Feb. 23, 1937. H. A. PIGGOTT ET AL 2,071,899

SENSITIZED PHOTOGRAPHIC FILM, PLATE, AND EMULSION

Filed Dec. 4, 1935

Fig. 1.

SENSITIVITY RANGE OF PHOTOGRAPHIC EMULSION TREATED WITH DYESTUFF OF EXAMPLE 1.

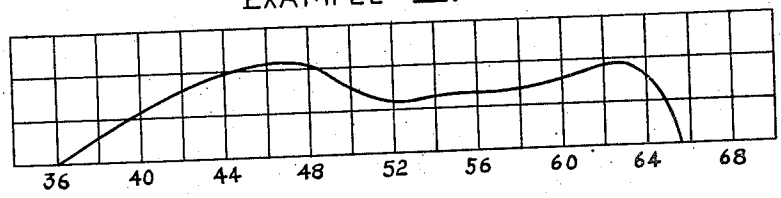


Fig. 2.

SENSITIVITY RANGE OF PHOTOGRAPHIC EMULSION TREATED WITH DYESTUFF OF EXAMPLE 2.

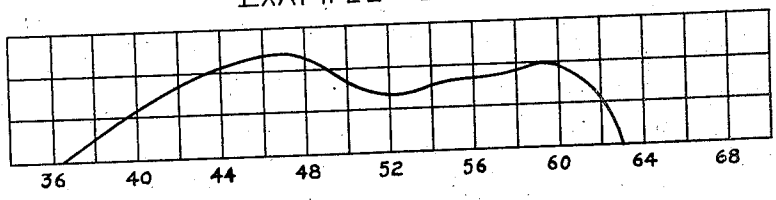
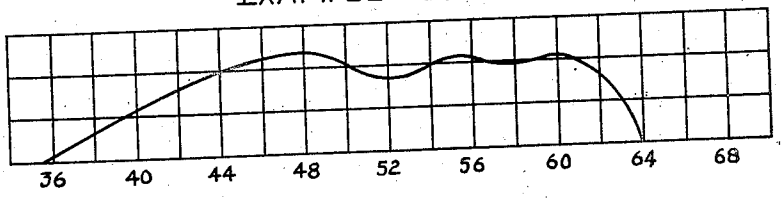


Fig. 3.

SENSITIVITY RANGE OF PHOTOGRAPHIC EMULSION TREATED WITH DYESTUFF OF EXAMPLE 4.



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SENSITIZED PHOTOGRAPHIC FILM, PLATE, AND EMULSION

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In Great Britain May 31, 1930

2 Claims. (Cl. 95—7)

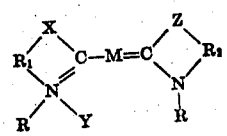
This invention relates to photographic sensitizing compositions and to photographic preparations, such as emulsions or plates or films coated with emulsions, comprising such compositions.

This application is a continuation-in-part of our co-pending application Serial No. 540,810 filed in the United States May 28, 1931, and in Great Britain May 31, 1930.

It is known that a standard photographic emulsion is sensitive to light rays only within the wave-length range of about 360 to 500 millimicrons, and that by suitable treatment, e. g., by bathing a photographic plate in a dilute solution of a sensitizer, the emulsion becomes sensitive to light of other wave-lengths, but it is still a matter of difficulty to increase or decrease the sensitivity at will in any desired degree.

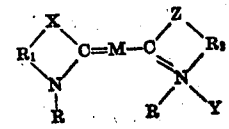
It is an object of this invention to produce new and improved sensitized photographic emulsions. A further object is to provide sensitizing compositions which will render photographic emulsions sensitive to light rays in the red and infra-red region of the spectrum. It is a further object of this invention to provide photographic emulsions sensitive to red and infra-red light rays. It is also an object of this invention to provide plates and films coated with such sensitized emulsions. Other objects will appear in the description and claims.

These objects are achieved according to this invention by the employment of unsymmetrical polymethine dyestuffs such as can be obtained by condensing a heterocyclic nitrogen compound containing an external reactive methylene group with an intermediate compound obtainable by the process described in our British Patent No. 344,409. In general, the sensitizing dyes employed in accordance with the present invention are characterized by having the general formula:

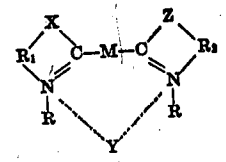


wherein X represents a member of the oxygen group of elements or dialkyl methylene, Z represents a member of the oxygen group of elements, dialkyl methylene, or vinylene and is different from X, R_1 and R_2 represent the same or different ortho-aromatic nuclei which may or may not be substituted by monovalent auxochromic substituents, e. g., by alkyl and alkoxy groups and/or halogen atoms such as chlorine and bromine in the meta- and para-positions, R represents an aliphatic hydrocarbon radical (not necessarily the same), Y represents the negative radical of an acid (e. g., halogen, sulfate, oxalate, nitrate, chlorate, etc.), and M represents a methenyl chain which may or may not be substituted by monovalent auxochromic substituents, for instance, by alkyl, alkoxy or aryl groups or by halogen atoms such as chlorine, bromine or iodine.

It will be recognized that this formula may also be written:



or



The position of the acid residue Y is not definitely known and it may be in equilibrium between the two nitrogen atoms.

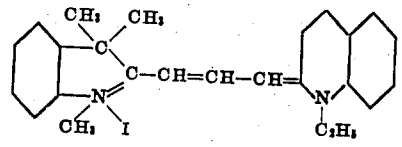
In carrying our invention into practical effect, we treat a photographic emulsion with unsymmetrical polymethine dyestuffs as described above, e. g., by bathing a photographic plate in a dilute aqueous solution of the dyestuff. The dyestuff may be added to typical photographic emulsions, such as gelatino silver halide emulsions, in a manner well known in the art. Preferably, a solution of about 1 part of dyestuff in about 2000 parts of 50% aqueous alcohol is prepared. This stock solution is diluted for use with about 20 parts of water. Approximately 100 cc. of the diluted solution are then taken for each full size photographic plate to be treated and the plate is immersed in the solution which is agitated gently and kept in contact with the plate for a period of about five minutes. The plate is then washed with water and dried. It will be apparent to those skilled in the art that the proportions of dyestuff and photographic emulsion may be varied in order to obtain the desired effect.

The accompanying drawing illustrates the sensitivity curves of photographic emulsions treated with certain of the unsymmetrical dyestuffs hereinafter described.

The invention will be further illustrated but is not limited by the following examples, in which the parts are by weight.

Example I

An intermediate compound was prepared by condensing together 60 parts of quinaldine ethiodide and 40 parts of diphenyl formamidine in accordance with Example 2 of the provisional specification of our British Patent No. 344,409 or Example 6 of the complete specification. Approximately 16 parts of this product were condensed with 7 parts of 1:3:3-trimethyl-2-methyleneindoline by boiling the two components under reflux for ten minutes in 2 parts of acetic anhydride. The reaction mixture was then cooled, somewhat diluted by 50 parts of hot water, and vigorously stirred. The dyestuff separated out and was filtered off and washed. This dyestuff has the formula

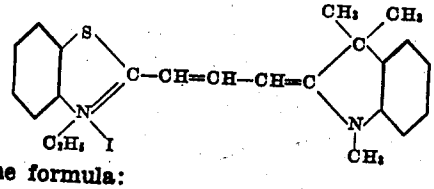


When a photographic plate was treated with a solution of the dyestuff as described above, it became sensitive to light of wave-lengths within the range of about 360 to about 653 millimicrons.

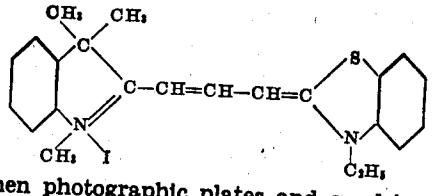
The procedure in preparing the above dyestuff may be varied. For instance, we may first prepare the intermediate compound from 2:3:3-trimethyl-indolenine-methiodide and diphenyl formamidine, as described in Example 1 of the complete specification of our British Patent No. 344,409, and then condense one molecular proportion of this with one molecular proportion of quinaldine ethiodide in the manner described above, with the addition of an acid-binding agent such as sodium acetate.

Example II

An intermediate compound was prepared by condensing 9 parts of 2-methyl-benzothiazole-ethiodide and 66 parts of diphenyl formamidine in 500 parts of acetic anhydride, as described in Example 5 of our British Patent No. 344,409. Twenty-four parts of this product were then condensed with 18 parts of 2:3:3-trimethyl-indolenine-methiodide in 160 parts of acetic anhydride to which 5 parts of sodium acetate had been added. The condensation was effected by boiling the solution under reflux for about fifteen minutes. The mixture was then diluted by a solution of 50 parts of water and the precipitated dyestuff purified by lixiviation with ether. It may be given the formula:



or the formula:

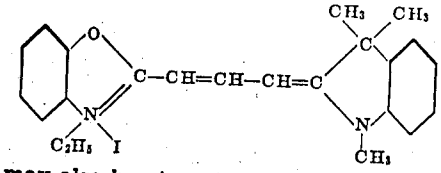


When photographic plates and emulsions are treated with the dyestuff as previously described the sensitivity range is from about 360 to about 630 millimicrons.

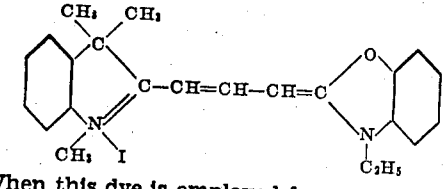
An alternate method of preparing the dyestuff is to produce the intermediate compound from 2:3:3-trimethyl-indolenine-methiodide and diphenyl formamidine, as described in Example 1 of our British Patent No. 344,409, and then reacting equi-molecular proportions of said compound and 2-methyl-benzothiazole-ethiodide in 160 parts of acetic anhydride and 5 parts of sodium acetate with boiling for fifteen minutes.

Example III

An intermediate product was prepared by boiling 58 parts of 2-methyl-benzoxazole-ethiodide and 66 parts of diphenyl formamidine in 250 parts of acetic anhydride for twenty minutes, as described in Example 4 of our British Patent No. 344,409. The dyestuff is prepared by condensing about 18 parts of this product with 18 parts of 2:3:3-trimethyl-indolenine-ethiodide by boiling under reflux in a solution of 160 parts of acetic anhydride to which 5 parts of sodium acetate have been added. After boiling for fifteen minutes, the mixture is diluted with 150 parts of hot water and the precipitated dyestuff is purified by lixiviation with ether. This dye has the formula:



and may also be given the formula:



When this dye is employed for sensitizing photographic plates and emulsions, as previously described, it extends the wave-length range and the plate becomes sensitive to wave-lengths of light within the range of 360 to about 600 millimicrons.

An alternative method of preparing the dyestuff described above is to prepare the intermediate compound from 2:3:3-trimethyl-indolenine-ethiodide and diphenyl formamidine, as described in our Example 1 of British Patent No. 344,409, and then boil under reflux equi-molecular proportions of said compound and 2-methyl-benzoxazole-ethiodide in 160 parts of acetic anhydride and 5 parts of sodium acetate for fifteen minutes. The dyestuff may be separated as previously described.

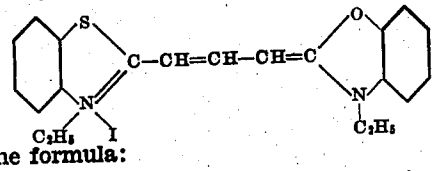
Example IV

An intermediate compound was prepared by boiling 90 parts of 2-methyl-benzothiazole-ethiodide and 66 parts of diphenyl formamidine in 500 parts of acetic anhydride for fifteen minutes, as described in British Patent No. 344,409. Approximately 26.92 parts of this intermediate product were then boiled under reflux with about 17.92 parts of 2-methyl-benzoxazole ethiodide in 160 parts of acetic anhydride to which 5 parts of sodium acetate had been added. After boiling for fifteen minutes, the mixture was diluted with 150 parts of hot water and the precipitated dyestuff was purified by lixiviation with ether.

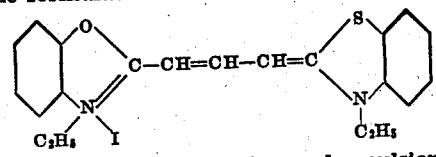
Alternately, the dyestuff may be prepared by making the intermediate product from 2-methyl-

benzoxazole-ethiodide, as described in Example 4 of our British Patent No. 344,409, and then condensing equi-molecular proportions of this intermediate product and 2-methyl-benzothiazole-ethiodide in the presence of acetic anhydride and sodium acetate as previously described.

The dyestuff may be given the formula:



or the formula:



When photographic plates and emulsions are treated with the above identified dyestuff in the manner previously described, the range of sensitivity to light is extended and the plate becomes sensitive to a wave-length range from 360 to about 640 millimicrons.

It wil be apparent that the present invention is applicable to the treatment of photographic plates and emulsions with other unsymmetrical dyestuffs of the type described in the examples, namely, those characterized by having dissimilar heterocyclic nuclei connected by a methenyl chain. By "dissimilar nuclei" we mean nuclei which are substantially different, either in having dissimilar hetero atoms (as, for instance, an oxazole, thiazole or selenazole nucleus) connected through a methenyl chain to an indoline nucleus or a quinoline nucleus. Thus, in Examples II and III, we have described dyestuffs in which a thiazole and an oxazole nucleus are connected through a methenyl chain to an indoline nucleus. By substituting chemically equivalent proportions of 2-methyl-benzoselenazole-ethiodide for 2-methyl-benzothiazole-ethiodide or 2-methyl-benzoxazole-ethiodide in these examples, it will be apparent that we can obtain dyestuffs containing a selenazole nucleus connected through a methenyl chain with an indoline nucleus, said dyestuffs also being characterized by excellent sensitizing properties. Similarly, by reacting chemically equivalent proportions of ethiodides of 2-methyl-benzoxazole, 2-methyl-benzothiazole or 2-methyl-benzoselenazole with the quinaldine ethiodide-diphenyl formamidine condensation product of Example I in the presence of acetic anhydride and sodium acetate, we may prepare dyes containing an oxazole, thiazole or selenazole nucleus connected through a methenyl chain to a quinoline nucleus.

It will also be apparent that we may employ dyes containing various combinations of oxazole, selenazole and thiazole nuclei. Thus, our preferred dyes are those in which the two heterocyclic nuclei are dissimilar in that they contain dissimilar atoms from the oxygen group of elements. Such a dye is described in Example IV in which a thiazole and an oxazole nucleus are connected by a methenyl chain. Instead of 2-methyl-benzoxazole-ethiodide in Example IV, we may employ the chemically equivalent proportions of 2-methyl-benzoselenazole-ethiodide to produce a dye in which a selenazole nucleus is connected through a methenyl chain to a thiazole nucleus; or, we may prepare the intermediate compound from 2-methyl-benzoxazole-ethiodide and diphenyl formamidine, as described in Example 4 of our British Patent No. 344,409, and boil together equi-molecular proportions of this compound and 2-methyl-benzoselenazole-ethiodide in 160 parts of acetic anhydride containing 5 parts of sodium acetate, as in Example IV, and obtain a dye containing an oxazole and a selenazole nucleus connected by a methenyl chain.

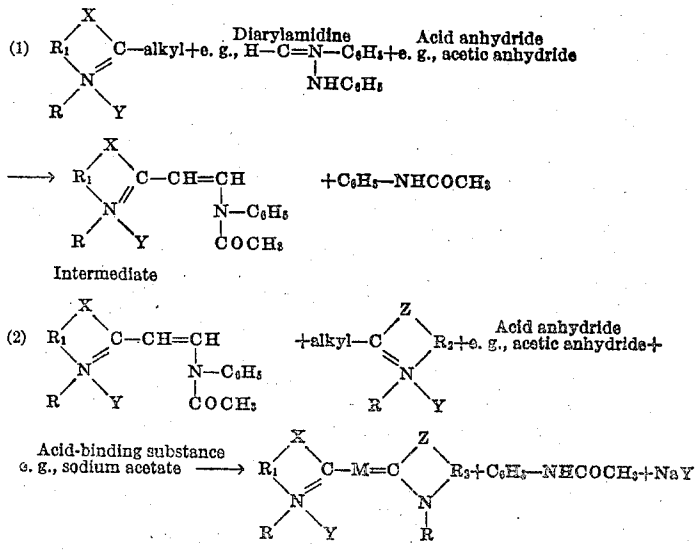
For simplicity in describing the invention, we have heretofore referred specifically to the unsubstituted benzoxazoles, benzothiazoles and benzoselenazoles, but it will be apparent to those skilled in the art that dyestuffs containing auxochromic substituents, such as halogen atoms (e. g., chlorine or bromine), alkyl groups (e. g., methyl, ethyl, isopropyl, butyl and higher homologues), and/or alkoxy groups (e. g., methoxy, ethoxy, butyloxy, etc.) may be present in the aromatic nucleus in any position, or positions, but the ortho positions which are already fully substituted by the bonds from the heterocyclic ring. The method of preparing the dyestuffs from the substituted derivatives is the same as from the unsubstituted derivatives, except that an intermediate is employed in which a substituent is already present. For instance, a 2-methyl-benzoselenazole ethiodide or a 2-methyl-benzothiazole-ethiodide in which the position para to the carbon atom connected to the selenium, sulfur or oxygen atom is occupied by an atom or group such as chlorine, bromine, methyl, ethyl, methoxy or ethoxy. Instead of the aromatic nucleus of the oxazole, selenazole or thiazole being a benzene nucleus, it may be a naphthalene nucleus, either substituted or unsubstituted.

Unsymmetrical dyes of the type described containing dissimilar heterocyclic nuclei connected by a penta-methenyl chain may be prepared as described in our British Patent No. 355,693, by reacting a beta-anilino-acrolein-anil and 2:3:3-trimethyl-indolenine-alkyl-iodide or 2-methyl-benzothiazole-alkyl-iodide or 2-methyl-benzoselenazole-alkyl-iodide or 2-methyl-benzoxazole-alkyl-iodide in acetic anhydride to form an intermediate compound, and then condensing said intermediate compound with a 2-methyl-benzothiazole-alkyl-iodide, 2-methyl-benzoxazole-alkyl-iodide or 2-methyl-benzoselenazole-alkyl-iodide in which the member of the oxygen group of elements is dissimilar from that employed in the formation of the intermediate. This condensation may be carried out in the presence of acetic anhydride and sodium acetate, as above described.

Unsymmetrical dyestuffs of the type described containing substituents on the methenyl chain may be prepared by employing alpha-substituted beta-anilino-acrolein-anils in the preparation of the intermediate bodies in accordance with British Patent No. 355,693, and then reacting the intermediate with the desired 2-methyl-benzothiazole ethiodide, 2-methyl-benzoxazole-ethiodide or 2-methyl-benzoselenazole-ethiodide, the choice of intermediate and/or reacting component being made so as to obtain a dye having dissimilar heterocyclic nuclei. The dye is obtained by reacting the intermediate, for example, an intermediate prepared by heating approximately equi-molecular proportions of alpha-chloro-beta-anilino-acrolein-anil in 200 parts of acetic anhydride to boiling for one hour as in Example 2 of British Patent No. 355,693, and then condensing the intermediate with an equi-molecular proportion

of 2-methyl-benzothiazole-ethiodide or 2-methyl-benzoxazole-ethiodide or 2-methyl-benzoselenazole-ethiodide in acetic anhydride containing potassium acetate, as in Example 4 of said patent. The resultant dyestuff will have a chlorine atom substituted on the methenyl chain. By employing the corresponding alpha-alkyl- and alpha-alkoxy-substituted beta-anilino-acrolein-anils or other alpha-substituted derivatives, the corresponding substituents may be obtained on the methenyl chain.

The course of reaction for the process of preparing the dyes as described in the examples may be illustrated by the following equations:



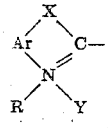
wherein R, R_1, R_2, X, Y, Z and M have the foregoing significance.

In the foregoing reactions, it will be recognized that equivalents may be employed, for example, propionic anhydride for acetic anhydride or sodium propionate for sodium acetate. The formation of the dye may also be effected in the presence of pyridine, alcohol or other solvents.

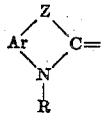
Preferred dyestuffs of the invention are such as may be represented by the general formula:

A—CH=CH—CH=B

where A is a monovalent heterocyclic nitrogen residue of the type:



in which Ar is an ortho-arylene group, R is alkyl, Y is an acid residue (such as halogen, sulfate, oxalate, etc.) and X stands for the bivalent atom or group of the oxygen group of elements, e. g., —O—, —S— or —Se—, or —CR'$_2$— (R' being alkyl), and B is a divalent heterocyclic nitrogen residue of the type



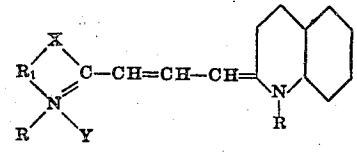
in which Ar and R have the same significance as before (though not necessarily representing identical groups), whilst Z stands for —O—, —S— or —Se—, or —CR'$_2$— (R' being alkyl) and is different from X.

It will be recognized that the results obtained with the different dyestuffs may vary. This is illustrated by the examples. The invention however, offers a wide selection of dyestuffs of a particular type with which it is possible to obtain new and improved sensitized photographic plates, films and emulsions.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

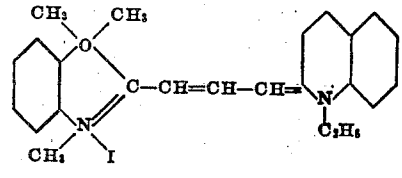
We claim:

1. Photographic gelatino-silver halide emulsions containing an unsymmetrical polymethine dyestuff having the following general formula:



in which X represents a member of the oxygen group of elements or dialkyl methylene, R_1 represents an aryl radical of the benzene series, R represents an alkyl radical, and Y represents the negative radical of an acid.

2. Photographic gelatino-silver halide emulsions containing an unsymmetrical polymethine dyestuff having the following general formula:



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