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METHOD OF COLOR-FORMING DEVELOPMENT

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1 Claim. (Cl. 95—88)

This invention relates to improvements in color-forming developers and in processes of color development for color photography.

It is known that a colored photographic image may be formed by developing a silver salt image with a developer which forms a colored compound on development. The colored compound thus formed is deposited adjacent 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 photographic developer solutions or by incorporating in a silver halide emulsion before or after exposure a compound which couples, during development of the silver salt, with the oxidation product of a primary aromatic amino developing agent and forms a coloring substance which is likewise deposited adjacent the silver grains of the silver image formed during development. Such a compound, which is so 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 color coupler. It is desirable that the dyes thus formed in color development should not readily wander from the place of formation. It is accordingly desirable that they should be insoluble in water. They are probably not physically attached to the silver grain.

The present invention concerns new and improved color forming developers comprising a primary aromatic amino compound, serving as the developing agent, and a color coupler as hereinafter defined, and also includes a new or improved photographic color development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in the presence of a color coupler as hereinafter defined, as well as the color photographic element resulting therefrom.

The silver can be removed from the image after the color development leaving a clear, transparent dye image.

Coupling components are able to couple with the oxidation products of developing agents in photographic development by virtue of what may be termed a "coupling function" in the molecule of the coupling component. Most of the coupling components heretofore proposed for photographic color development have been of two types, namely, those having a phenolic hydroxyl group, and those having a reactive methylene group.

In the case of a reactive methylene group, this group may carry certain substituents such as a halogen atom or carboxylic acid group if desired. These substituents are split off in the coupling reaction, and their presence does not interfere with dye formation. The term "reactive methylene" includes compounds having such substituents.

Numerous substances have hitherto been employed or proposed as color couplers among which may be mentioned phenols, naphthols, cresols, nitrophenylacetonitriles and acetoacetic esters. It has not, however, always been possible among those hitherto available to select one which exhibits all the desired combination of properties required for any specific case. In color-developing a silver-halide emulsion layer it is necessary to select a color coupler which will give just the desired shade in conjunction with the colors which are produced in other layers. It is moreover important to employ a color coupler which gives a colored compound which is resistant to the normal processing baths employed, although it may often be desirable to have one which gives a color which can be destroyed or removed if desired during some step in the processing.

Another disadvantage of the color couplers which have hitherto been employed in solution with coupling developing agents is that the indophenol or azomethine dyes which are formed on development are rather unstable. In particular, they are sensitive to the action of acids and are subject to decomposition by heat and light. In addition, the characteristics of such dyes are limited, because they are dependent not only upon the nature of the coupler but upon the nature of the developing agent used to form the dye.

It has now been found that color-forming developers can be made and used containing in solution a color coupler which has been prepared from a dyestuff or the leuco form of dyestuff by introducing into the molecule thereof a group containing one of the coupling functions hereinbefore described.

The dye formed on coupling with the oxidation products of a developing agent is an indophenol or azomethine but is also a derivative of the initial dye or leuco dye. Accordingly, it can be decomposed by hydrolysis, oxidation or reduction, to split off the group containing the coupling function and so leave the initial dye or another acid-stable dye in the areas where development has taken place. By the aid of the present invention images composed of suitable dyes which are resistant to most photographic processing baths can be obtained.

According to the present invention, therefore, the color coupler employed comprises a dyestuff or leuco form of a dyestuff having combined therewith an auxiliary group containing a coupling function, which auxiliary group is capable of being split off by hydrolysis, oxidation or reduction to liberate the original dye or its leuco form, which leuco form can in turn be oxidized to the final dye. On photographic developing of a silver salt image such coupler combines with the developing agent to form the intermediate dye image which contains the indophenol or indamine group and at any convenient stage in the subsequent processing it is treated to liberate the original dye or the leuco form thereof.

One advantage of the present invention is that it is possible to introduce into the auxiliary group containing the coupling function other substituents which will influence the solubility or coupling characteristics of the coupling component. For example, sulphonic acid groups may be introduced into the auxiliary group containing the coupling function so as to enhance the solubility of the color coupler to facilitate its solution in the developer and to facilitate removal of the undesired residue after the dyestuff has been split off by oxidation, reduction or hydrolysis. By this introducing solubilizing groups into the auxiliary group containing the coupling function, it is possible to enhance the solubility of the color coupler without increasing the solubility or altering the shade of the final dye.

The aromatic amino compounds which may be used as developing agents in the present invention include the mono-, di-, and tri-amino aryl compounds. Among the mono-amino compounds may be mentioned the aminophenols and aminocresols and their halogen substituted derivatives as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as paraphenylene diamine and its substitution products. Those developers may be substituted in one amino group or in the ring or in both, forming compounds such as the alkyl phenylene diamines toluylene diamines, alkyltoluylene diamines and amino-diphenylamines. These compounds are usually kept in the salt form, such as hydrochloride or sulphate, since these are more stable than the amines themselves. As examples of developing agents of this class, there may be mentioned diethyl paraphenylene diamine, mono-methyl paraphenylene diamine, and dimethyl paraphenylene diamine.

Since the final image dye obtained according to the present invention no longer contains the coupling function the shade of the color obtained by coupling is generally of no importance and on this account the nature of the developing agent employed is immaterial.

A developing formula which may be used is the following:

A

Diethyl para-phenylenediamine	grams	1
Sodium sulphite	do	0.5
Sodium carbonate	do	20
Water to	liter	1

B

Coupler.... The molecular equivalent of the developer or an excess, for example 3 to 5 times such equivalent

Water-miscible solvent such as acetone..cc.. 50

For use, B is added to A.

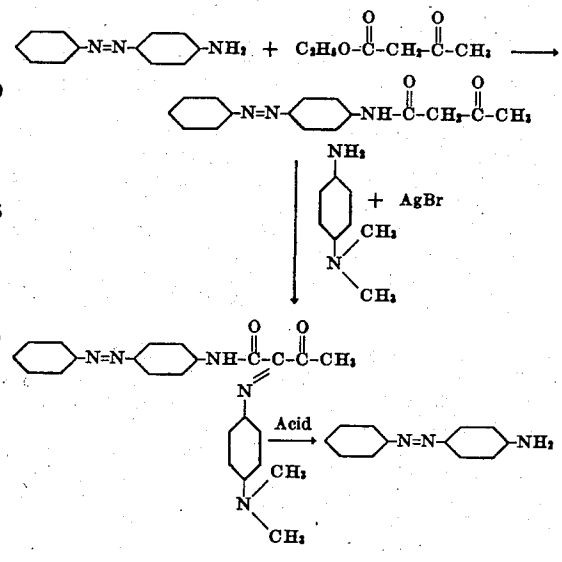
The developing agent and the proportions of the ingredients used in the above formulae may, of course, be varied. Solvents other than acetone, such as alcohols, may also be used, or the coupler may be dissolved in a small amount of alkali-metal hydroxide solution.

Instead of regenerating the original acid-stable dye in the layer, the dye formed by oxidation, reduction, or hydrolysis may be another acid-stable dye, such as a derivative of the original dye. Examples of color couplers for use in such a formula are:

Example 1

Para-aminoazobenzene, which is a suitable dye for use in a finished photographic image, is condensed with ethylaceto-acetate to give para-azophenylacetoacetanilide, which is a color coupler. This will couple with the developing agent such as para-aminodimethylaniline to give an azomethine dye in the regions where the developable silver salt is developed to silver by the paraaminodimethylaniline. This azomethine dye can readily be decomposed by acids to regenerate the original para-aminoazo-benzene.

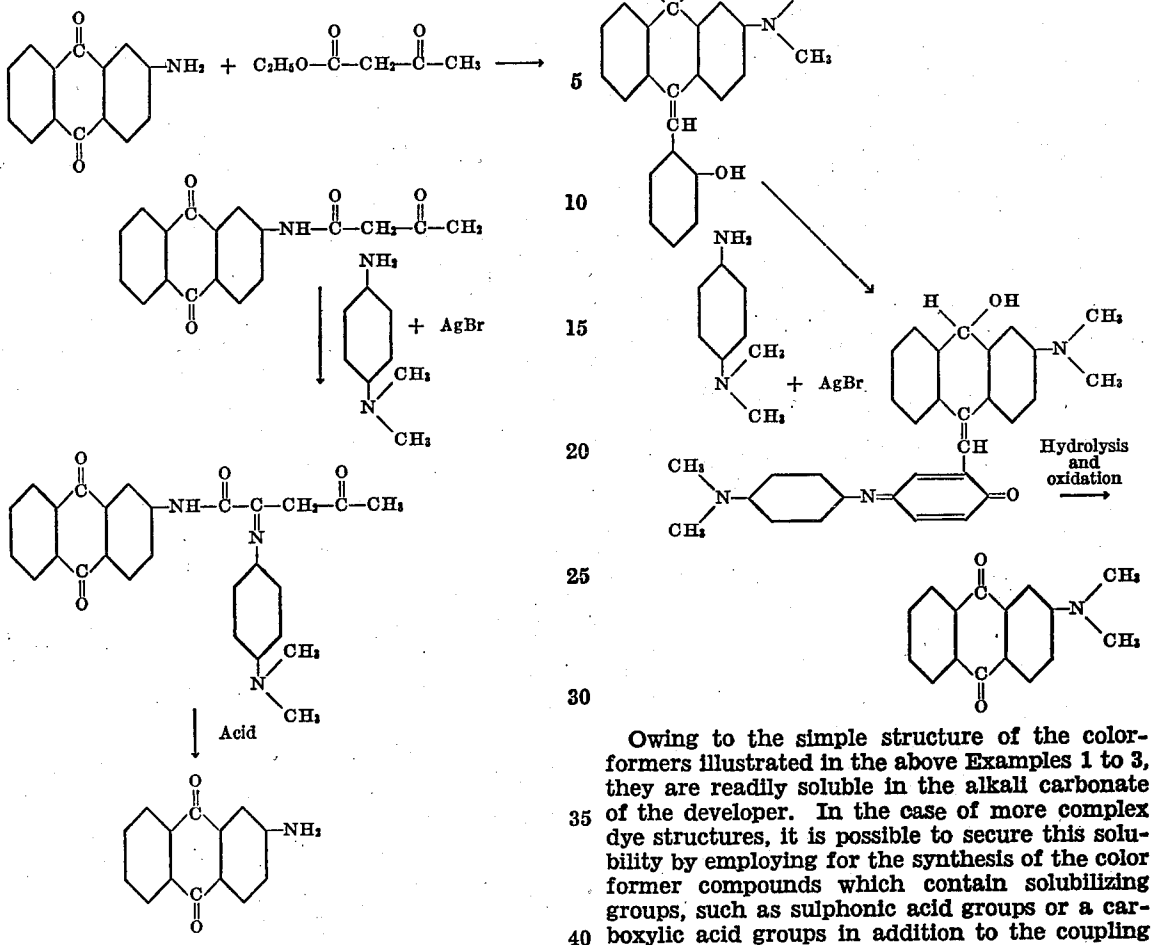
The reactions involved are as follows:



Example 2

2-aminoanthraquinone, which is a suitable dye for use in the finished picture, can be condensed with ethylacetoacetate and the product used as the color coupler.

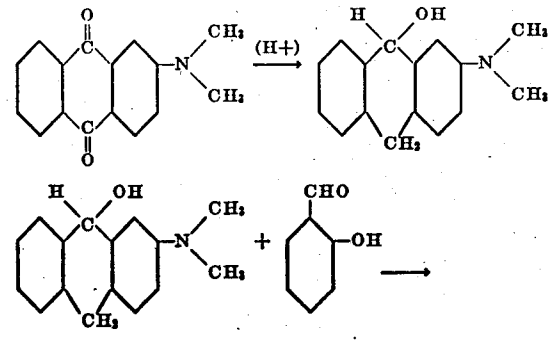
The reactions involved are as follows:



Example 3

2-dimethyl-aminoanthraquinone is reduced to the anthrone, and this is condensed with salicyl aldehyde to produce 2-dimethyl-amino-meso-salicylanthrone. Under these circumstances the aldehyde group combines with one of the carbonyl groups of the anthraquinone residue to give a phenolic derivative of the 2-aminoanthraquinone, which product can be used as the color coupler on development of a silver salt image with a developer containing this derivative and employing para-aminodimethylaniline as the developing agent. An indephenol dye is formed where the silver image develops. Hydrolysis of this indephenol liberates the leuco form of the original dye (anthrone), from which the original dye is readily formed by oxidation.

The reactions involved are as follows:



Owing to the simple structure of the color-formers illustrated in the above Examples 1 to 3, they are readily soluble in the alkali carbonate of the developer. In the case of more complex dye structures, it is possible to secure this solubility by employing for the synthesis of the color former compounds which contain solubilizing groups, such as sulphonic acid groups or a carboxylic acid groups in addition to the coupling function.

The present invention may be utilized in the formation of colored photographic images on plates or papers as well as on films employing gelatin or other carrier for the silver halide. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one side or on both sides of the support, and they may contain a sound-track.

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

We claim:

The method of forming a colored photographic image which comprises introducing a solubilizing coupling group into an insoluble acid stable dye to form a soluble coupling dye derivative, developing a silver halide layer in a developing solution containing the coupling dye derivative and a primary aromatic amino developing agent to form an intermediate dye, and removing the entire coupling group by hydrolysis from the intermediate dye to regenerate the original acid stable dye in the layer.

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