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UNITED STATES PATENT OFFICE

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HETEROCYCLIC COLOR COUPLERS

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6 Claims. (Cl. 95—6)

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The present invention relates to color photography and is particularly concerned with photographic color forming or color coupling components which are adapted to be incorporated in photosensitive emulsion layers in the production of photographic film, papers and the like.

This invention is an improvement in the process of color forming development which was first described in United States Patents No. 1,055,155 and No. 1,102,028 to Fischer, in accordance with which colored photographic images are produced by means of a coupling reaction between the oxidation product of a photographic developer containing free amino groups, for instance, phenolic diamines, especially the mono- or unsymmetrically disubstituted ones, like p-dimethylaminoaniline or methoxy-p-dimethylaminoaniline and the like, and an intermediate or coupling component. As is well known, this coupling occurs at those points where a silver image is produced by reduction of the silver halide by the color developer with resulting formation, at these points, of the oxidation product of the developer, which couples with the intermediate or coupling component. The coupling component can be present in the photographic developer. However, in accordance with the preferred methods for practicing this color forming development process, non-diffusible color forming or coupling components are employed which are incorporated in the photosensitive emulsion during manufacture. It is particularly desirable that such non-diffusible color forming or coupling components be employed in case several differently sensitized photosensitive emulsion layers are coated on a single support as is the case in three-color photographic processes in which the so-called integral tripack films are employed, since, in such cases, any wandering or diffusing of the color component from the layer in which it is incorporated would cause inaccurate color rendition, while attempts to employ the color coupling component in the color forming developer, in such cases, unnecessarily complicates the process of developing.

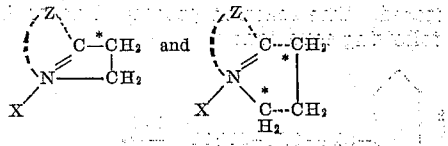
The present invention is particularly concerned with a novel type of color component having an active methylene group which will react with the oxidation product of the usual color developers.

It has heretofore been proposed that certain heterocyclics, having an quaternized nitrogen atom as the hetero atom in the ring and which have a methyl group as a substituent on the carbon atom adjacent to the quaternized nitrogen atom, can be employed as color forming components since the methyl group is relatively active and coupling with the color forming developer can occur through this methlyl group. The activity of the methyl group, however, is insufficient for compounds of this type to be entirely satisfactory as color components for use in color photographic processes of the type described above and, in general, compounds of this type are relatively weak color formers.

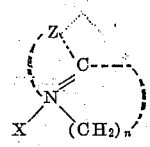
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It is an object of this invention to produce compounds related to those heretofore proposed but which are so modified as to increase the activity of the active groups therein. Other and further objects will be apparent as the present description progresses.

I have discovered that if the active group of a color forming component is a part of a ring structure, the activity of the reactive group is substantially increased and, on color forming development, greater coupling speed and more energetic coupling takes place. Therefore, in practicing my invention, I employ, in place of color forming components of the type which have heretofore been employed and in which the starred methylene group is the active group, related compounds of the following type



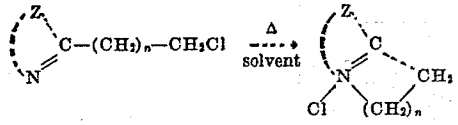
which may be represented by the following generic formula:



In the above formulas, Z represents the necessary atoms to make up a five or six membered N-hetero ring, which may be further substituted, *n* is 2, 3 or 4, and X represents halogen. It will be noted that in compounds of this type, the reactive methylene group or groups, which are starred, form a part of a ring.

Compounds of this type may readily be prepared by reacting an orthoalkyl halide-substituted N-hetero compound so as to quaternize the nitrogen atom and cyclicize the alkyl group. Thus, ortho-substituted N-hetero compounds, such as pyridine, quinoline, benzthiazole, benzoxazole, and the like, in which the carbon atom, adjacent to the heterogenous nitrogen atom, is

substituted by an alkyl halide group, having 2 to 4 carbon atoms in the chain, may readily be quaternized by conventional procedure, for instance, by heating to a temperature slightly above the melting point of the product, while dissolved in a suitable solvent so that the nitrogen atom is quaternized and a cyclic compound formed. This reaction proceeds in accordance with the following equation:

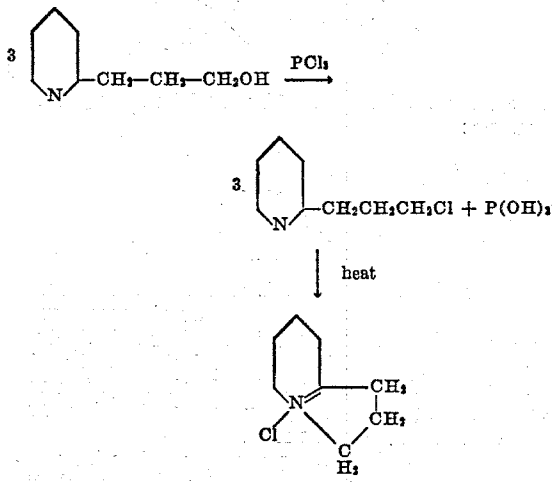


in which n is 1, 2 or 3 and Z stands for the necessary atoms to make up a five or six-membered ring which may be further substituted. These cyclic-substituted N-hetero compounds contain reactive methylene groups having a substantially enhanced activity since they form a part of a ring and coupling readily takes place through such reactive methylene groups with the usual color forming developers. The compounds may be readily incorporated in a photographic emulsion by any usual procedure, for instance, by dissolving a minor amount of the same in alkaline aqueous alcohol and incorporating such solution in a conventional gelatin photographic emulsion.

This invention will be readily understood by reference to the following specific examples, which illustrate typical compounds embraced in this invention. Numerous other compounds containing the essential features of the present invention will suggest themselves to those skilled in the art.

Example 1

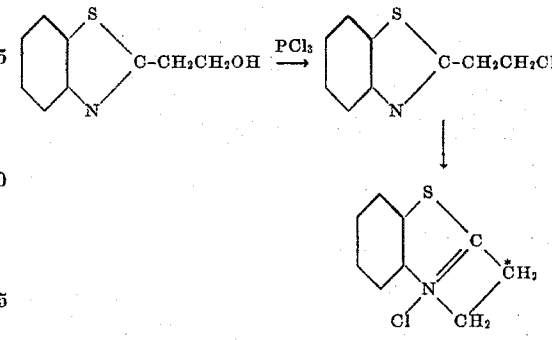
Orthohydroxypropylpyridine was treated with phosphorous trichloride in order to form the corresponding orthochloropropylpyridine. This was then dissolved in a suitable solvent, for instance, nitrobenzene, and was heated to a temperature above its melting point but below the boiling point of nitrobenzene. A corresponding quaternary ammonium compound was thus formed and, being insoluble in nitrobenzene, was precipitated. The reaction proceeded according to the following equation:



The thus obtained quaternized compound was then incorporated in a photographic emulsion by dissolving a small amount thereof, generally about 8 grams, in 3 cc. of sodium hydroxide of 40% strength, 25 cc. of methanol and 70 cc. of water and was then added to 500 cc. of a gelatin emulsion of 5% strength. When so incorporated in a photographic emulsion, the compound exerted no adverse effect on the emulsion. The emulsion was then coated on a glass plate in the usual manner for producing photographic plates and the plate exposed. On development with a color forming developer, for instance, p-diethylaminoaniline, a yellow picture was obtained.

Example 2

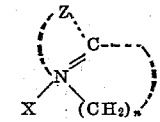
Hydroxyethylbenzthiazole was treated with phosphorous trichloride in order to obtain chlorethylbenzthiazole. This was then dissolved in nitrobenzene and heated to a temperature slightly above its melting point but below the boiling point of nitrobenzene, a temperature of 120–180° C. being satisfactory. The nitrogen atom of the thiazole group was quickly quaternized and the quaternary compound so formed precipitated from the nitrobenzene and was removed and washed. This reaction proceeded according to the following equation:



The thus obtained quaternary ammonium compound was incorporated in a conventional gelatino photographic silver halide emulsion in the manner specified in Example 1 above and the emulsion then coated on a glass plate and dried. The plate was then exposed and the image developed by a reversal process, a color forming developer, p-diethylaminoaniline, being employed in the second developing batch. A magenta picture was thus obtained.

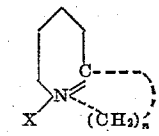
I claim:

1. A photographic silver halide emulsion having incorporated therein, as a color forming development component, a compound having the following formula:



wherein Z represents the necessary atoms to make up a radical selected from the group consisting of 5 and 6-membered N-hetero rings, and n is a whole number of from 2 to 4, and X represents halogen.

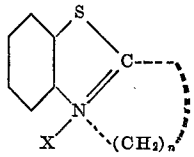
2. A photographic silver halide emulsion having incorporated therein a color forming development component having the following formula:



wherein X represents halogen and n is a whole number of from 2 to 4.

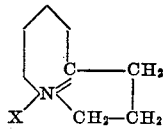
3. A photographic silver halide emulsion hav-

ing incorporated therein a color forming development component having the following formula:



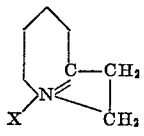
wherein X represents halogen and n is a whole number of from 2 to 4.

4. A photographic silver halide emulsion having incorporated therein, as a color former, a compound having the following formula:



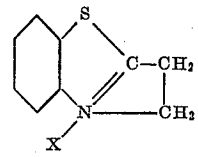
wherein X represents halogen.

5. A photographic silver halide emulsion having incorporated therein, as a color former, a compound having the following formula:



wherein X represents halogen.

6. A photographic silver halide emulsion having incorporated therein, as a color former, a compound having the following formula:



wherein X represents halogen.

ABRAHAM BAVLEY.

REFERENCES CITED

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

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536,673	British	May 22, 1941