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PHOTOGRAPHIC COLOR FORMER DISPERSIONS

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This invention relates to color photography and particularly to a method for incorporating couplers in silver halide emulsion layers.

Color-forming compounds of the water-insoluble type which are capable of coupling with the oxidation product of primary aromatic amino developing agents are usually incorporated in silver halide emulsions by first dissolving them in an organic solvent, dispersing this solution in aqueous gelatin and mixing the resulting dispersion with the silver halide emulsion. Processes of this type are described in Jelley and Vittum U.S. Patent 2,322,027 and Fierke and Chechak U.S. Patent 2,801,171. The Fierke and Chechak patent describes a process whereby the ratio of coupler solvent to coupler may be considerably reduced so that the final coating does not contain a large amount of organic solvent.

One of the difficulties encountered in these methods of incorporating the coupler in the emulsion is the tendency of the coupler to crystallize in the emulsion. When the auxiliary solvent has appreciable water-solubility, some of this solvent dissolves in the gelatin solution during the disperson operation, and this may take place so rapidly that there is insufficient solvent in the coupler phase to keep the coupler in solution. Some of the coupler then crystallizes. This crystallization of the coupler is undesirable because the coupler reacts less readily in the color-forming reaction when crystalline and therefore yields less dye.

It is therefore an object of the present invention to provide a novel method for incorporating color couplers in photographic emulsions. A further object is to provide a method for decreasing the tendency of the coupler to crystallize when incorporated in the emulsion. Other objects will appear from the following description of my invention.

These objects are accomplished by dissolving the coupler in a solvent which may include both a "regular" solvent and an "auxiliary" solvent, or which may include one or more auxiliary solvents without the regular solvent, dispersing the solution in gelatin to which auxiliary solvent has been added, chilling and setting the gelatin dispersion, removing substantially all of the auxiliary solvent from the dispersion by washing or drying, and mixing the dispersion with a gelatino-silver halide emulsion.

Couplers which may be used according to my invention are those disclosed in Jelley and Vittum U.S. Patent 2,322,027 and Fierke and Chechak U.S. Patent 2,801,171. More specifically I may employ 2-(α-di-tert.amylphenoxy-n-butyrylamino)-4,6-dichloro-5-methylphenol as a cyan-forming coupler, 1-(2',4',6'-trichlorophenyl)-3-[3"-(2"',4"'-di-tert.amylphenoxyacetamido) - benzamido]-5-pyrazolone as a magenta-forming coupler and N-(4-benzoylacetaminobenzenesulfonyl) - N - (γ-phenylpropyl)-p-toluidine as a yellow-forming coupler.

According to my process the coupler is first dissolved in an organic solvent which is a mixture of a regular solvent and an auxiliary solvent, or which may be one or more auxiliary solvents alone.

The "regular" solvent is a high-boiling, organic, crystalloidal coupler solvent, substantially water-insoluble, of low molecular weight, having a boiling point above about 175° C. at atmospheric pressure, having a high solvent action for the coupler and for dyes formed therefrom, and being permeable to photographic developer oxidation products. Coupler solvents of this class include (1) alkyl esters of phthalic acid in which the alkyl radical preferably contains less than 6 carbon atoms, e.g., methyl phthalate, ethyl phthalate, propyl phthalate, n-butyl phthalate, di-n-butyl phthalate, n-amyl phthalate, isoamyl phthalate and dioctyl phthalate, (2) esters of phosphoric acid, e.g., triphenyl phosphate, tricresyl phosphate and diphenyl mono-p-tert. butyl phenyl phosphate, and (3) alkyl amides or acetanilide, e.g., N,n-butylacetanilide and N-methyl-p-methyl acetanilide. The regular coupler solvent should have a water solubility of less than about 0.1 part of solvent in 100 parts of water, and is generally used in an amount less than one part of coupler solvent per part of coupler by weight.

The "auxiliary" solvents with which the present invention is useful should have a water solubility within the range of about 2.5 to 100 parts of solvent in 100 parts of water. If the water solubility of the solvent is less than about 2.5 parts of solvent in 100 parts of water, the loss of solvent to the aqueous gelatin solution becomes too small to be important. If the water solubility of the solvent is greater than about 100 parts of solvent in 100 parts of water, it is difficult to saturate the gelatin solution with the solvent and thereby to prevent loss of solvent to the gelatin solution from the coupler dispersion. Suitable auixilary solvents include esters of aliphatic alcohols with acetic or propionic acid, e.g., ethyl acetate, isopropyl acetate, ethyl propionate, β-ethoxyethyl acetate, and β-butoxy-β-ethoxyethyl acetate. Typical solvents of this class together with their boiling points and water solubilities are as follows:

Water-soluble solvents	B.P. (° C.)	Water Solubility (parts/100 at approx. 20° C.)
β-ethoxyethyl acetate	156.3	22
β-butoxy-β-ethoxyethyl acetate	127–130 (16 mm.)	6.5
Di-(Tetrahydrofurfuryl) adipate	200–205 (3 mm.)	3.5
Ethyl acetate	76–77°	9
Isopropyl acetate	86–88	3
Ethyl propionate	98–100	2.5
Methyl-n-propyl-ketone	103.3	6

After dissolving the coupler in the coupler solvent or mixture of coupler solvents, the solution is dispersed in a solution of gelatin. Prior to adding the coupler solution to the gelatin, there is added to the gelatin solution enough auxiliary solvent to saturate the gelatin solution. The coupler solution is dispersed in the gelatin by passing the mixture through a colloid mill or homogenizer and the coupler dispersion in gelatin is then chilled and set. The gelatin dispersion is then noodled, washed and dried. If an auxiliary solvent of appreciable water-solubility has been employed, washing removes substantially all of this solvent; or if a low-boiling solvent has been used, drying removes most of this solvent and at least 90% of the water. The dispersion may be kept in this form for an appreciable time and when it is to be used it is remelted, or if previously dried, redispersed in water, and mixed with the gelatino-silver halide emulsion in the usual manner. If a high-boiling regular solvent has been employed, it is retained in the coupler dispersion and is then incorporated in the final silver halide emulsion. It is usually desirable to have some regular solvent in the final coating.

A suitable ratio of coupler to regular coupler solvent would be 40 grams of coupler to 20 grams of regular solvent or a ratio of 1:½. The following example contains di-n-butyl phthalate as the regular solvent and β-ethoxyethyl acetate as the auxiliary solvent, although other mixtures and ratios may obviously be employed.

Example

Forty grams of the coupler, 2-(α-di-tert. amylphenoxy-n-butyrylamino)-4,6-dichloro-5-methyl phenol, were dissolved in a solution of 20 grams of di-n-butyl phthalate and 60 grams of β-ethoxy ethyl acetate at 280° F. A gelatin solution was prepared containing 272 grams of 10% gelatin solution in water, 40 cc. of 7½% Alkanol B solution and 80 grams of β-ethoxyethyl acetate, dissolved at 120° F. The coupler solution was poured into the gelatin solution, stirred for about one minute and passed through a colloid mill five times. The dispersion was set up on a chill plate at 40° F., noodled and washed for 6 hours in cool water to remove the auxiliary solvent. After remelting, the coupler dispersion was incorporated in a gelatino-silver halide emulsion. Eight grams of the coupler dispersion was added to a gelatino-silver halide emulsion containing approximately 0.046 mole of silver halide, and after coating on a film support the emulsion was exposed and processed in a developer of the following composition to produce a cyan image.

	Grams
p-Amino diethylaniline sulfate	2
Sodium sulfite, anhydrous	5
Sodium carbonate, anhydrous	20
Potassium bromide	2
Benzyl alcohol	10
Water to 1 liter.	

Compounds other than couplers such as antistain agents and ultraviolet light absorbers may be dispersed in gelatin by my method. Suitable antistain agents which can be incorporated in this way are 2,5-di-iso-octyl hydroquinone and 2,5-di-n-octyl hydroquinone. A suitable ultraviolet light absorber which can be incorporated by my method is o-methosulfobenzyl-3-phenyl-2-phenyl-amido-4-thiazolidone.

It will be understood that my invention is to be taken as limited only by the scope of the appended claims.

What I claim is:

1. The method of incorporating a color coupler in a gelatino-silver halide emulsion, which comprises dissolving a water-insoluble color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development to form a dye, in a solvent including (*a*) at least an auxiliary solvent having a solubility of at least 2.5 parts of solvent in 100 parts of water and not more than 100 parts of solvent in 100 parts of water, said auxiliary solvent being selected from the group consisting of ethyl acetate, isopropyl acetate, ethyl-propionate, β-ethoxyethyl acetate, β-butoxyethyl β-ethoxyethyl acetate, methyl-n-propyl ketone and di(tetrahydrofurfuryl) adipate and (*b*) less than about one part per part of color-forming compound of a substantially water-insoluble, low molecular weight, organic crystalloidal solvent for the color-forming compound, said crystalloidal solvent having a boiling point above about 175° C. and a solubility of less than about 0.1 part of solvent in 100 parts of water and having a high solvent action for the color-forming compound and for dyes formed therefrom, and being permeable to photographic developer oxidation products, dispersing the solution in aqueous gelatin previously approximately saturated with at least one of said auxiliary solvents, chilling and setting the gelatin dispersion, removing substantially all of said auxiliary solvent from the dispersion and mixing the dispersion with a gelatino-silver halide emulsion.

2. The method of incorporating a color coupler in a gelatino-silver halide emulsion, which comprises dissolving a water-insoluble color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development to form a dye, in a solvent mixture of di-n-butyl phthalate and β-ethoxyethyl acetate, dispersing the solution in aqueous gelatin previously approximately saturated with β-ethoxyethyl acetate, chilling and setting the gelatin dispersion, removing substantially all of said β-ethoxyethyl acetate from the dispersion and mixing the dispersion with a gelatino-silver halide emulsion.

3. The method of incorporating a color coupler in a gelatino-silver halide emulsion, which comprises dissolving 2-(α-di-tert. amylphenoxy-n-butyrylamino)-4,6-dichloro-5-methyl phenol in a solvent mixture of di-n-butyl phthalate and β-ethoxyethyl acetate, dispersing the solution in aqueous gelatin previously approximately saturated with β-ethoxyethyl acetate, chilling and setting the gelatin dispersion, removing substantially all of said β-ethoxyethyl acetate from the dispersion and mixing the dispersion with a gelatino-silver halide emulsion.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,787,544	Godowsky et al.	Apr. 2, 1957
2,801,171	Fierke et al.	July 30, 1957