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ELIMINATION COUPLING WITH AZO-SUBSTITUTED COUPLERS

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5 Claims. (Cl. 95—6)

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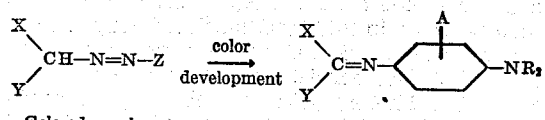
This invention relates to color photography and particularly to a method for producing stable dye images in photographic layers.

Colored couplers having an azo-substituted reactive methylene group or reactive ethenol group, that is, a carbon atom ortho or para to the hydroxyl group of a phenolic hydroxyl group, are described in Glass, Vittum and Weissberger U. S. patent applications Serial Nos. 533,930, 533,931, and 533,932, filed May 3, 1944. Such couplers react with the development product of primary aromatic amino developing agents to form colored photographic images just as the couplers containing unsubstituted reactive methylene or ethenol groups. The azo group is removed during coupling and an azomethine or indophenol dye is produced.

In Jelley and Vittum U. S. patent application Serial No. 533,933, filed May 3, 1944, now Patent Number 2,434,272, issued January 13, 1948, a method of producing stable photographic images from such couplers is described. According to the method of the Jelley and Vittum application, the emulsion layer containing the colored coupler is developed in the usual way with a coupling developing agent, such as diethyl p-phenylene diamine, and the layer is then treated with an acid bath which destroys the coupling bond and removes the colored dye from the emulsion layer. The original coupler containing the azo group is not affected by the acid bath, and the original colored coupler constitutes the final dye image.

We have found that stable colored images may be produced in a simple way by a method somewhat analogous to that of the Jelley and Vittum application. According to the present method, there is in the original coupler from which the colored coupler is produced, or in the developing agent used to develop an azomethine or indophenol dye from the colored coupler, or both, a group which renders the coupled dye soluble in the developing solution. The coupled dye may therefore be removed from the emulsion layer by reason of its solubility in the developing solution without the necessity of a separate acid treatment.

The principle involved in our invention may be illustrated by the following general reaction:



Colored coupler (non-diffusing) — Azomethine (soluble)

X and Y represent the portions of the usual coupler molecule and may contain a group which confers solubility in aqueous alkaline solution such as —COOH, —SO_3H, or —SO_2NH_2.

2

Z represents a group attached to the azo portion of the molecule such as phenyl, p.-tert. amylphenoxy phenyl, etc. If the X or Y portion of the molecule contains a solubilizing group, the Z portion of the molecule should contain one or more substituents of such molecular size that the colored coupler is non-diffusing in the emulsion layer in spite of the presence of the solubilizing group in the other portion of the molecule.

The primary aromatic amino developing agent may contain a group represented by A in the coupled dye which confers solubility in aqueous alkaline solution, on the coupled dye. This may be a group such as —COOH, or —SO_3H.

It will be apparent that the solubilizing groups may be present either in the X or Y portions of the original colored coupler or in the A portion of the developer or both.

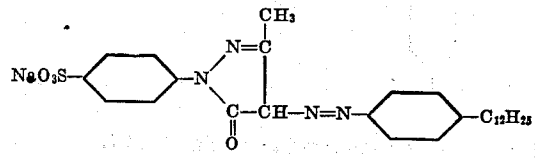
Our invention will be illustrated more fully by reference to the following examples which are illustrative only:

Example 1

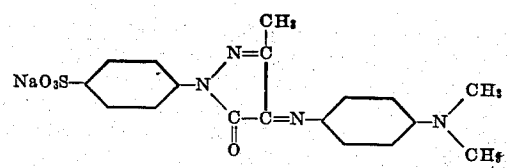
To a liter of a normal silver bromide emulsion is added a solution in 100 cc. of water of 5 g. of the sodium salt of 1-p-sulfophenyl-3-methyl-4-p-laurylphenylazo-5-pyrazolone (I), and the mixture is coated onto a suitable support, and dried in the normal manner. For processing, this material is developed, after exposure, in a solution of the following composition:

p-Aminodimethylaniline sulfate	grams	4
Sodium sulfite (anhydrous)	do	4
Sodium carbonate (monohydrate)	do	20
Potassium bromide	do	1
Water to	cc.	1,000

Where development occurs, the non-diffusing azo dye (I) is converted into the water-soluble, diffusible azomethine dye (II) which will wash out of the film. Development is followed by fixing and the usual silver removal baths, leaving a reversed image of the yellow azo dye I.



I



II

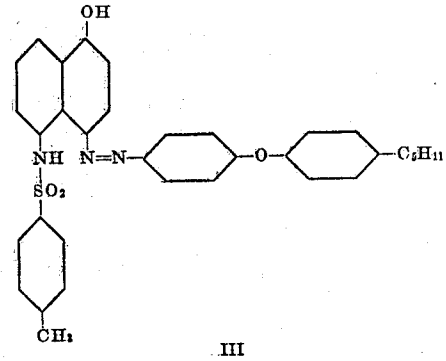
Example 2

5 g. of the orange-red dye, 4-p-(p'-tert-amyl) phenoxybenzeneazo - 5 -p-toluenesulfonamido-1-naphthol (III), is dissolved in a mixture of 10 cc. of a melted AgBr emulsion. To the emulsion is then added enough 10% citric acid solution to bring the pH to about 7. The mixture is coated and dried in the normal way.

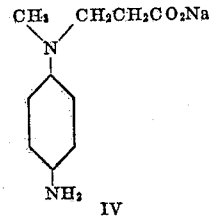
Development is carried out with the following solution:

N-methyl-N(p-aminophenyl) - B - amino-propionic acid (IV)	grams	5
Sodium sulfite (anhydrous)	do	1
Sodium carbonate (monohydrate)	do	20
Sodium hydroxide	do	2
Potassium bromide	do	5
Water to	cc.	1,000

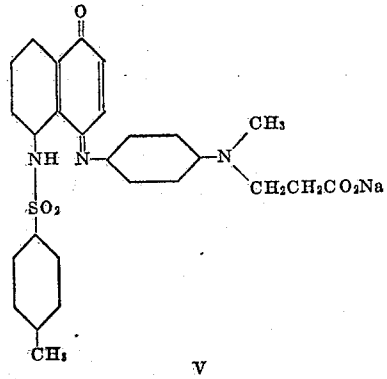
During development, the orange-red azo dye III couples with the oxidation product of the developer IV to yield the indoaniline dye V which is soluble in the alkaline developer solution and washes out of the layer, leaving a reversed image of orange-red dye III.



III



IV

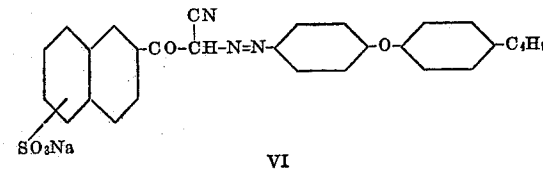


V

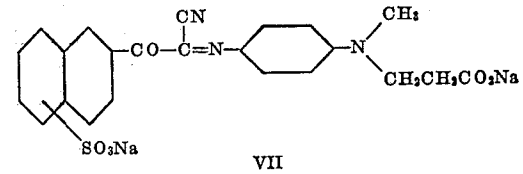
Processing is completed as in Example 1.

Example 3

The bright yellow azo dye VI obtained by coupling 2-cyano-acetylnapthalene-x-sulfonic acid with diazotized p-tert.butylphenoxyaniline is added to a silver halide emulsion layer exactly as in Example 1, and development is effected with the developer of Example 2. In this way, the yellow azo dye VI is transformed into the magenta azomethine VII which is soluble in the developer and washes out of the layer.



VI



VII

Our process can be adapted to single layer or multi-layer materials. In the latter case, the material may be arranged in the known manner to give natural color reversal pictures. For example, the red-sensitive layer containing cyan-colored coupler would be coated on the support followed by the green-sensitive layer containing magenta colored coupler and the blue-sensitive layer containing yellow colored coupler. In this material it will be advantageous to have sensitivity maxima which do not correspond to the absorption maxima of the colored couplers. Our process may also be adapted to other known arrangements, such as those leading to false colored pictures.

It is advantageous in certain cases when using multi-layer materials to incorporate the colored coupler in only a single layer or in less than all of the emulsion layers of the coating. The remaining emulsion layers might contain colorless couplers incorporated directly in the emulsion layer in the usual way or incorporated in water-permeable water-insoluble solvents as described in Mannes and Godowsky 2,304,940 or in Jelley and Vittum U. S. Patent 2,322,027. It might also be advantageous to have one or more of the layers of the multi-layer coating free of coupler, so that the dye image could be formed in this layer by means of a coupler dissolved in the developing solution. One or more of the emulsions may be a direct positive emulsion, such as that described in Leermakers U. S. Patent 2,184,013, granted December 19, 1939.

It will be understood that our invention is capable of numerous modifications not herein specifically mentioned and that our invention is to be taken as limited only by the scope of the appended claims.

The emulsions containing couplers, or the material including layers containing couplers and layers free of coupler, may be developed directly in the color developer or may be developed in a non-coupling, black-and-white developer, followed by color development to produce a positive image.

We claim:

1. The method of producing a colored image in a silver halide emulsion layer, which comprises incorporating in said layer a colored coupler having an azo-substituted reactive group selected from the class consisting of aromatic azo-substituted and heterocyclic azo-substituted methylene groups and aromatic azo-substituted and heterocyclic azo-substituted carbon atoms in a position other than meta to the hydroxyl group of a phenolic hydroxyl group, said azo substituent rendering the coupler non-diffusing in the emulsion layer, exposing said layer and devel-

oping it with a primary aromatic amino developing agent, thereby splitting off said azo-substituted reactive group and coupling said coupler at the point of splitting, with the development product of said developing agent, to form a silver image and a coupled dye possessing a group rendering the coupled dye soluble in the developing solution, and simultaneously removing said coupled dye from the region of said silver image in the emulsion layer by dissolving it in an alkaline solution, leaving the original colored coupler having the azo group in the remaining portions of the layer.

2. The method of producing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a colored coupler possessing a group which confers solubility on the coupler in alkaline solution and having an azo-substituted reactive group selected from the class consisting of aromatic azo-substituted and heterocyclic azo-substituted methylene groups and aromatic azo-substituted and heterocyclic azo-substituted carbon atoms in a position other than meta to the hydroxyl group of a phenolic hydroxyl group, said azo substituent rendering the coupler non-diffusing in the emulsion layer, exposing said layer and developing it with a primary aromatic amino developing agent, thereby splitting off said azo-substituted reactive group and coupling said coupler at the point of splitting with the development product of said developing agent, to form a silver image and a coupled dye in the exposed regions, which dye is soluble in an alkaline solution by reason of said solubilizing group, and simultaneously removing said dye from the region of the emulsion layer in which a silver image and a dye were formed, by dissolving it in said alkaline solution, leaving the original coupler having the azo group in the remaining portions of the layer.

3. The method of producing a colored image in a silver halide emulsion layer, which comprises incorporating in said layer a colored coupler having an azo-substituted reactive group selected from the class consisting of aromatic azo-substituted and heterocyclic azo-substituted methylene groups and aromatic azo-substituted and heterocyclic azo-substituted carbon atoms in a position other than meta to the hydroxyl group of a phenolic hydroxyl group, said azo substituent rendering the coupler non-diffusing in the emulsion layer, exposing said layer and developing it with a primary aromatic amino developing agent possessing a group which confers solubility on the coupled dye, thereby splitting off said azo-substituted reactive group and coupling said coupler at the point of splitting with the development product of said developing agent to form a silver image and a coupled dye in the exposed regions, which dye is soluble in an alkaline solution by reason of said solubilizing group and is removed, simultaneously with the development, from the region of the emulsion layer in which a silver image and a dye were formed, leaving the original coupler having the azo group in the remaining portions of the layer.

4. The method of producing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a colored coupler

possessing a group which confers solubility on the coupler in alkaline solution and having an azo-substituted reactive group selected from the class consisting of aromatic azo-substituted and heterocyclic azo-substituted methylene groups and aromatic azo-substituted and heterocyclic azo-substituted carbon atoms in a position other than meta to the hydroxyl group of a phenolic hydroxyl group, said azo substituent rendering the coupler non-diffusing in the emulsion layer, exposing said layer and developing it with a primary aromatic amino developing agent, thereby splitting off said azo-substituted reactive group and coupling said coupler at the point of splitting with the development product of said developing agent, to form a silver image and a coupled dye in the exposed regions, which dye is soluble in the developing solution by reason of said solubilizing group and simultaneously removing said dye from the emulsion layer by dissolving it in said developing solution, leaving the original coupler having the azo group in the unexposed portions of the layer.

5. The method of producing a colored image in a silver halide emulsion layer, which comprises incorporating in said layer a colored coupler having an azo-substituted reactive group selected from the class consisting of aromatic azo-substituted and heterocyclic azo-substituted methylene groups and aromatic azo-substituted and heterocyclic azo-substituted carbon atoms in a position other than meta to the hydroxyl group of a phenolic hydroxyl group, said azo substituent rendering the coupler non-diffusing in the emulsion layer, exposing said layer and developing it with a primary aromatic amino developing agent possessing a group which confers solubility on the coupled dye, thereby splitting off said azo-substituted reactive group and coupling said coupler at the point of splitting with the development product of said developing agent to form a silver image and a coupled dye in the exposed regions, which dye is soluble in the developing solution by reason of said solubilizing group and is removed, simultaneously with the development, from the emulsion layer, leaving the original coupler having the azo group in the unexposed portions of the layer.

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