

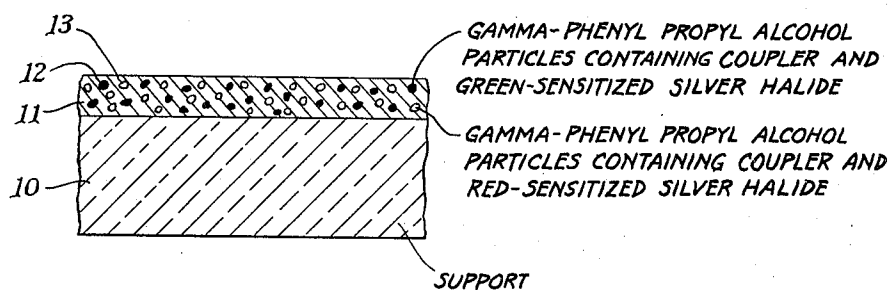
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MIXED GRAIN PHOTOGRAPHIC EMULSIONS

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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.

There have been many suggestions for mixed grain photographic emulsions in which a multi-colored image is obtained in a single emulsion layer by a single development step. In such emulsions, when a color coupler is incorporated in the coating, the coupler and sensitized silver halide must be kept in a particle separate from differently sensitized silver halide and its accompanying coupler in the same layer. Gelatin or other water-permeable colloid is ordinarily used as the continuous phase of the layer and since this colloid is also ordinarily used to disperse the silver halide, it is difficult to keep the sensitized silver halide particles separated from differently sensitized silver halide particles in the emulsion layer. The particles containing sensitized silver halide and coupler should be in a water-insoluble but water-permeable medium so that it can be dispersed in the gelatin or other hydrophilic colloid. Since the silver halide is ordinarily dispersed in gelatin, this dispersion or emulsion of silver halide and gelatin is not compatible with the water-insoluble material used to dissolve the coupler and difficulties therefore arise in making the mixed grain emulsion layers.

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 in which the silver halide is dispersed or peptized with a water-insoluble material which is soluble in the solvent used to dissolve the coupler. Other objects will appear from the following description of our invention.

These objects are accomplished by dispersing or peptizing the silver halide in zein and dissolving the zein-peptized silver halide, together with the color coupler, in a liquid solvent such as γ -phenyl propyl alcohol and dispersing the mixture in gelatin or other hydrophilic colloid.

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

According to the present invention, there is provided a photographic layer having two or more differently colored-sensitive photographic emulsions dispersed therein in a liquid solvent containing a color coupler. The liquid solvent must be a solvent for the zein or material used as the vehicle for the silver halide, and a solvent for the coupler and it should allow adequate op-

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tical sensitization of the silver halide. In addition, it should not interfere with the peptizing action of the colloid.

The emulsion used in our process is preferably a silver bromide positive type emulsion prepared in a solution of zein in benzyl alcohol or other organic solvent as the peptizing medium as described in Lowe U. S. application Ser. No. 47,753, filed September 3, 1948. This emulsion differs from the usual gelatino silver halide emulsion in that it contains no water and is compatible with the liquid coupler solvent to be used in the process. Gelatin cannot be used as the peptizing medium 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.

We prefer to use γ -phenyl propyl alcohol as the coupler solvent. A suitable amount of optical sensitizing dye is dissolved in a portion of γ -phenyl propyl alcohol and is stirred into the zein peptized emulsion. A suitable amount of color coupler is also dissolved in a portion of γ -phenyl propyl alcohol and stirred into the sensitized emulsion. This produces a sensitized emulsion of silver halide containing zein and color coupler, in solution in the γ -phenyl propyl alcohol.

The emulsion mixture is then poured slowly into a gelatin solution with stirring to form a dispersion of γ -phenyl propyl alcohol containing color coupler, sensitized silver halide and zein. The particle size of the dispersed particles is critical and the dispersion should not be run through a colloid mill because the particles are then too finely divided and color separation is poor when the dispersion is mixed with a differently sensitized dispersion. After the dispersion is firmly set, it is shredded and washed in cold water to remove unwanted salts and benzyl alcohol. Similar dispersions are made using different optical sensitizing dye and color coupler and these are mixed with the first made dispersion to produce a mixed grain photographic layer. Two or three dispersions made in this way may be mixed as desired, to form either a two-color or 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-colored image in the layer. Suitable developing agents are diethyl-p-phenylene diamine, dimethyl-p-phenylenediamine, 2-amino-5-diethylamino toluene, and N-ethyl-N-methyl sulfonamido ethyl p-phenylene diamine. In order to produce satis-

factory color density, the developing solution should have a pH of at least 10.5.

Numerous coupler compounds are suitable for use in our invention. The couplers should have a molecular size and shape so that, although they are soluble in the γ -phenyl propyl alcohol or other coupler solvent used, they do not readily diffuse in gelatin and in the dispersion in which we incorporate them.

The following couplers are suitable for use according to our 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. amyl sulfonanilide
- 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 examples illustrate methods of forming sensitive photographic layers according to our 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-pyrazolone 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 -naphthothiazolyldiene)- 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-chloro-phenol 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 75 grams of dispersion (a) to 150 grams of a 10% gelatin solution 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. Blue light must be excluded since the emulsion is sensitive to the blue region. The exposed layer was developed in the following developing solution.

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

Cyan and magenta images were obtained in the portions of the plate which had been exposed to red and green light, respectively.

Example 2

A three-color emulsion coating was made as follows:

(a) A green-sensitive emulsion containing magenta coupler was made as described in Example 1 (a) but using silver chloride instead of silver bromide.

(b) A red-sensitive emulsion containing cyan coupler was made as in Example 1 (b) but using a silver chloride emulsion instead of silver bromide.

(c) To 50 grams of a silver bromide positive type emulsion prepared in a 10% solution of zein-benzyl alcohol as the peptizing medium, there was added a solution of 1.9 grams of yellow coupler N(4-benzoyl acetamino benzene sulfonyl)-N'-(γ -phenylpropyl)-p-toluidine dissolved in 65 cc. of γ -phenylpropyl alcohol and stirred for 5 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 two hours in cold water to remove soluble salts and benzyl alcohol.

A coating was prepared by mixing 25 grams of emulsion (c) with 150 grams of 10% gelatin solution and adding 25 grams of emulsion (a) and 25 grams of emulsion (b) with thorough mixing. A

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coating was made at the rate of 10 grams of the mixture to a 5 x 7 inch plate.

Because silver chloride was used for the red-sensitive and green-sensitive emulsions, these emulsions were not appreciably sensitive to blue light. For this reason, they are affected by the red light and green light which they are intended to record and the silver bromide emulsion being unsensitized, was affected only by blue light.

The coating was exposed through red, green and blue filters and a step wedge over the light source. The exposed layer was developed in the same developer as used in Example 1 and good color separation was obtained.

The mixed grain emulsions made according to our invention may be coated on transparent, translucent or opaque supports such as glass, cellulose ester, synthetic resin or suitable coated paper. A single layer emulsion containing three types of dispersed particles as described in Example 2 may be used or an emulsion layer containing two types of dispersed particles as described in Example 1 may be overcoated with a single emulsion layer containing a yellow coupler. Suitable filter layers may be used to restrict the effect of undesired light in a manner well known in the art or a filter dye, for example, a yellow filter dye, may be incorporated in the emulsion coating itself.

Our 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 particles 12 of coupler solvent containing zein, sensitized silver halide and coupler. In the same layer, there are particles 13 of coupler solvent containing zein, differently sensitized silver halide and different coupler.

The method of exposing and developing this element will be understood by reference to the specific examples above.

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

What we claim is:

1. A light-sensitive layer for producing a colored image, comprising a layer of water-soluble, water-permeable colloidal material having dispersed therein particles of γ -phenylpropyl alcohol containing silver halide and color coupler.

2. A light-sensitive layer for producing a colored image, comprising a layer of gelatin having dispersed therein particles of γ -phenylpropyl alcohol containing silver halide and color coupler.

3. A photographic element for producing multi-color photographic images, comprising gelatin having dispersed therein particles of γ -phenylpropyl alcohol containing differently-sensitized, zein-peptized silver halides containing different color couplers.

4. A photographic element for producing multi-color photographic images, comprising a gelatin layer having dispersed therein particles of γ -phenylpropyl alcohol containing green-sensitized, zein-peptized silver halide and magenta-forming coupler, and separate particles of γ -phenylpropyl alcohol containing red-sensitized, zein-peptized silver halide and cyan-forming coupler.

5. The method of making a mixed grain photographic emulsion, which comprises adding to one portion of a zein-peptized silver halide emulsion a solution of an optical sensitizer for green light and a magenta-forming coupler in γ -phenylpropyl alcohol, and adding to another portion of said emulsion a solution of an optical sensitizer for red light and a cyan-forming coupler in γ -phenylpropyl alcohol, and dispersing said mixtures separately in gelatin.

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No references cited.