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NONDIFFUSING COUPLERS FOR COLOR PHOTOGRAPHY

Abraham Bavley, Binghamton, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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2 Claims. (Cl. 95—6)

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This invention relates to color photography and is particularly concerned with a process of color photography and photographic color forming or coupling compounds which are non-diffusing when incorporated in photosensitive gelatin emulsion layers.

The present invention relates to the photographic color process in which a color photographic image is produced by means of a coupling reaction between a photographic developer and an intermediate or coupling compound, as has been described in Patents No. 1,055,155 and No. 1,102,028 to Fischer. In one method of carrying out a color forming of this type the coupling compound is incorporated in the sensitive emulsion layer prior to coating it on the support. When this is done it is highly desirable that the coupling compound should not wander or diffuse from the layer in which it is incorporated, particularly when two or more layers are superimposed and are differentially sensitive, as such diffusion of a coupling component causes inaccurate color rendition. It is also important that the coupling compound which is incorporated in the sensitive layer should not desensitize or otherwise adversely affect the sensitive emulsion layer.

It is therefore an object of this invention to provide a photographic color forming or coupling compound which may be incorporated in a sensitive emulsion without any adverse effect on such emulsion and which when so incorporated is non-diffusible therein. Other and further objects will be apparent as the description progresses.

I have found that known color coupling compounds which contain an acidic radical, either a sulfonic acid substituent or a carboxyl group, may be rendered non-diffusing without any adverse effect on the tendency of the coupling compound to desensitize or otherwise adversely affect the sensitive emulsion by reacting such color coupling compounds with a long chain amine, in order to form an amine salt of the color former

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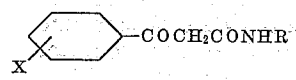
and employing the thus obtained amine salt as a color forming or coupling component which is incorporated in a photographic emulsion.

As the coupling component I may employ any known coupling component which contains an acidic substituent. As is well known, the coupling components ordinarily employed in color forming development are compounds which contain an active methylene group. In general aceto-acetic acid ester and its derivatives are employed for the production of yellow and green dye images, for the blue-reds, or magentas it is customary to employ a pyrazolone, and various phenols and naphthols are employed for the production of blue dye images. Many of these known coupling components contain sulfonic acid or carboxylic acid substituents and these may readily be reacted with a long chain aliphatic amine in order to produce the corresponding amine salt which is non-diffusing.

As known color forming or coupling components which contain an acidic group, and which, therefore, are suitable for use in practicing the present invention, may be named, for example, β-ketonic acid esters of the following type:



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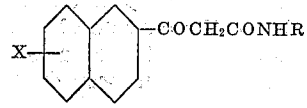
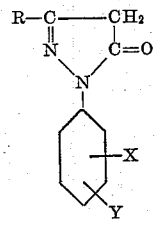
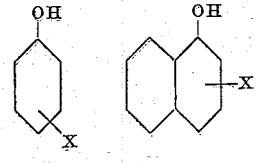


in which X stands for a sulfonic or carboxylic acid group and R is alkyl, aryl or aralkyl. Specific exampes of such esters are benzoylacetanilide-p-sulfonic acid and naphthoyl-2-acetanilide-5-sulfonic acid. These compounds are suitable for the production of yellow images. For the production of red or magenta images, pyrazolones which contain a sulfonic or carboxylic acid group

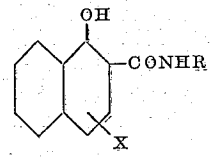
may be employed. Thus, pyrazolones of the following type:



in which X stands for a sulfonic or carboxylic acid group and Y stands for hydrogen or a sulfonic or carboxylic acid group, and R is alkyl, aryl or aralkyl, are suitable for use in practicing the present invention. Typical specific examples of compounds of this type are: 1-(3'-sulfophenyl)-3-methyl-5-pyrazolone; 1-(5'-sulfophenyl)-3-methyl-5-pyrazolone. For the production of blue colors, phenols and naphthols, containing a sulfonic or carboxylic acid group, may be employed. The following types of compounds are suitable:



and



in which X stands for sulfonic or carboxylic acid group and R is alkyl, aryl or aralkyl. Specific examples of such compounds are: α-hydroxy naphthoyl aminobenzene-3-sulfonic acid; an α-hydroxy naphthoyl aminonaphthalene-6-sulfonic acid.

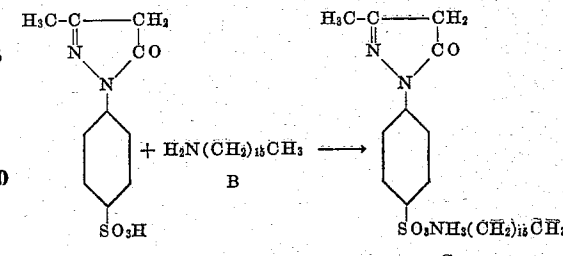
The amines which I react with these color coupling compounds in order to produce the amine salt which is non-diffusing are preferably primary aliphatic amines containing at least 8 carbon atoms. While I prefer to employ the primary aliphatic amines it should be understood that the secondary amines are operative in the present invention and if desired, branched chain amines may be employed. The essential feature of the amine in accordance with the present invention, is that it contains a sufficient number of carbon atoms, at least 8, in order to impart non-diffusibility to the coupling compound.

The present invention will be readily understood from the following specific examples which are given only for the purpose of illustrating the present invention and it should be understood that the invention is in no way limited to these examples.

Example 1

A typical example of a known color forming pyrazolone containing a sulfonic acid or carboxylic acid group is 1-p-sulfonic phenyl-3-methyl pyrazolone. This compound may readily be reacted with an amine, for instance, hexadecylamine, in order to produce the corresponding amine salt compound C in Equation I below:

Eq. I.



This amine salt may readily be incorporated in a conventional gelatino silver halide photosensitive emulsion and when so incorporated is non-diffusing and is without adverse effect on the emulsion.

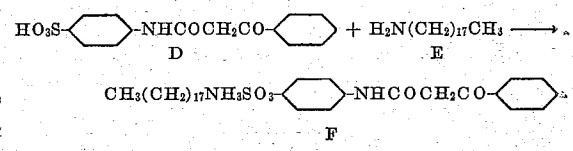
Other known pyrazolones, such as those mentioned previously in this specification, which contain a sulfonic acid or carboxylic acid group, may be substituted for the 1-p-sulfonic-phenyl-3-methyl pyrazolone mentioned above and reacted with an alkyl amine in order to produce the corresponding amine salt which may readily be incorporated in a sensitive photographic emulsion in the usual manner.

The thus obtained amine salt was incorporated in a conventional gelatino silver halide photographic emulsion in the usual way by dissolving a small amount of this amine salt, about 8 grams, in 3 cc. of sodium hydroxide of 40 percent strength, 25 cc. of methanol, and 70 cc. of water and this solution was then added to 500 cc. of a gelatin silver halide emulsion of 5 percent strength. When so incorporated in a photographic emulsion, the amine salt exerted no adverse effect on the emulsion and was non-diffusing therein. The thus obtained emulsion was cast on a film support, in accordance with conventional practice, and the film exposed. By developing with a color forming developer, for instance, p-diethylaminoaniline, a magenta picture was obtained.

Example 2

A typical known color forming compound containing a sulfonic acid group which is a derivative of aceto-acetic acid ester is benzoyl acetanilide-p-sulfonic acid. This was readily reacted with an aliphatic amine, for instance, octadecyl amine, in order to produce the corresponding amine salt F, as illustrated in Equation II below:

Eq. II.



This amine salt F may readily be incorporated in a photographic sensitive emulsion and the emulsion cast on a photographic film support, in the same manner as in Example 1, and when so incorporated therein is without adverse effect on the emulsion and when so incorporated is non-diffusing therein. By developing with a color forming developer, a yellow picture is obtained.

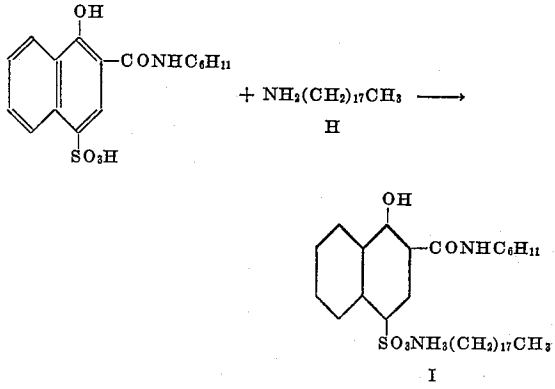
Other derivatives of aceto-acetic acid ester which contain an acidic group and which are known to have color forming properties, for instance those of the type heretofore mentioned, may be treated in a like manner and non-diffus-

ing amine salts, which are suitable for use as non-diffusing color compounds, are thus obtained.

Example 3

A known naphthol color forming or coupling compound for the production of blue pictures is α-naphthoylaminocyclohexane-4-sulfonic acid. This may be reacted with a primary amine, for instance, octadecylamine, as illustrated in Equation III, to produce the corresponding amine salt I.

Eq. III.



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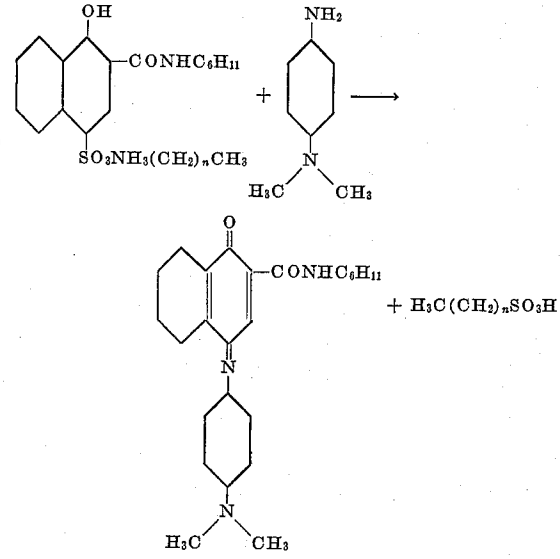
This amine salt may readily be incorporated in a photographic emulsion as a coupling compound, in the same manner as in Example 1, and when so incorporated exerts no adverse effect on the emulsion and is non-diffusing therein. By developing with a color forming developer, a blue picture is obtained.

Other known phenols and naphthols which are color coupling compounds and which contain an acidic group, for instance, those mentioned above, may be treated in a like manner to produce the corresponding amine salt and the amine salt used as a non-diffusing coupling compound.

It should be noted that the amine salts of naphthols and phenols which contain a sulfonic acid group in the para-position, with respect to the hydroxyl group, are particularly advantageous for use as non-diffusing coupling compounds. Many of the dyes obtained by coupling a naphthol or phenol with a photographic color developer, for instance, an aryl amine or diamine, are quite insoluble with the result that on color forming development clumping of the dye occurs. This is particularly true if the naphthol or amine coupling compound has been treated in order to render it non-diffusing by methods heretofore known in the art. As is well known in the art of color forming development, coupling between a naphthol or phenol coupling compound and the aryl amine employed as the developing agent takes place at the para-position with respect to the hydroxyl group. In accordance with the present invention, this coupling results in the sulfonic acid or carboxylic acid group being split off as illustrated in Equation IV below:

Eq. IV.



This resulting dye is sufficiently soluble in the emulsion layer that clumping does not occur. On the other hand, the coupling component is sufficiently non-diffusible prior to color forming development and the resulting coupling that it does not diffuse from the sensitive emulsion in which it has been incorporated.

I claim:

1. A photographic silver halide emulsion containing a color former fast to diffusion, said color former comprising the salt of a primary aliphatic amine containing at least 8 carbon atoms and a color former selected from the class consisting of phenols and naphthols having an acidic group selected from the class consisting of carboxylic and sulfonic acid groups in para-position.

2. A photographic silver halide emulsion containing a color former fast to diffusion, said color former comprising the salt of a primary aliphatic amine containing at least 8 carbon atoms and a color former selected from the class consisting of phenols and naphthols having a sulfonic acid group in para-position.

ABRAHAM BAVLEY.

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

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