

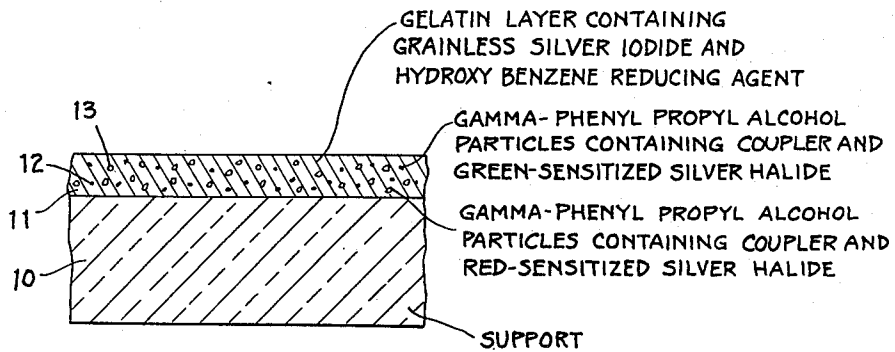
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MIXED GRAIN PHOTOGRAPHIC EMULSIONS

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MIXED GRAIN PHOTOGRAPHIC EMULSIONS

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This invention relates to color photography and particularly to mixed grain photographic emulsions.

Mixed grain photographic emulsions in which a multicolored image is obtained in a single emulsion layer by a single development step are well known. Fierke and Chechak U. S. Patent 2,490,749 granted December 6, 1949, describes such process in which the silver halide used as the sensitive material is dispersed or peptized in zein and the zein-peptized silver halide together with a color coupler is dissolved in a liquid solvent such as γ -phenylpropyl alcohol and the mixture dispersed in gelatin or other hydrophilic colloid. Portions of the silver halide are preferably optically sensitized so that different portions of the visible spectrum may be recorded in the emulsion layer to permit formation of a natural color photographic image.

One of the difficulties with mixed grain photographic processes is that there is color degradation or color contamination of the emulsion layer. In processes using color couplers in the emulsion layer, a considerable amount of the color contamination is due to the wandering of the active or coupling form of the oxidized developer, produced during the development of the silver in one set of particles, through the gelatin and into another set of particles containing a coupler different from that in the first set. For example, in the process of the Fierke and Chechak Patent 2,490,749, the active developer produced in the green-sensitive particles begins to couple with the magenta coupler in those particles but some of it diffuses out of the green-sensitized particles before it has had time to couple, travels through the gelatin and enters an adjacent particle containing cyan coupler and red-sensitive silver halide. Cyan dye is thereby produced in the red-sensitive particle, even though there has been no exposure of the red-sensitive particle.

It is therefore an object of the present invention to provide a novel mixed-grain photographic material and process. A further object is to provide a mixed grain material containing differently sensitized silver halide particles associated with color couplers, in which color contamination due to wandering of the oxidized developer is reduced or prevented. Other objects will appear from the following description of my invention.

These objects are accomplished according to the broader aspects of my invention by incorporating in a layer containing differently sensitized silver halide particles having color couplers associated with them, a material having a very large surface such as grainless silver iodide

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and a non-color-forming hydroxy benzene reducing agent. My invention is particularly useful with a mixed grain process in which the sensitive silver halide is contained in particles of γ -phenylpropyl alcohol containing color coupler.

In the accompanying drawing, the single figure is an enlarged view of a photographic film made according to my invention.

According to my invention, there is provided a photographic layer of gelatin or other water-permeable colloidal material having two or more differently color-sensitive photographic emulsions dispersed therein. Preferably the differently color sensitive photographic emulsions are contained in dispersed particles of a liquid solvent containing a color coupler. The liquid solvent should, according to the preferred embodiment of my invention, be a solvent for zein or other material with the vehicle for the silver halide and a solvent for the coupler and it should allow adequate optical sensitization of the silver halide. In addition, it should not interfere with the peptizing action of the zein or other colloidal material used to disperse the silver halide.

The sensitive emulsions used in my process are preferably silver bromide positive type emulsions prepared in a solution of zein-benzyl alcohol or other organic solvent as the peptizing material as described in Lowe U. S. application Ser. No. 47,753, filed September 3, 1948. These emulsions differ from the usual gelatino-silver halide emulsions in that they contain no water and are compatible with the liquid coupler solvent to be used in the process. In the process of the Lowe application, gelatin cannot be used as the peptizing material because it is insoluble in benzyl alcohol or other organic solvent and contains a considerable amount of water which makes it incompatible with the liquid coupler solvent.

When using γ -phenylpropyl alcohol as the coupler solvent, a suitable amount of optical sensitizing dye is dissolved in a portion of the γ -phenylpropyl alcohol which is then stirred into the zein-peptized emulsion. A suitable amount of color coupler is also dissolved in a portion of γ -phenylpropyl alcohol and stirred into the sensitized emulsion. This produces a sensitized emulsion of silver halide containing zein and color coupler in solution in γ -phenylpropyl alcohol.

The emulsion mixture is then poured slowly into a gelatin solution with stirring to form a dispersion of γ -phenylpropyl alcohol containing color coupler, sensitized silver halide and zein. According to my invention, the gelatin solution contains a non-color-forming benzene reducing

agent and grainless silver iodide. The particle size of the dispersed particles of γ -phenylpropyl alcohol containing color coupler and sensitized silver halide is determined by the amount of dispersing agent used. I prefer particles about 5 to 6 microns in diameter. The dispersion should not be run through a colloid mill because the particles are then too finely divided resulting in poor color separation when the dispersion is mixed with a differently sensitized dispersion. After the dispersion is firmly set, it is chilled and washed in cold water to remove unwanted salts and benzyl alcohol. Similar dispersions are made sensitized to other portions of the spectrum and containing appropriate color couplers and these dispersions are blended to produce a mixed grain photographic layer. Two or three dispersions made in this way may be mixed to form either a two-color or a three-color layer.

The layer made in this way may be exposed and developed in a primary aromatic amino color developing solution to produce a multi-color image in the layer.

Suitable developing agents are diethyl-p-phenylene diamine, dimethyl-p-phenylenediamine, 2-amino-5-diethylamino toluene, and N-ethyl-N-methylsulfonamidoethyl - p - phenyleneamido diamine. In order to produce satisfactory color density, the developing solution should have a pH of at least 10.5.

The hydroxy benzene reducing agents used according to my invention should not couple with the oxidized developer, or if they couple, the coupled product should be readily soluble so that it washes out of the layer. The reducing agents which I propose to use are therefore non-color-forming reducing agents. These include amyl hydroquinone, diamyl hydroquinone, lauryl hydroquinone, heptyl hydroquinone, dioctyl hydroquinone, resorcinol, 1-hydroxy-8-amino naphthalene-3,6-disulfonic acid and the like. In general, the emulsion layer may contain from 0.02 gram to 0.20 gram of reducing agent per square foot of coated emulsion surface. In the case of using non-diffusing reducing agent such as diamyl hydroquinone and dioctyl hydroquinone, the reducing agent must be dispersed before addition to the gelatin. For example, a dispersion of dioctyl hydroquinone is produced as follows:

8.0 g. dioctyl hydroquinone is dissolved at about 60° C. in 8.0 cc. dibutyl phthalate and is run, with stirring, at 40° C., into 54.0 cc. of 10% gelatin in water containing 6.4 cc. of a 5% aqueous solution of alkanol B. By means of a colloid mill, the particle size of the dispersion is reduced until the particles are of the order of 1 or 2 microns. The dispersion is then made up to a total weight of 100 g. with distilled water.

The grainless silver iodide used according to my invention has a very large surface and therefore has a strong adsorptive affinity for the active oxidized form of the developer. Materials such as activated aluminum oxide and diatomaceous earth may also be used but I prefer to use grainless silver iodide which can be easily removed during processing of the photographic layer. The silver iodide may be prepared by a simple formula such as the following:

- A. 100 cc. of 10% gelatin
10 cc. of 6.8% silver nitrate solution
- B. 100 cc. of 10% gelatin
10 cc. of 6.65% potassium iodide solution

Pour B rapidly into A at about 40° C.

The silver iodide should be used in amounts of 0.01 gram to 0.1 gram per square foot of coated emulsion.

My invention is applicable not only to mixed grain emulsions of the type described in Fierke and Chechak Patent 2,490,749, but also to other types of mixed grain emulsions such as those described in Godowsky U. S. application Serial No. 715,605, filed December 11, 1946 and Baines et al. U. S. application Serial No. 789,294, filed December 2, 1947.

When my invention is used in the preferred form in the mixed grain process of Fierke and Chechak Patent 2,490,759, numerous coupler compounds may be employed. The couplers should have molecular sizes and shapes so that although they are soluble in the γ -phenylpropyl alcohol or other coupler solvents used, they do not readily diffuse in gelatin and in the dispersion in which they are incorporated.

The following couplers are suitable for use according to the invention. It will be understood that this list is not intended to be exhaustive but merely to illustrate compounds which may be used.

Couplers producing cyan images

- 2-[α -(4'-tert.amylphenoxy) - butyrylamino]-phenol
- 5-(p-amylphenoxybenzenesulfonamino)-1-naphthol
- 2-chloro - 5 - (N - n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
- 2,4-dichloro-5-palmitylamino-1-naphthol
- 2-lauryl-4-chlorophenol
- 2-[α - (4'-tert.amylphenoxy) - butyrylamino]-6-phenylphenol
- 5-(p-laurylbenzenesulfamido)-1-naphthol

Couplers producing magenta images

- 1-phenyl-3-palmitylamino-5-pyrazolone
- 2-cyanoacetyl coumarone-5 - (N - n-amyl-p-sec.-amylsulfanilide)
- 2-cyanoacetyl coumarone - 5 - (N-n-amyl-p-tert.-amylsulfanilide)
- 2-cyanoacetyl coumarone - 5-(N- γ -phenylpropyl)-p-tert.amylsulfonanilide
- 2-cyanoacetyl coumarone-5-sulfon-N-(p-isopropylphenyl)-N-(γ -phenylpropyl)-amide
- 1-p-laurylphenyl-3-methyl-5-pyrazolone
- 1-phenyl-3-pentadecyl-5-pyrazolone

Couplers producing yellow images

- N-(4 - anisoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
- N-(4 - benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
- N-(4 - benzoylacetaminobenzenesulfonyl) - N-n-amyl-p-toluidine
- ω -Benzoylacetylaniline-p-nonyl-sulfonate

The following example illustrated a method of forming sensitive photographic layers according to my invention.

Example 1

- (a) To 50 grams of a silver bromide positive type emulsion prepared in a 10% solution of zein and benzyl alcohol as described in Lowe U. S. application Ser. No. 47,753, there was added at 50° C. a solution of 7.5 mg. of green sensitizer 3-ethyl-5-[(3-ethyl-2-(3)-benzoxazolyldiene)-isopropylidene]-rhodanine in 10 cc. of γ -phenylpropyl alcohol. The mixture was stirred for one hour at 50° C. To this was added 1.9 grams of magenta coupler, 1-phenyl-3-pentadecyl-5-py-

razolone dissolved in 65 cc. of γ -phenylpropyl alcohol and stirred for five minutes at 50° C. While stirring well, this emulsion mixture was then slowly poured into 300 cc. of 10% gelatin solution at 40° C. to which had been added 7.5 cc. of a 5% solution of sodium alkyl naphthalene sulfonate (alkanol B). Stirring was continued for five minutes at 40° C. The dispersion was firmly set, shredded and washed for two hours in cold water to remove soluble salts and benzyl alcohol. The total weight of the dispersion was about 500 grams.

(b) A second portion of 50 grams of the silver bromide emulsion made as described above was taken and to it was added a solution of 1.25 mg. of red sensitizer, 3-ethyl-5-[(1-ethyl-2-(1- β -naphthothiazolylidene)- α -ethylethylidene]-2-(3- β -hydroxy- β -ethoxy- β -ethoxyethyl-4-oxo-2-thiono-5-thiazolidylidene)4-thiazolidone) dissolved in 1.3 cc. pyridine and 10 cc. γ -phenylpropyl alcohol. The mixture was stirred for one hour at 50° C. To this was added 1.9 grams of cyan coupler 2-lauryl-4-chlorophenol dissolved in 65 cc. of γ -phenylpropyl alcohol and stirred 15 minutes at 50° C. While stirring well, the emulsion mixture was slowly poured into 300 cc. of 10% gelatin solution at 40° C. to which had been added 7.5 cc. of a 5% solution of sodium alkyl naphthalene sulfonate. Stirring was continued for 5 minutes at 40° C. The dispersion was firmly set, shredded and washed for 2 hours in cold water to remove soluble salts and benzyl alcohol. The total weight of the dispersion was about 500 grams.

A coating was prepared by adding 5.0 grams of dioctyl hydroquinone dispersion and 5 grams of grainless silver iodide emulsion prepared as described above to 150 grams of a 10% gelatin solution and then adding 75 grams of dispersion (a) with stirring. To this there was added 75 grams of dispersion (b) and the whole was thoroughly mixed. Suitable coatings were obtained by coating at the rate of 10 grams of emulsion to a 5 x 7 inch plate.

The dried coating was exposed to an image through red and green filters. It is necessary to exclude blue light since the emulsion is sensitive to the blue region and is intended to record only red and green light. The exposed layer was developed in the following developing solution.

	Grams
2-amino-5-diethylamino toluene hydrochloride	2
Sodium sulfite	2
Sodium carbonate	20
Potassium bromide	2
Water to 1 liter.	

Cyan and magenta images of satisfactory color separation were obtained in the portions of the plate which should be exposed to red and green light, respectively.

A three-color emulsion coating was made as described in Example 2 of Fierke and Chechak U. S. Patent 2,490,749 by adding 5.0 grams of dioctyl hydroquinone dispersion and 5 grams of grainless silver iodide emulsion to the 150 grams of 10% gelatin solution before adding the silver chloride and silver bromide emulsions to it.

The mixed grain emulsions made according to my invention may be coated on transparent, translucent or opaque supports such as glass, cellulose ester, or suitably coated paper. A single-layer emulsion containing three types of dispersed particles may be used or an emulsion layer containing two types of dispersed particles may be overcoated with a single emulsion layer containing the third color coupler to produce a natural color image. Suitable filter layers may be used to restrict the effect of undesired light in the manner well-known in the art, or a filter dye, for example a yellow filter dye, may be incorporated in the emulsion coating itself.

My invention will now be described by reference to the accompanying drawing. As shown therein, a support 10 of any suitable material is coated with a layer of gelatin 11 containing grainless silver iodide and a hydroxy benzene reducing agent. Layer 11 contains particles 12 of coupler solvent such as γ -phenylpropyl alcohol containing coupler and green-sensitized silver halide. In the same layer, there are similar particles 13 of coupler solvent containing coupler and red sensitizer silver halide. The method of exposing and developing this element will be understood by reference to the specific example above.

It will be understood that the examples included herein are illustrative only and that numerous variations may be made within the scope of the appended claims.

I claim:

1. A light-sensitive layer for producing a colored photographic image upon exposure and development, comprising a layer of water-permeable colloidal material having dispersed therein (1) particles of γ -phenylpropyl alcohol containing sensitive silver halide and a color coupler, (2) grainless silver iodide and (3) a non-color-forming hydroxy benzene reducing agent.

2. A light-sensitive layer for producing a colored photographic image upon exposure and development comprising a layer of gelatin having dispersed therein (1) particles of γ -phenylpropyl alcohol containing sensitive silver halide and a color coupler, (2) grainless silver iodide and (3) dioctyl hydroquinone.

3. A light-sensitive layer for producing a colored photographic image upon exposure and development comprising a layer of gelatin having dispersed therein (1) particles of water-insoluble, developer-permeable colloidal material containing optically sensitized silver halide and a color coupler, (2) grainless silver iodide and (3) dioctyl hydroquinone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,318,597	Davey et al.	May 11, 1943
2,490,749	Fierke et al.	Dec. 6, 1949