

UNITED STATES PATENT OFFICE

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PREVENTING CRYSTALLIZATION OF COUPLERS

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1 Claim. (Cl. 95-6)

This invention relates to color photography and particularly to the incorporation of color couplers in photographic emulsion layers.

It is known that colored photographic images may be formed by using a developer which forms a colored compound on development. The colored compound thus formed is deposited adjacent to the silver grains of the silver image during the development. It is also known that a colored image may be formed by adding to certain developer solutions or by incorporating in the gelatino-silver-halide emulsion before or after exposure a compound which couples during development with the oxidation product of the developing agent and forms a coloring substance which is likewise deposited adjacent to the silver grains of the silver image during development. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a coupling component or coupler.

Difficulties are frequently encountered in attempting to disperse coupling compounds uniformly in photographic emulsions. These compounds are apt to crystallize badly or form conglomerate masses when incorporated in the emulsion without the aid of dispersing agents and in many instances the commercial wetting or dispersing agents are of little or no value for this particular purpose.

It is known that the incorporation in emulsions of couplers of similar but not identical structure would reduce the melting point and crystallization tendency of the couplers but generally these properties are not sufficiently reduced to make the method suitable for use in overcoming the crystallization tendency of couplers in emulsion layers.

It is, therefore, the principal object of the present invention to provide a method for reducing the crystallization tendency of couplers when incorporated in photographic emulsions.

The object of the invention is accomplished by mixing with the coupler a non-coupling compound or dispersing agent having a structure or configuration similar to that of the coupler.

Couplers containing a "coupling function" that is, a functional or reactive group common to coupler compounds, react with primary aromatic amino developing agents. This reactive group takes the form of a reactive methylene or reactive ethenol group, as well known in the art. Crystallization is evident in the case of couplers

also having one or more aromatic rings or ring structures.

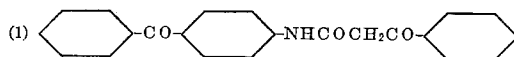
Non-coupling compounds or dispersing agents which we have found suitable for reducing the crystallization tendency of couplers in photographic emulsions have three component parts in their molecule:

1. One or more ring systems of exactly the same structure or configuration as that of the coupler with which it is to be used and therefore compatible with the coupler.

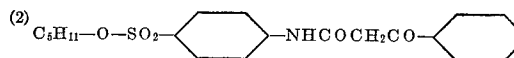
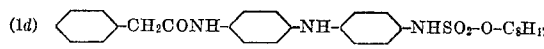
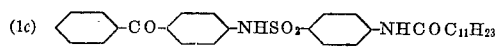
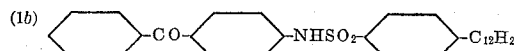
2. One or more polar groups which contribute to dispersability and solubility such as sulfate, sulfonic acid, sulfonamide, hydroxyl and quaternary nitrogen salts.

3. One or more alkyl groups having a straight carbon chain of at least five carbon atoms.

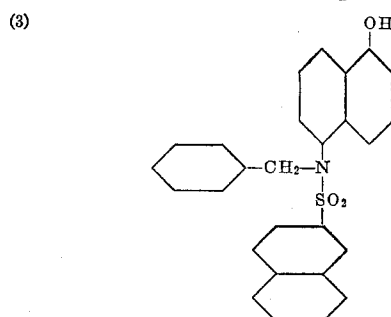
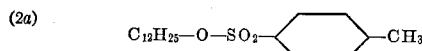
The following examples illustrate combinations of couplers and non-couplers which may be employed according to our invention:



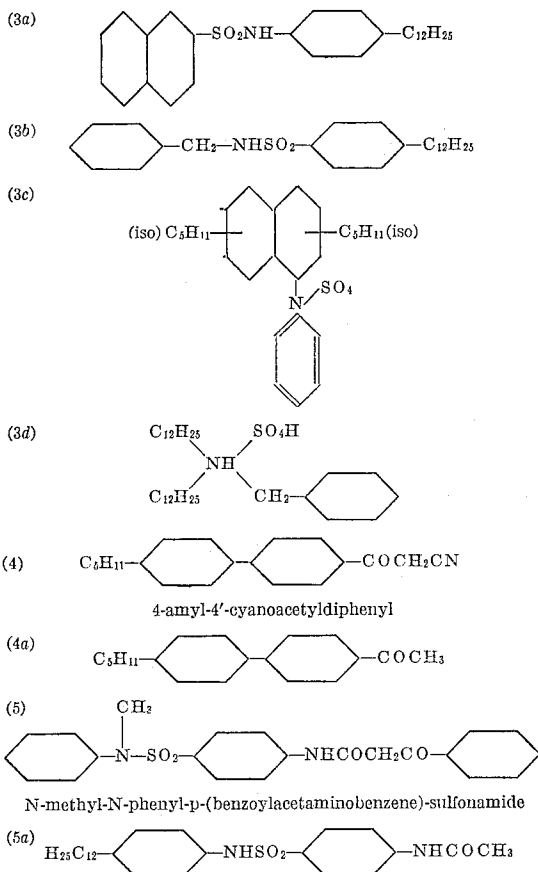
Benzoyl-acetamino-p-benzoylbenzene



n-Amyl-p-benzoylacetaminobenzene sulfonate



5-(N-benzyl-β-naphthalenesulfonamido)-1-naphthol



The yellow coupler benzoylacetamino-p-benzoylbenzene (1) crystallizes badly when incorporated in an emulsion layer of a multi-layer photographic element. A large variety of dispersing agents fails to eliminate this fault. However, if an equal weight of the compound 1a is incorporated in the emulsion simultaneously with the coupler 1, the crystallization tendency of the coupler is greatly diminished. Likewise, compounds 1b, 1c and 1d may be used alternatively with the coupler 1 to prevent crystallization in the emulsion.

Analogously, the coupler n-amylyl-p-benzoylacetamino-benzene sulfonate (2) crystallizes in emulsions. If an approximately equal weight of the compound 2a is incorporated with it, this tendency to crystallize is greatly diminished.

The coupler 5 (n-benzyl-β-naphthalenesulfonamide)-1-naphthol (3) is a cyan coupler which tends to crystallize in the emulsion. The compounds 3a, 3b, 3c or 3d may be incorporated with it in order to decrease its tendency to crystallize. In a similar manner the compound 4a may be used with the coupler 4 and the compound 5a with the coupler 5 to decrease their respective crystallization tendencies.

This decrease in crystallization tendency of the various couplers may be explained on the basis of the structure or configuration of the non-coupling compound employed with it. In the case of the coupler 1, for example, which contains a benzoylbenzene group, the non-coupling compounds used with it may contain a similar group or even a simple phenyl group which renders the auxiliary compound compatible or miscible with the coupler. The auxiliary compound contains a sulfonamide group which contributes to its dispersability and solubility in the emulsion

and also contains an alkyl group preferably of five or more carbon atoms to render the compound non-diffusing in the emulsion layer. In a similar manner, it will be seen that the various dispersing agents or auxiliary compounds employed with the various couplers have configurations rendering them compatible with the coupler with which they are used and also contain groups contributing to solubility and groups designed to reduce diffusion tendency. The dispersing agents which we employ are, therefore, designed for use with a specific coupler compound or group of coupler compounds having like structure. They do not possess general dispersing or solubilizing characteristics but are specific to a particular coupler compound. The following example will illustrate a method by which the couplers and dispersing agents may be incorporated in a photographic emulsion.

A solution of the coupler 2 was prepared by dissolving 5 grams of coupler in a mixture of 65 cc. of ethyl alcohol and 5 cc. of 20% sodium hydroxide solution. To this solution there was added 5 grams of the compound 2a. The solution was then mixed with 500 cc. of a melted gelatino silver halide emulsion and enough citric acid solution added to bring the pH of the emulsion to its original value. The emulsion was coated and dried in the usual manner.

The auxiliary compounds or dispersing agents employed in conjunction with couplers according to our invention may be used in greater or less amount than the coupler itself. We prefer to use an amount of the dispersing agent approximately equal to the amount of coupler although in certain cases the amount of dispersing agent may be as little as $\frac{1}{10}$ of that of the coupler or as great as five times the amount of coupler.

The specific compounds referred to herein may be prepared in any suitable manner. Generally, the sulfonic acid amides and carboxylic acid amides are prepared by the reaction of a suitable sulfonic acid chloride with an amine by the well known Schotten-Baumann reaction. The esters are prepared by the interaction of a sulfonyl chloride with the appropriate alcohol in the presence of one equivalent of pyridine. The coupler 2 is described in Porter and Weissberger U. S. Patent 2,289,805 and the couplers 3 and 5 are described in Porter and Weissberger U. S. Patent 2,289,443.

It will be understood that emulsion layers prepared according to our invention may be developed after exposure with any of the customary aromatic amino developing agents such as diethyl-p-phenylenediamine hydrochloride or suitable p-aminophenols. The compounds may be incorporated in single emulsion layers although the invention is most useful in the case of multi-layer coatings where two or more emulsion layers are coated in superposed relation on a single photographic support. Although gelatin is customarily used as the carrier for the silver halide, other colloidal materials such as colloidal cellulose organic esters or synthetic resins may also be employed. The emulsion layers may be supported by a transparent medium such as glass, cellulose ester or a non-transparent reflecting medium such as paper or an opaque cellulose ester. Superposed emulsion layers may be differentially sensitized to form natural color photographic images in the well-known manner.

The examples and compounds set forth in the present specification are illustrative only and it

is to be understood that our invention is limited only by the scope of the appended claim.

We claim:

The method of preventing the crystallization of couplers incorporated in photographic silver halide emulsions which comprises incorporating in said emulsion a mixture of a coupler normally

tending to crystallize and having a benzoylbenzene group and a benzoyl acetamino group, and a non-coupling compound having a benzoylbenzene group, a sulfonamide group, and an alkyl group of at least 5 carbon atoms.

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