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SILVER HALIDE PHOTOGRAPHIC EMULSION WITH DEVELOPER AND COLOR COUPLER DISPERSED THEREIN

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1 Claim. (Cl. 95—6)

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This invention relates to color photography and particularly to a photographic method in which color-forming or coupling compounds are incorporated in a sensitive emulsion layer.

The method of incorporating couplers or color-forming compounds in a silver halide emulsion layer by dissolving them in a solvent for the coupler which is insoluble in the gelatin or other colloid of the emulsion, and dispersing the mixture in the emulsion, is described in Martinez U. S. Patent 2,269,158, January 6, 1942, Mannes and Godowsky U. S. Patents 2,304,939 and 2,304,940, December 15, 1942, and in our U. S. Patent 2,322,027, June 15, 1943. In all of these processes a multi-layer material having differently sensitized superposed emulsion layers contains different couplers which produce different dyes upon development with a single color-forming developer. One disadvantage of these processes is that the dye images formed in the separate emulsion layers must be derived from the same developing agent. It is frequently desirable to form the dye images from different developing agents since this affords a wider choice of dye colors and properties.

It is therefore an object of the present invention to provide a method of color photography which retains the advantages of the incorporated coupler processes such as those of our prior Patent 2,322,027 and at the same time affords a wider choice of color-forming developers for the separate layers. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating a color-forming developer base in the mixture of coupler and coupler solvent and dispersing the whole in the silver halide emulsion. We have found that it is possible to incorporate certain types of color-forming developer in the coupler-coupler solvent mixture and produce colored images in the separate layers of a multilayer system. This result is unexpected inasmuch as color-forming developing agents, when added to a photographic layer in the absence of a protecting medium act as powerful desensitizers of the photographic emulsion.

According to our invention, we add the color-forming developer as the free base to the mixture of coupler and coupler solvent before it is dispersed in the colloid mill. The following color developer bases are suitable for this purpose.

p-Amino diethylaniline
2-amino-5-diethylaminotoluene
p-Amino-N-ethyl-N - β - (methylsulfonamido) - ethylaniline

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3-methyl-4-amino-N-ethyl-N-β - (methylsulfonamido) -ethylaniline
p-Amino-di-n-propylaniline
p-Amino-di-n-butylaniline
2-amino-5-di-n-propyl-amino-toluene

The coupler solvents may be resins such as those of Martinez U. S. Patent 2,269,158, cellulose esters such as those of Mannes and Godowsky U. S. Patent 2,304,940 or liquid high-boiling solvents such as those of our prior Patent 2,322,027. All of these coupler solvents are water-insoluble, water-permeable organic materials, as dispersed in the silver halide emulsion having gelatin or other water-soluble colloid as the continuous phase. Typical coupler solvents are acetyl-n-butyl aniline, N-n-amyl-phthalimide, methyl phthalate, n-butyl phthalate, benzyl phthalate, triphenyl phosphate, p-toluene sulfonyl dimethylamide, etc.

The couplers used in our process may be any of those described on page 3 of our U. S. Patent 2,322,027.

Our invention will be further described by reference to the following examples which are illustrative only.

Example I

A solution was made by dissolving 1 gram of the coupler 5-[p-(p'-amylphenoxy)-benzenesulfonamido]-1-naphthol, 3 grams of triphenyl phosphate (coupler solvent) and 1 gram of p-amino-diethylaniline in 40 cc. of ethyl acetate. To this solution there was added 60 cc. of 0.1% solution of sodium alkyl sulfate and the mixture passed one or more times through a colloid mill or homogenizer until the globules of the non-aqueous dispersed phase were of the required degree of fineness. The dispersion was then evaporated to about 50 cc. to remove the volatile solvent, ethyl acetate. The evaporated dispersion was then added to 100 cc. of a gelatino silver halide emulsion of the required characteristics such as grain size, speed and color sensitivity, to yield a color-forming sensitive layer for use in a single layer or multi-layer photographic system. The emulsion was then coated.

Example II

A solution was made by mixing 1 gram of 1-p-sec. amylphenyl-3-n-amyl-5-pyrazolone, 4 grams of methyl phthalate (coupler solvent) and ½ gram of 2-amino-5-diethylaminotoluene base and warming gently until a homogeneous liquid was obtained. The warm liquid was then poured

into the following solution which had previously been heated to 40° C.

	Grams
Gelatin	3
Sodium alkyl sulfate	½
Water to 70 cc.	

The mixture was passed one or more times through a colloid mill or homogenizer until the globules of the non-aqueous dispersed phase were of the required degree of fineness. The dispersion was then added directly to a gelatino silver halide emulsion of the required properties to yield a color-forming sensitive layer for use in single-layer or multi-layer photographic systems.

The method of processing sensitive layers prepared by the present method depends on the physical properties of the developer base, particularly its partition coefficient between the disperse coupler-developer-solvent phase and the continuous photographic emulsion phase. For example, a photographic layer containing p-amino-diethylaniline base such as that of Example I gives a satisfactory dye image when developed in an alkaline solution which does not in itself contain a developing agent, such as the following:

	Grams
Sodium sulfite (anhydrous)	1
Potassium bromide	1
Sodium carbonate (monohydrate)	10
Sodium metaborate	40
Water to one liter	

The developer bases having a very low solubility in water and a high solubility in the coupler-coupler solvent disperse phase, do not develop in an alkaline solution such as the above but may be caused to do so by adding a suitable non-color-forming developer to the above formula. Thus, a photographic layer containing p-amino-di-n-butylaniline as the color developer base in addition to a color coupler develops to give a normal dye image in the following solution:

	Grams
Sodium sulfite (anhydrous)	1
Potassium bromide	1
Hydroxyphenyl glycine	2
Sodium carbonate (monohydrate)	10
Sodium metaborate	40
Water to one liter	

For this use the developer incorporated in the alkaline solution must be one which is in itself incapable of coupling either with the developer or the coupler in the disperse phase of the photographic layer.

A color-forming developer such as p-amino-N-ethyl-N-β-(methyl sulfonamido) ethylaniline may be used in the developing solution in which case its action appears additive, more dye being produced than with a photographic layer containing the coupler without the developer base.

The residual developer bases used in the present method are removed from the photographic material after formation of the color image by treating it in a weakly acid solution such as 1% acetic acid solution or an acid hardening stop bath. After this acid treatment which requires from 5 to 10 minutes, the silver is removed from the developed material by treatment with a ferricyanide-bromide bleach bath followed by hypo or by treatment in a solution containing an oxidizing agent such as potassium dichromate, or quinone and an acid such as sulfuric acid or hydrochloric acid. Any unchanged silver halide is removed with hypo.

While the development methods described above give a negative image the present method may also be used for reversal processing by developing first in a non-color-forming developer containing a high percentage of sulfite and after a fogging exposure using a second developer such as described above.

Our proposed method has a number of definite advantages. In a multi-layer system each layer may contain a different developing agent best suited for the production of a dye of the required absorption properties, light fastness and stability to heat and humidity so that there is no need to subject the process to the restriction of working with a single color-forming developer. Moreover, color-forming developers having too low solubility in alkaline solution to be used in any existing color process may be incorporated in the coupler-coupler solvent mixture according to the present process. A still further advantage is that the developing solutions need not contain developing agents producing skin irritation.

It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claim.

We claim:

A multi-layer photographic element comprising at least one gelatino silver halide emulsion containing finely-divided liquid particles of a solution of color former, p-amino dialkyl aniline color developing agent base, and a water-permeable, substantially water-insoluble, low molecular weight organic crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color former, the developing agent and the dye formed therefrom and being permeable to photographic processing solutions, the nature and proportions of the color former, developing agent and crystalloidal material being so chosen that the particles thereof are liquid under conditions of coating and processing the emulsion, said particles being dispersed in the emulsion.

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