Sensitized Photographic Emulsion Containing Color Couplers

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2 Claims. (Cl. 95 — 7)

1. This invention relates to spectrally—(optically) sensitized photographic silver halide emulsions containing color couplers.

In general, in subtractive color photography, blue, green and red sensitive photographic silver halide emulsions are employed. The green and red sensitivities are obtained by the use of sensitizing dyes adsorbed to the silver halide grains. When couplers or dispersers of couplers are incorporated in the dye-sensitized emulsions, it is necessary that they do not alter the spectral (optical) sensitization produced by the dyes.

With the very great majority of sensitizing dyes, the molten sensitized silver halide emulsions in combination with the color couplers or dispersors of color couplers are not stable enough to permit the obtaining of uniform sensitivity throughout the period of coating; the emulsions losing the sensitivity conferred by the dye to a considerable degree during the coating operation.

We have now found that certain combinations of silver halide emulsions sensitizing dyes and color couplers are, in fact, stable and that the melted emulsions can be coated without appreciable loss in dye-sensitivity.

It is, accordingly, an object of our invention to provide stable combinations of silver halide emulsions sensitizing dyes and color couplers. A further object is to provide a process for preparing such combinations. Still other objects will become apparent hereinafter.

In accordance with our invention, we prepare an emulsion for color photography comprising a red-sensitive silver halide emulsion containing a color-former (coupler) for the cyan image (i.e., a color-former capable of forming a quinonimine dye with a phenylenediamine developer), said red-sensitive emulsion being sensitized with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formulas:

\[
I. \quad \text{R} \quad \text{R} \quad \text{Z} \quad \text{Z} \\
\text{II.} \quad \text{R} \quad \text{R} \quad \text{Z} \quad \text{Z} \\
\text{III.} \quad \text{R} \quad \text{R} \quad \text{Z} \quad \text{Z}
\]

wherein D and D₁ each represents a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, e. g., methylene, ethylene, ethylidene, trimethylene, tetramethylene, etc., R and R₁ each represents a member selected from the group consisting of a hydrogen atom and an alkyl group, containing from 1 to 4 carbon atoms, e. g., methyl, ethyl, n-propyl, isobutyl and n-butyld.

Z and Z₁ each represents a non-metallic atom or groups of atoms necessary to complete a heterocyclic nucleus, selected from the group consisting of heterocyclic nuclei of the benzothiazole series, heterocyclic nuclei of the benzoxazolone series, heterocyclic nuclei of the phenanthroline series and heterocyclic nuclei of the naphthoquinone series, e. g., the benzothiazole nucleus, the 5-methoxybenzothiazole nucleus, the 5-methoxybenzoxazolone nucleus, the 5-ethylbenzothiazole nucleus, the 5-ethylbenzoxazolone nucleus, the 5-phenylbenzothiazole nucleus, the 5-chlorobenzothiazole nucleus, the 5-bromobenzothiazole nucleus, the benzoxazolone nucleus, the 5-chlorobenzoxazolone nucleus, the α-naphthoquinone nucleus, the α-naphthoquinone nucleus, the α-naphthoquinone nucleus, the α-naphthoquinone nucleus, etc., R₂ and R₃ each represent an alkyl group containing from 1 to 2 carbon atoms, i.e., methyl and ethyl, R₄ represents a monocylic aryl group of the benzene series, e. g., phenyl, p-methoxyphenyl, m-tolyl, p-chlorophenyl, p-ethoxyphenyl, p-tolyl, p-bromophenyl, and X represents an anion, e. g., chloride, bromide, iodide, methylsulfate, ethylsulfate, p-toluenesulfate, benzenesulfonate, acetate, propionate, thiocyanate, perchlorate, etc.

In accordance with our invention, we prepare a yellow-green sensitive silver halide emulsion containing a color-former (coupler) for the magenta image (i. e., a color-former capable of forming an azomethine dye with a phenylenediamine developer), said yellow-green sensitive silver halide emulsion being sensitized with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formulas:

\[
IV. \quad \text{R} \quad \text{Z} \quad \text{Z} \\
\text{V.} \quad \text{R} \quad \text{Z} \quad \text{Z}
\]
wherein R4 and R5 each represents an alkyl group containing from 1 to 4 carbon atoms, e. g. methyl, ethyl, n-propyl, n-butyl, isobutyl, etc., X1 represents an anion, e. g. benzenesulfonate, p-toluene-

sulfonate, chloride, bromide, iodide, perchlorate, methylsulfate, ethylsulfate, thiocyanate, acetate, propionate, etc., X2 and X3 each represents a divalent hydrocarbon radical containing from 1 to 4 carbon atoms, e. g. methylene, ethylene, propylene, triethylene, tetramethylene, etc., and Z2 represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the quinoline series, e. g. the quinoline nucleus, the 6-methylquinoline nucleus, the 6-ethylquinoline nucleus, the 6-methoxyquinoline nucleus, the 6-ethoxyquinoline nucleus, the 6-chloroquinoline nucleus, etc.

In the preparation of photographic elements for color photography employing our new emulsions, any of the customary procedures can be used. Thus, the emulsions can be coated on a support as separate layers, e. g. a support (of cellulose acetate film, resin film, paper, etc.) can be coated with a layer of the red-sensitive emulsion containing a color former (as described above) and upon this, a layer of the yellow-green sensitive emulsion containing a color former (as described above) can be coated. Upon the yellow-
green sensitive layer, a yellow filter layer can then be coated and upon the filter layer a layer of a blue sensitive emulsion containing a color former which produces a yellow image or picture. Typical multi-emulsion photographic elements (consisting of color-formers in the emulsion) to which our invention is applicable are described in United States Patents 1,055,155, dated March 4, 1913; 2,304,940, dated December 15, 1942, and 2,322,027, dated June 15, 1943.

Our invention is also applicable to color photographic emulsion material wherein the emulsions are mixed instead of disposed in separate layers. Moreover, our invention is also applicable for producing single emulsions containing color-formers for making component color pictures. In addition to the sensitizing crystallloid materials, the emulsions employed in our invention can also contain the usual additions to emulsions, e. g. stabilizers, etc.

Our invention is especially useful where the emulsions contain, in addition to a color-former, a dispersing agent for the color-former, e. g. the water-insoluble but water-permeable materials set forth in U. S. Patents 2,304,940 and 2,322,027, such as water-insoluble but water-permeable cellulose esters, e. g. water-insoluble, but water-permeable cellulose acetate, cellulose acetate-phthalate, cellulose nitrate, etc., water-insoluble, but water-permeable cellulose ethers, water-in-

soluble but water-permeable natural and synthetic resins, high-boiling, substantially water-insoluble crystallloid materials, such as N-n-amyldichloride, tetrahydrofurfuryl benzole, triphenyl phosphate, n-buty1 sulfate, ethyl-NN-di-n-butylecarbamate, ethyl-N-phenylcarbamate, tetrahydrofurfuryl succinate, ethyl benzo malonate, methyl phthalate, n-buty1 phthalate, n-amy1 phthalate, a-methoxyethoxy phthalate, a-ethoxyethyl phthalate, a-butoxyethyl phthalate, butyl a-methoxybenzoate, n-hexyl benzole, benzophenone, p-sec-amylbenzophenone, tri-
cresyl phosphate, diphenyl mono-p, tert. butyl phenyl phosphate, monophenyl di-o-chlorophenyl phosphate, tri-o-phenylphosphinyl phosphates, p-
toluene-sulfonyl methyl-o-toluidine, p-toluene-sulfonyl dimethylamid, p-di-n-amyldichlorosul-
fonamide, p-toluene-sulfonyl di-n-butyl amide, N,N'-diethyl-N,N'-diphenyl urea, N,N-di-n-butyl urea, etc.

Our invention is especially useful with emulsions in which the color-former is dispersed in one or more of the aforesaid substantially water-insoluble, high-boiling crystallloid materials. These crystallloid materials are organic and have boiling points above about 175° C. These crystallloid materials have a high solvent action for the color-formers and for the dyes formed therefrom and are permeable to photographic processing solutions. These crystallloid ma-
terials have been referred to as "oil formers" because they have the property of producing an oily or liquid solution when mixed with the coupler, even though the coupler is a solid. The crystallloid materials are generally liquid at ordinary temperatures or low melting solids (be-
low 100° C.). The most useful compounds contain one or more polar groups such as halogen, hydroxyl, carboxylic acid, amide, ketone, etc.

The following couplers are suitable for use in our invention. It is to be understood that this list is not exhaustive, but merely to typify com-

pounds which may be used.

Couplers producing cyan images

5-(p-amyloxybenzenesulfonamido) -1-naph-
thol
5-(N- benzyl - N - naphthalene sulfonamido) -1-naphthol
5-(n-benzyl-N,n-valerylamino) -1-naphthol
5-caproylamino-1-naphthol
2-chloro-5-(N-n-valeryl - N - p-isopropylbenz-
lyaminol) -1-naphthol
2-dichloro-5(p-nitrobenzoyl-γ-hydroxyeth-
ylamino) -1-naphthol
2-dichloro-5-palmitamino-1-naphthol
2,2'-dihydroy-5,5'-dibromostilbene
5-diphenylethersulfonamido-1-naphthol
1-hydroxy-2-(N-isomy1-N-phenyl) naphthamide
1-hydroxy-2-(N-sec. amylphenyl) naphtham-
ide
8-hydroxy-1,1-epoxythyl - 1,2,3,4 - tetrahydroy-
quinoline
2-lauryl-4-chlorophenol
1-naphthol-2-carboxylic-o-naphthalde
1-naphthol-5-sulfocyclohexylamide
5-phenoxycetacamin-1-naphthol
5-γ-phenylpropionamino-1-naphthol
Monochlor-5-(N-γ-phenylpropyl-N-sec.amyl-
benzylamino)-1-naphthol
2-acetylamin-5-methylphenol
2-benzoylema-5-dimethylphenyl
2-γ-(p-tert. amyloxy) N - butyrylamino-5-
methylphenol
Couplers producing magenta images

1-p-sec. amylphenyl-3-n-amyl-5-pyrazolone
2-cyanoacetyl - 5 - (p-sec. amylphenoxylamino) - coumarone
2-cyanoacetylcoumarone - 5 - (n-n-amyl-p-sec. amylsulfinilide)
2-cyanoacetylcoumarone - 5 - (N-n-amyl-p-tert. amylsulfinilide)
2-cyanoacetylcoumarone - 5 - sulfon-N-n-butylinilide
2-cyanoacetyl-5-benzoyl-coumarone
2-cyanoacetylcoumarone-5-sulfondimethylamid
2-cyanoacetylcoumarone-5-sulfon-N-methylandilide
2-cyanoacetylnaphthalene sulfon-N-methylandilide
2-cyanoacetylcoumarone-5-(N-γ-phenylpropyl) - p-tert. amylsulfinilide
1-p-laurylphenyl-3-methyl-5-pyrazolone
1-β-naphthyl-3-amyd-5-pyrazolone
1-p-nitrophenyl-3-n-amyl-5-pyrazolone
1-p-phenoxphenyl-3-n-amyl-5-pyrazolone
1-phenyl-3-n-amyl-5-pyrazolone
1-4-phenylene bis-3-(1-phenyl-5-pyrazolone)
1-phenyl-3-acetylamin-5-pyrazolone
1-phenyl-3-propionylamin-5-pyrazolone
1-phenyl-3-n-valerlamino-5-pyrazolone
1-phenyl-8-chloroacetalamino-5-pyrazolone
1-phenyl-8-dichloroacetalamino-5-pyrazolone
1-phenyl-8-benzoylalamino-5-pyrazolone
1- phenyl-3 -(3-amino-3-benzoyl) aminol-5-pyrazolone
1-phenyl-3-(p-sec. amylbenzoxylamino) -5-pyrazolone
1-1phenyl-3- (p-sec. amylbenzoxylamino) -5-pyrazolone
1-phenyl-3-diamylbenzoylamin-5-pyrazolone
1-phenyl-3-kynyl-3-aminopyrazolone
1-phenyl-3-phenylcarbamoylamino-5-pyrazolone
1-phenyl-3-palmitylamino-5-pyrazolone
1-phenyl-3-benzenesulfonylamino-5-pyrazolone
1-phenyl-3-pheoxynylphenyl - 3 - (p-tert. amylbenzoxylamino) - amino-5-pyrazolone.

Of course, for photographic elements involving: a blue-sensitive, as well as a yellow-green sensitive, and a red-sensitive emulsion, color-felters, which produce yellow images are employed. and,
any of the color-formers producing yellow images can be used, e. g.

**Couplers producing yellow images**

N-amyl-\(p\)-benzoylaceticaminobenzensulfonate
N-(4-anisoylaceticaminobenzensulfonate)-N-benzyl-m-toluidine
N-(4-benzoylaceticaminobenzensulfonate)-N-benzyl-m-toluidine
N - (4 - benzoylaceticaminobenzensulfonate) - N-amyl-p-toluidine
N-(4-benzoylaceticaminobenzensulfonate)-N-benzylamine
\(\omega\)-(p-Benzoylbenzoyl) acetanilide
\(\omega\)-Benzylacet-2,5-dichloroanilide
\(\omega\)-Benzoyl-p-acet, amy lacetanilide
N,N'-di-(\(\omega\)-benzoylacetyl)-p-phenylenediamine
N,N'-di-(acetoacetamino)-diphenyl
4,4',di-(Acetoacetamino)-3,3'-dimethyl diphenyl
p,p'-di-(Acetocacetoamin)-diphenylmethane
Ethyl-p-benzoylaceticaminobenzesulfonate
Nonyl-p-benzoylaceticaminobenzesulfonate
N-phenyl-N'-p-(acetoacetamidophenyl)-urea
n-Propyl - p - benzoylaceticaminobenzesulfonate
acetoacetiperidide
\(\omega\)-Benzoylaceticiperidide
N(\(\omega\)-benzoylacetyl)-1,2,3,4-tetrahydroquinoline
N-(\(\omega\)-benzoylacetyl) morpholine

The aforesaid couplers give color development with color developers, such as N,N-dimethyl-p-phenylenediamine, N,N-diethyl - p - phenylenediamine, N-carbamidomethyl-N-methyl-p-phenylenediamine, N'-carbamidomethyl-N'-tetrahydrofurfuryl-2-methyl-p-phenylenediamine, N'-ethyl-N'-carboxymethyl-2-methyl-p-phenylenediamine, N'-carbamidomethyl-4'-ethyl-2-methyl-

**EXAMPLE 1**

![Chemical structure](image)

**TABLE A**

<table>
<thead>
<tr>
<th>Dye</th>
<th>VIII</th>
<th>VIII-A</th>
<th>IX</th>
<th>IX-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>Speed</td>
<td>Speed</td>
<td>Speed</td>
<td>Speed</td>
</tr>
<tr>
<td>289</td>
<td>1.63</td>
<td>69.5</td>
<td>1.98</td>
<td>425</td>
</tr>
<tr>
<td>67.5</td>
<td>1.06</td>
<td>67.5</td>
<td>1.06</td>
<td>18</td>
</tr>
<tr>
<td>(5)</td>
<td>63.0</td>
<td>1.07</td>
<td>(9)</td>
<td>170</td>
</tr>
<tr>
<td>(5)</td>
<td>38.0</td>
<td>1.23</td>
<td>(7)</td>
<td>130</td>
</tr>
</tbody>
</table>

1 Concentration of sensitizing dye was 50 mg. per liter of emulsion in all cases.
2 Red speed too low to measure.

From the data in the above table it is apparent that two otherwise excellent red sensitizers (dyes VIII and IX) do not give emulsions which are sufficiently stable to be coated in the presence of color formers, whereas dyes VIII-A and IX-A give emulsions of satisfactory stability.

**EXAMPLE 2**

![Chemical structure](image)
From the data in the above Table B it is apparent that two otherwise excellent red sensitizers (dyes X and XI) do not give emulsions which are sufficiently stable to be coated in the presence of color formers, whereas dyes X-A and XI-A give emulsions of satisfactory stability.

### Table C

(Exposure through a minus blue filter which transmits substantially no light of wavelength shorter than 600 m.)

<table>
<thead>
<tr>
<th>Dye</th>
<th>XII</th>
<th>XIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>γ</td>
<td>Speed</td>
</tr>
<tr>
<td>←labase-silver-bromodate-¢emulsion sensitized with dye...</td>
<td>70</td>
<td>0.48</td>
</tr>
<tr>
<td>←same, gelatin-silver-bromolodide-¢emulsion sensitized with same dye and containing a dispersion of a pyrazolone coupler for magenta image, held 1 hr. at 40°C.</td>
<td>78</td>
<td>0.65</td>
</tr>
<tr>
<td>←same gelatin-silver-bromolodide-¢emulsion sensitized with same dye and containing a dispersion of a 5-pyrazolone coupler for magenta image, held 2 hrs. at 40°C.</td>
<td>1</td>
<td>1.68</td>
</tr>
</tbody>
</table>

*1 Concentration of dye in all cases, 30 mg. per liter of emulsion.*
The data in the above Table C show two yellow-green sensitizers either of which gives an emulsion containing a coupler for the magenta image, which emulsions are satisfactory for coating purposes.

EXAMPLE 4

![Diagram](image)

TABLE D

<table>
<thead>
<tr>
<th>Dye</th>
<th>Speed γ</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with dye XIV</td>
<td>165</td>
<td>0.44</td>
</tr>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with dye XIV and containing a dispersion of an o-acylaminoazophenol color coupler</td>
<td>215</td>
<td>0.44</td>
</tr>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with dye XIV and containing a dispersion of an o-acylaminoazophenol color coupler</td>
<td>185</td>
<td>0.43</td>
</tr>
</tbody>
</table>

1 Concentration of sensitizing dye is 30 mg. per liter of emulsion in all cases.

In the above Table D it is shown that dye XIV gives a stable emulsion in the presence of color couplers for the cyan image.

EXAMPLE 5

![Diagram](image)

TABLE E

<table>
<thead>
<tr>
<th>Dye</th>
<th>Speed γ</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with dye XV</td>
<td>520</td>
<td>0.55</td>
</tr>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with same dye and containing a dispersion of an o-acylaminoazophenol color coupler for cyan image, held at 40°C, for 1 hr.</td>
<td>460</td>
<td>0.54</td>
</tr>
<tr>
<td>gelatine-silver-bromide emulsion sensitized with same dye and containing a dispersion of an o-acylaminoazophenol color coupler for cyan image, held at 40°C, for 2 hrs.</td>
<td>370</td>
<td>0.55</td>
</tr>
</tbody>
</table>

1 Concentration of dye in all cases, 30 mg. per liter of emulsion.

In the above Table E it is shown that dye XV gives a fairly stable emulsion in the presence of color couplers for the cyan image.

In preparing emulsions in accordance with our invention, the sensitizing dyes can be added to the emulsions in accordance with customary procedures, i.e., by adding a solution of the dye in an appropriate solvent to the emulsion. In the case of the dyes of Formulas II, III and IV, the dyes are advantageously dissolved in methyl alcohol and a volume of the methyl alcohol solution (which may be diluted with water) containing from 5 to 100 mg. of the dye or dyes is slowly added to 1000 cc. of emulsion with stirring. In the case of the dyes of Formulas I, V, VI and VII, a water-soluble salt of the dye is advantageously formed and dissolved in water, methyl alcohol or ethyl alcohol. The resulting solution of the water-soluble salt is then dispersed in the emulsions. The water-soluble salts are advantageously formed by adding to the dye or dyes (wet with a little water, methyl alcohol or ethyl alcohol), an alkali metal hydroxide, e.g. sodium or potassium hydroxide, or ammonium hydroxide, or an amine, e.g. methylamine, ethylenimine, dimethylamine, diethylenimine, trimethylamine, triethylenimine, ethanamine, diethanamine, triethanamine, pyridine, N-methylpyridine, N-propylenimine, isopropylenimine, n-butyamine, p-ethoxyethylamine, etc. The salt which forms is then taken up in a suitable solvent, e.g., water, methyl alcohol, ethyl alcohol, a mixture of methyl alcohol and water, a mixture of ethyl alcohol and water, etc. As in the case of the dyes of Formulas I, II, III and IV, the dyes of Formulas I, V, VI and VII are ordinarily employed in a concentration of from 5 to 100 mg. per liter of emulsion. In the case of any of the sensitizing dyes employed in our invention, the optimum sensitizing effect is ordinarily obtained at a concentration of from 5 to 50 mg. of dye per liter of emulsion.

The sensitizing dyes in most cases should be added to the emulsions before the coupler of coupler dispersion is added.

The color-formers (couplers) are incorporated in the emulsions in the customary manner, e.g., by adding a dispersion of the coupler in a water-insoluble but water-permeable material (see above) to the emulsion, or by adding a dispersion of the alkali metal of the coupler in water. When employing dispersions of couplers in the aforesaid colloidal materials, the coupler (color-former) which has been mixed with the high-boiling organic colloidal material to produce an oil-like mixture can be dispersed in water or gelatin solution or in any aqueous binder of colloidal character which is miscible with the silver halide emulsion. The dispersion so produced may be worked with the aid of a homogenizer, colloid mill or the like, and the dispersions can be stabilized by the addition of emulsifying agents such as those of the well-known higher fatty alcohol sulfate type. The dispersion may also be formed by dispersing a solution of coupler and colloidal material in a solvent of low boiling point such as butyl acetate with water or gelatin solution and subsequently removing the low-boiling solvent by evaporation. Here also an emulsifying agent can be used. It is important that the mixture of coupler and colloidal material be a liquid at ordinary temperatures, so that liquid particles are formed when the mixture of coupler and colloidal material is emulsified in water and mixed with the emulsion, the particles retaining the coupler in solution, yet being readily penetrated by the photographic developing solution and other processing baths. The nature and proportions of the coupler and the colloidal material should be chosen so that the particles are liquid under the conditions of coating and processing the emulsion. With the aforesaid colloidal materials, there is little or no tendency to crystallization even when the coupler is present in a proportion amounting to 50% or more of the high-boiling colloidal material. The colloidal ma-
The materials should also be substantially colorless and stable toward light, heat and moisture, in addition to being inert to the various processing baths which may be encountered, such as developers, oxidized developers, silver removal baths and fixing baths. They should have a sufficiently low refractive index so that solutions of the couplers in them have approximately the same refractive index as gelatin, thereby minimizing the opacity or light scattering of the coating. Most couplers themselves have high refractive indices, so for this reason it is desirable that the oil formers have low refractive indices. The crystalloidal materials should be easily disperseable in the emulsions and should be chemically inert toward the couplers and dye formed therefrom.

Our invention is directed primarily to the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloroiodide, -iodochloride, -bromide and -bromiodide developing-out emulsions. These ordinarily employed silver-halide developing-out emulsions are emulsions which form "surface" latent image (see British Patent 581,772, accepted October 24, 1945). However, silver halide emulsions which form latent image mostly inside the silver halide grains (see British Patent 581,772 supra) can also be employed in practicing our invention.

The dyes set forth under Formula II above are described in the copending application of Leslie G. S. Brooker and Frank L. White, Serial No. 312,314, filed January 22, 1944, now U. S. Patent 2,478,366, issued August 9, 1949. The dyes set forth under Formula III above are described in United States Patent 2,319,238, dated September 3, 1943. The dyes set forth under Formula I above can be prepared as described in United States Patent 2,381,638, dated February 11, 1945, by condensing a cyclammonium carboxyalkyl quaternary salt containing a reactive methyl group with ethyl orthophosphate, ethyl orthosacetate, ethyl orthoproponate, ethyl orthobutyrate or ethyl orthoacrylate. The dyes set forth under Formulas IV-VIII above are prepared as described in the copending application of Gertrude Van Zandt and Leslie G. S. Brooker, Serial No. 711,816, filed November 22, 1946, now U. S. Patent 2,815,913, issued July 18, 1950.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A red sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a phenolic color-former for the cyan image capable of forming a quinonemine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystalloidal material having a boiling point above about 175 °C., said crystalloidal material containing a high solvent action for the color former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formula:

\[
\text{HO-CH=CH-CH=CH-CH=CH-CH=CH-OH}
\]

wherein D and Z each represent a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, R and R each represent a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 2 carbon atoms, X and Z each represent a non-metallic atom; necessary to complete a heterocyclic nucleus selected from the group consisting of heterocyclic nuclei of the benzothiazole series, heterocyclic nuclei of the benzisoxazole series and heterocyclic nuclei of the naphthoselenazole series, R and R each represent an alkyl group containing from 1 to 2 carbon atoms, R each represents a monomeric aryl group of the benzene series, and Z represents an anion.

2. A yellow-green sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a ketomethylene color-former for the magenta image capable of forming a quinonemine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystalloidal material having a boiling point above about 175 °C., said crystalloidal material containing a high solvent action for the color former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said yellow-green sensitive emulsion containing said sensitizing dye selected from the group consisting of those dyes represented by the following general formula:

\[
\text{HO-CH=CH-CH=CH-CH=CH-OH}
\]

wherein D and Z each represent a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, R and R each represent a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 2 carbon atoms, X and Z each represent a non-metallic atom; necessary to complete a heterocyclic nucleus selected from the group consisting of heterocyclic nuclei of the benzothiazole series, heterocyclic nuclei of the benzisoxazole series and heterocyclic nuclei of the naphthoselenazole series, R and R each represent an alkyl group containing from 1 to 2 carbon atoms, Z each represents a monomeric aryl group of the benzene series, and Z represents an anion.
wherein R₄ and R₅ each represents an alkyl group containing from 1 to 4 carbon atoms, Xₖ represents an anion, Dₑ and Dₚ each represents a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and Zₖ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the quinoline series.

3. A red sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of an o-acylamino phenol color-former for the cyan image capable of forming a quinonemine dye with a phenylendiamine developer, and a substantially water-insoluble, low molecular weight, organic crystallloid material having a boiling point above about 175°C, said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formulas:

$$\text{OOC-D-N=CH=CH=CH-N-D-COOH}$$

wherein D represents a saturated divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, R represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 4 carbon atoms, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series.

5. A red sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of an o-acylamino phenol color-former for the cyan image capable of forming a quinonemine dye with a phenylendiamine developer, and a substantially water-insoluble, low molecular weight, organic crystallloid material having a boiling point above about 175°C, said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following formula:

$$\text{OOC-D-N=CH=CH=CH-N-D-COOH}$$

wherein D and Zₖ each represents a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and Zₖ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series, heterocyclic nuclei of the benzoxadiazole series, heterocyclic nuclei of the benzothiadiazole series and heterocyclic nuclei of the naphthothiazole series, Rₖ and Zₖ each represents an alkyl group containing from 1 to 2 carbon atoms, and X represents an anion.

4. A red sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of an o-acylamino phenol color-former for the cyan image capable of forming a quinonemine dye with a phenylendiamine developer, and a substantially water-insoluble, low molecular weight, organic crystallloid material having a boiling point above about 175°C, said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formula:

$$\text{OOC-D-N=CH=CH=CH-N-D-COOH}$$

wherein Rₖ represents an alkyl group containing from 1 to 2 carbon atoms, Rₖ represents a mono-
cyclic: aryl group of the benzene series, $Z$ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series; and $X$ represents an anion.

7. A red sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a 5-phenylazo-phenol color-former for the cyan image capable of forming a quinonesulfonine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic crystallloid material having a boiling point about 175° C., said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following formula:

\[
\text{CH}_2\text{CH}_2\text{CH}_2\\text{N}-\text{SO}_2\text{H}
\]

8. A yellow-green sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a 5-pyrazolone color-former for the magenta image capable of forming an azomethine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystallloid material having a boiling point above about 175° C., said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said yellow-green sensitive emulsion being sensitized to the yellow-green with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formula:

\[
\begin{align*}
N-\text{SO}_2\text{H} \\
\text{C-CH=CH-C}=N-\text{SO}_2\text{H}
\end{align*}
\]

wherein $R_1$ and $R_2$ each represents an alkyl group containing from 1 to 4 carbon atoms, $X_1$ represents an anion, $D_2$ and $D_3$ each represents a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and $Z_1$ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the quinoline series.

9. A yellow-green sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a 5-pyrazolone color-former for the magenta image capable of forming an azomethine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystallloid material having a boiling point above about 175° C., said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said yellow-green sensitive emulsion being sensitized to the yellow-green with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formula:

\[
\begin{align*}
N-\text{SO}_2\text{H} \\
\text{C-CH=CH-C}=N-\text{SO}_2\text{H}
\end{align*}
\]

wherein $D_2$ represents a divalent saturated aliphatic radical containing from 1 to 4 carbon atoms, $R_5$ represents a primary alkyl group containing from 1 to 4 carbon atoms, $X_1$ represents an anion and $Z_2$ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the quinoline series.

10. A yellow-green sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely divided liquid particles of a mixture of a 5-pyrazolone color-former for the magenta image capable of forming an azomethine dye with a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystallloid material having a boiling point above about 175° C., said crystallloid material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystallloid material be-
19. A sensitive silver halide emulsion for color photography selected from the group consisting of (I) a red sensitive silver halide emulsion containing dispersed therein finely divided liquid particles of a mixture of a phenolic color-former for the cyan image capable of forming a quinonimine dye with a phenylenediamine developer, and a 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 and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said red sensitive emulsion being sensitized to the red with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formulas:

\[ \text{formula} \]

wherein \( R_1 \) and \( R_2 \) each represents an alkyl group containing from 1 to 4 carbon atoms, \( R_3 \) and \( R_4 \) represent a member selected from the group consisting of a hydrogen atom and an alkyl group consisting from 1 to 4 carbon atoms, and \( X \) represents an anion, \( Y \) represents a divalent aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and \( Z \) represents a member selected from the group consisting of heterocyclic nuclei of the benzothiazole series, heterocyclic nuclei of the benzisoxazole series, heterocyclic nuclei of the naphthothiazole series and heterocyclic nucleus of the napthoselenazole series, \( R_5 \) and \( R_6 \) each represents a monocyclic aryl group of the benzene series, and \( X \) represents an anion, and (II) a yellow-green sensitive silver halide emulsion containing dispersed therein finely divided liquid particles of a mixture of a ketomethylene color-former for the magenta image capable of forming a quinonimine dye with a phenylenediamine developer, and a 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 and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said yellow-green sensitive silver halide emulsion being sensitized to the yellow-green with at least one sensitizing dye selected from the group consisting of those dyes represented by the following general formulas:

\[ \text{formula} \]