application Serial No. 766,097, filed August 4, 1947. The dyestuff 5-hydroxy-3-phenylisoxazolyl - alpha - carbethoxy - alpha' - methyltrimethine-3-phenylisoxazolone-5 may be prepared as follows: 0.02 mol phenylisoxazolone, 0.01 mol sodium acetyl pyruvic acid ethyl ester and 60 cm.<sup>3</sup> methyl alcohol are heated on the water bath for two hours whereafter the intensive-violet colored mixture is poured into 400 cm.<sup>3</sup>

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of a 20 per cent potassium bromide solution. The precipitated dyestuff is then drained. The dyestuff obtained is probably of the formula given in Example 3.

The dyestuff barbituryl - pentamethine - hydroxyuracil is prepared in the following way: 0.04 mol barbituric acid, 0.02 mol glutacondialdehydianilido-hydrobromide and 0.04 mol triethylamine are mixed in 60 cm.<sup>3</sup> of alcohol whereupon the mixture is heated on the water bath for thirty minutes and then cooled. Next the dyestuff is drained and recrystallized from water. The absorption maximum of this violet dyestuff, which is probably the dyestuff of Example 4, lies at about 592 mμ.

The dyestuff (1-oxo-3-oxyhydrindyl-2)-beta-chlorotrimethine-indandione is prepared as follows: 0.02 mol indandione, 0.04 mol chloromalon-dialdehyde dianilhydrochloride and 0.02 mol sodium hydroxide are mixed in 250 cm.<sup>3</sup> methylalcohol and allowed to remain for two days. Then the formed crystals are drained and washed with ether. The dyestuff obtained is probably that of Example 5.

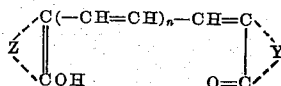
The preparation of the pseudo and carbocyanines to be used according to our invention is sufficiently known from the respective literature.

In order to carry out our invention, the dyestuffs may be mixed with the emulsion either individually or in combinations.

It is believed that the general method and the specific examples of our invention, as well as the advantages thereof, will be apparent from the foregoing detailed description. It will also be apparent that while we have shown and described preferred examples of our invention, changes may be made without departing from the spirit of the invention, as sought to be defined in the following claims.

We claim:

1. Photographic silver halide emulsion having incorporated therein a supersensitizing dyestuff composition comprising at least one sensitizing dyestuff and at least one polymethine dyestuff, said sensitizing dyestuff being selected from the group consisting of 3,3' - diethyl - 2,2' - cyanine iodide and 3,3',9-triethyl-6,7,6',7'-dibenzoxocarbocyanine iodide, said polymethine dyestuff having the following general formula:



wherein Z and Y are the non-metallic atoms required to complete a ring selected from the group consisting of a heterocyclic ring and an isocyclic ring,  $n$  is a positive integer of from 1 to 2, and the hydrogen atoms of the open chain may be replaced by substituents selected from the group consisting of hydrocarbon groups, halogen and carbon-containing bridges.

2. A photographic silver halide emulsion having incorporated therein a supersensitizing dyestuff composition comprising 3,3' - diethyl - 2,2' - cyanine iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - methyl - trimethine - 1-phenyl-3-methyl-5-pyrazolone - p - p' - di-ammonium sulphonate.

3. A photographic silver halide emulsion having incorporated therein a supersensitizing dyestuff composition comprising 3,3' - diethyl - 2,2' - cyanine iodide and 1-phenyl-3-methyl-5-hydroxypyrazolyl - alpha' - beta - butylene - trimethine - 1-phenyl-3-methyl-5-pyrazolone-

p,p'-di-ammonium sulphonate.

4. A photographic silver halide emulsion having incorporated therein a supersensitizing dye-stuff composition comprising 3,3' - 9 - triethyl-6,7,6',7' - dibenzoxocarbocyanine iodide and 1-phenyl - 3 - methyl - 5 - hydroxypyrazolyl - alpha' - methyl - trimethine - 1 - phenyl - 3-methyl - 5 - pyrazolone - p - p' - di - ammonium sulphonate.

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