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3,469,987

METHOD OF SPECTRALLY SENSITIZING PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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ABSTRACT OF THE DISCLOSURE

Photosensitive silver halide is spectrally sensitized by forming a dispersion of a substantially water-insoluble spectral sensitizing dye in a hydrophilic colloid, and incorporating the dispersion of dye in colloid in a light sensitive system comprising photosensitive silver halide dispersed in a hydrophilic colloid.

This invention relates to new processes for spectrally sensitizing photographic materials, and to new compositions useful in such processes.

In one aspect of this invention, photosensitive materials dispersed in a hydrophilic colloid which are sensitized in accordance with this invention tend to exhibit lower fog and generally higher sensitized speed than similar emulsions spectrally sensitized in accordance with prior art procedures. In addition, such sensitized photographic materials may be coated at high speeds without the occurrence of coating defects caused by organic solvents in the system. Organic solvents were previously necessary in fairly large quantities in order to introduce the sensitizing dye in the emulsion.

As is well known, most spectral sensitizing dyes for photosensitive materials, such as silver halide, are highly insoluble in water. For many purposes, it is desirable to incorporate these water-insoluble dyes in aqueous systems, such as a dispersion of a photosensitive material, e.g., silver halide, in a hydrophilic binder such as gelatin. Most of these dyes are so insoluble that large quantities of organic solvent are required to dissolve the dye for incorporation into the aqueous system. When large quantities of organic solvent are introduced in hydrophilic colloid systems, serious problems are encountered, such as coating defects when coating the hydrophilic colloid system on a support. It would, therefore, be highly desirable if an improved process could be provided for incorporating water-insoluble dyes in hydrophilic systems.

This invention solves the problem of excess solvent when incorporating water-insoluble dyes in hydrophilic colloids containing photosensitive materials, and in addition normally provides an unexpected reduction in fog and, generally, an increase in sensitized photographic speed. Since only extremely small quantities of organic solvent are employed in the process of the invention, difficulties such as coating problems arising from prior art techniques are avoided.

One object of this invention is to provide a novel process for spectrally sensitizing photosensitive materials. A further object of this invention is to provide a novel process for dispersing sensitizing dyes in hydrophilic colloids containing photosensitive materials, such as silver halide. Still another object of this invention is to provide a process for making dispersions of sensitizing dye in hydrophilic colloids. Another object of this invention is to provide novel dispersions of dye in hydrophilic colloids. Other objects of this invention will be apparent from the description herein and the appended claims.

These and other objects of this invention are accom-

plished by novel processes and compositions which are interrelated, and will be more apparent from the following disclosure and claims.

In one embodiment of this invention, photosensitive materials are spectrally sensitized by forming a dispersion of a spectral sensitizing dye in a hydrophilic colloid, and the photosensitive material is then contacted with said dispersion.

In another embodiment of this invention, a spectral sensitizing dye is incorporated in a hydrophilic colloid by dissolving the dye in an organic solvent, and then adding the dissolved dye to a hydrophilic colloid.

In still another embodiment of this invention, novel compositions are provided comprising dispersions of spectral sensitizing dye in a hydrophilic colloid which is essentially free from photosensitive materials, the particles of the dye in the colloid having an average diameter of less than about 1.0 micron.

This invention will be further illustrated by the following examples which show the spectral sensitization of photosensitive materials by contacting them with a dispersion of spectral sensitizing dye in a hydrophilic colloid. Preferably, the solvent is heated to dissolve the dye in as high a concentration as possible. The solution of dye is then combined with a hydrophilic colloid, such as an aqueous gelatin solution. A wetting agent may advantageously be employed to aid in dispersing the dye in the hydrophilic colloid. The dispersion of dye in hydrophilic colloid may be milled or homogenized. In Examples 1-4, the solvent employed to dissolve the dyes is a substantially water-immiscible organic solvent which has a sufficiently high vapor pressure to volatilize from the dispersion upon drying. After forming the dispersion of dye in hydrophilic colloid, the dispersion is dried to remove essentially all of the solvent.

EXAMPLE 1

A negative speed gelatino-silver bromiodide emulsion is digested to optimum sensitivity with a mixture of labile sulfur compound and a soluble gold salt, and divided into two portions. These portions are spectrally sensitized in the 5000 to 6000 Å. range as follows:

(a) Dye I, a benzothiazolylidene-isopropylidene-oxazolidinedione merocyanine dye of the type described in Example 7 of U.S. Patent 2,165,338, is added to the melted emulsion with good agitation at the rate of 0.132 g. per mole of silver halide from an acetone solution.

(b) Dye I is predispersed in aqueous gelatin as follows:

Dye I	-----g--	0.130
Acetic acid	-----cc--	3
Ethyl acetate	-----cc--	70
10% aqueous gelatin	-----cc--	200
5% aqueous alkanol B	-----cc--	75

using the method outlined above, dried and added to the emulsion as the plumped and melted dispersion at the rate of 0.132 g. of dye per mole of silver halide. The wetting agent used in this example is an alkyl-naphthalene sodium sulfonate product sold as Alkanol B by Du Pont.

Each emulsion is further treated by the addition of a magenta-forming coupler of the pyrazolone type suitably dispersed in a high boiling solvent. The emulsions are then coated on a suitable support. The resulting coatings are exposed for 1/25 second to the light emitted by a 500-watt tungsten lamp adjusted to 2650° K. in an intensity scale sensitometer further modified by a Wratten No. 15 filter and processed by the color negative process disclosed by Hanson, Jr., and Kisner in "Journal of the Society of Motion Picture and Television Engineers,"

vol. 61 (1953), pages 667-701, at page 683. The following results are obtained:

Feature	Relative speed	Minimum density
Sensitized as in (a) (12 min. dev.)	100	.36
Sensitized as in (b) (12 min. dev.)	155	.12
Sensitized as in (a) (14 min. dev.)	79	.44
Sensitized as in (b) (14 min. dev.)	159	.17
Sensitized as in (a) (16 min. dev.)	76	.53
Sensitized as in (b) (16 min. dev.)	178	.24

It may be seen from the above table that a substantial increase (over 50%) in sensitized speed is realized with the sensitizing technique of this invention. In addition, the results show a great reduction in fog (D_{\min}) over the same emulsions sensitized in accordance with the prior art method of spectrally sensitizing. Similar results are obtained when the light sensitive material is TiO_2 or ZnO instead of silver halide, and the hydrophilic colloid, instead of gelatin, is cellulose ether phthalate, polyvinyl alcohol, or polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of 0.25 to 1.5, and mixtures thereof. The dispersions of sensitizing dye in gelatin (and the other hydrophilic colloids) give good sensitization of binder-free silver halide films prepared by vacuum depositing silver halide on a support.

EXAMPLE 2

A negative speed gelatino-silver bromiodide emulsion digested to optimum sensitivity with a mixture of liable sulfur compound and a soluble gold salt is divided into two portions. These portions are optically sensitized in the 5000 to 6000 A. region as follows:

(c) With dye I as described in Example 1(a) above.

(d) Predispersing dye I according to the following formula:

Dye I	g	0.130
Benzene	cc	10
Ethyl acetate	cc	65
10% aqueous gelatin	cc	200
5% aqueous alkanol B	cc	75

The dispersion is formed as in Example 1(b), dried and added to the emulsion as the plumped and melted dispersion at the rate of 0.132 g. of dye per mole of silver halide.

Each emulsion is further treated by the addition of a magenta forming coupler of the pyrazolone type suitably dispersed in a high boiling solvent. The emulsions are then coated on a suitable support.

The resulting coatings are exposed for $\frac{1}{25}$ second to the light emitted by a 500-watt tungsten lamp adjusted to 2650° K. in an intensity scale sensitometer further modified by a Wratten No. 15 filter and processed as in Example 1. The following results are obtained:

Feature	Relative speed	Minimum density
Sensitized as in (c) 12 min. dev.	100	.65
Sensitized as in (d) 12 min. dev.	100	.18
Sensitized as in (c) 14 min. dev.	110	.84
Sensitized as in (d) 14 min. dev.	110	.84
Sensitized as in (c) 16 min. dev.	126	1.06
Sensitized as in (d) 16 min. dev.	132	.39

The above results show the lower fog, and increased sensitized speed upon extended development, of the emulsion spectrally sensitized in accordance with this invention.

EXAMPLE 3

A positive speed gelatino-silver chlorobromide emulsion digested to optimum sensitivity with labile sulfur compounds is divided into two portions. These portions are then spectrally sensitized in the 6000 to 7000 A. range as follows:

(e) Dye II, a thiazolylidene - 2 - butenylidene-2-thiohydantoin mercyanine dye of the type described in U.S. Patent 2,177,403, is added slowly to the emulsion

with good agitation from acetone-methanol solution at the rate of 0.060 g./mole of silver halide.

(f) Dye II is predispersed as in Example 1 according to the following formula:

Dye in (e)	g	0.066
Benzene	cc	25
Ethyl acetate	cc	75
10% aqueous gelatin solution	cc	200
5% aqueous alkanol B solution	cc	100

The predispersed dye is added to the emulsion as a plumped and melted dispersion at the rate of 0.060 g. of dye per mole of silver halide.

Each emulsion was further treated by the addition of a phenolic cyan forming coupler dispersed in a high boiling solvent and coated on suitable supports.

The resulting coatings are exposed for 1 second to the light emitted by a 500 w. tungsten lamp adjusted to 3200° K. in an intensity scale sensitometer further modified by a Wratten 29 filter, and processed as in Example 1. The following results are obtained:

Feature	Relative speed	Minimum density
Example 3(e)	100	.06
Example 3(f)	142	.06

These results show a substantial increase in relative speed of the emulsion sensitized in accordance with the invention.

EXAMPLE 4

Antifoggant action of dispersion sensitization is also evident in reversal processing of emulsions in the process described in U.S. Patent 2,294,898, col. 11, as "Color Process 1." Slightly larger amounts of dye are used to increase the speed of the reference coating. Substantial antifoggant action is evident at these higher concentrations of dye and is found in the black and white developing step as lower D_{\min} and in full reversal color process as higher D_{\max} .

The following results are obtained on coatings prepared as in Example 2 above with the exception of the higher concentration of dye as indicated.

Feature	Black and white		Color reversal	
	D_{\min}	Relative speed	D_{\max}	Speed
(c) (Above)	.26	100	1.60	100
(d) (Above) at rate of 0.198 g. dye/mole AgX	.15	100	1.86	100

The procedure of Example 5 shows a preferred method of dispersing spectral sensitizing dyes in hydrophilic colloids. In this method, the dye is first dissolved in a high-boiling, partially water-miscible solvent. Advantageously, the dye is dissolved in heated solvent to provide as high a concentration of dye in the solvent as possible. The concentrated solution of dye is then dispersed in an aqueous hydrophilic colloid, and the mixture is preferably milled or homogenized. This procedure results in an oil-in-water emulsion featuring small particle size globules of solvent containing the dye. This dispersion of dye in hydrophilic colloid may be used to sensitize photosensitive materials. If desired, the dispersion can be set and stored until it is desired to use the dispersion to sensitize a photographic material.

EXAMPLE 5

Dye A (a thiocyanine dye of the type described in Brooker et al. U.S. Patent 2,231,658) and dye B (an oxacarbocyanine dye of the type described in U.S. Patent

2,295,276) were dissolved in methanol and in the high boiling solvent phenoxy ethanol as shown below:

	Prior art	Dispersion method
Dye A (grams).....	1.5	1.5
Dye B (grams).....	0.9	0.9
Methanol for dye A (ml.).....	887.0
Methanol for dye B (ml.).....	1,065.0
Phenoxy ethanol for dye A (ml.).....	75.0
Phenoxy ethanol for dye B (ml.).....	45.0
Total solvent (ml.).....	1,952.0	120.0

It should be noted that dye A is normally dissolved in methanol at 0.05 g. per fl. oz. of methanol, and dye B at 0.025 g. per fl. oz. of methanol. The phenoxyethanol was heated to 220° F. for dye A and 180° F. for dye B in the above samples. It will be seen that prior art methods resulted in the introduction of 1952 ml. of organic solvent into an emulsion, whereas to introduce the same concentration of dyes, only 120 ml. of organic solvent are introduced into the system. The high boiling solvent solution of dye is, while hot, mixed into an aqueous solution of gelatin containing a surfactant, and milled or homogenized. The resulting dispersion is allowed to set and may be stored, e.g., at about 40 to 50° F. The set gel is added directly to a warm silver halide emulsion, where it is dissolved causing the sensitizing dye to precipitate as a crystalline or amorphous solid dispersion of very fine, uniform particle size (average diameter is under 1 micron). The very fine dye dispersion obtained has a high surface area to mass ratio which promotes dye dissolving and transfer to the silver halide grains. Similar results are obtained when the phenoxyethanol is replaced with n-butanol, and with ethyl acetate.

The lower fog and higher sensitized speed of emulsions sensitized with the dispersion of Example 5 are shown in Examples 6 and 7.

EXAMPLE 6

Two multilayer color films are prepared as described in Example 1 of Van Campen U.S. Patent 2,956,879. The green sensitive emulsion is spectrally sensitized with an oxazole-thiohydantoin dye of the type described in Example 3 of Brooker U.S. Patent 2,282,116 using about 180 mg. per mole of silver halide. In one case the dye is added from a solution consisting of 25 mg. of dye per 30 ml. of acetone-methyl alcohol 1:1. In the second case the dye is in the form of a dispersion in gelatin containing 2 g. of dye per pound of dispersion prepared as described in Example 5 (the set dispersion of dye in gelatin is added to the warmed emulsion).

The coated films are exposed and developed for 25 minutes in a developer of the type described in Example 1 of U.S. Patent 2,956,879 and processed as described in this patent with the following results.

Green sensitized with:	Magenta fog
Dye solution22
Dye dispersion11

The following example illustrates the increase in sensitivity that can be obtained using sensitizing dye dispersions.

EXAMPLE 7

Two multilayer coatings containing dye-developers are prepared as described in Example 1 of Weyerts and Salminen U.S. Patent 3,146,102. The red sensitive emulsion is spectrally sensitized with a thiocarbocyanine dye of the type described in Example 9 of Sprague U.S. Patent 2,503,776 using about 140 mg. of the dye per mole of silver halide. In one case the dye is added from a solution consisting of 120 mg. of dye per 30 cc. of methyl alcohol. In the second case the dye is added in the form of a dispersion containing 2 g. of dye per pound of dispersion prepared as described in Example 5 (the set dis-

persion of dye in gelatin being added to the warm emulsion).

The coated films are exposed and processed as described in U.S. Patent 3,146,102 using an activator similar to activator IVQ described in this patent. The following results were obtained.

Relative speed of the red sensitive emulsion layer	
Red sensitized with:	
Dye solution	100
Dye dispersion	151

Results similar to those in Examples 6 and 7 are obtained when the solvent is n-butanol and instead of gelatin, the hydrophilic colloid is polyvinyl alcohol.

The preparation of sensitizing dye dispersions and sensitizing photosensitive materials is further illustrated in the following example. This example shows the technique of dissolving a spectral sensitizing dye in a volatile, water-miscible solvent, and adding this solution to a heated aqueous solution of hydrophilic colloid, which is then chilled and set. The solvent vaporizes from the colloid, leaving a fine dispersion of dye crystals in the colloid. This dispersion may then be used to spectrally sensitize photosensitive materials. No milling or homogenizing of the dispersion is necessary in this method to get very fine crystals of dye.

EXAMPLE 8

A cyanine dye (a 2,2'-cyanine) (1.6 grams) is refluxed in 4.2 fl. oz. of methanol, and when it is dissolved the hot solution is immediately poured into 18 fl. oz. of well agitated 5% aqueous gelatin solution at 95° F. The resulting dispersion is immediately cooled and set. This dispersion is then added to a gelatin silver halide emulsion to spectrally sensitize the silver halide, with results similar to those of the above examples.

This invention is applicable to spectral sensitizing dyes which are substantially insoluble in aqueous solutions. Spectral sensitizing dyes with which this invention are concerned generally have a solubility in water (at 20° C.) of less than about 1%. Among the useful spectral sensitizing dyes are the cyanine dyes, the hemicyanine or merocyanine dyes, styryl dyes and the like, such as:

3,3'-diethylthiocarbocyanine iodide;
1',3-diethyl-7-methylthia-2'-cyanine iodide;
2-p-dimethylaminostyrylbenzothiazole ethiodide;
[2-(3-ethylthiazoline)][4-(2-acetamino)-5(4)-thiazolone]dimethinemerocyanine;
Oxonal dyes such as 3-hydroxy-3'-oxy-2,2'-methenyldithionaphthene; phthaleins such as erythrosine;

and other dyes containing the amidinium-ion-auxochromophore system, such as rhodamine, pinacyanol and pinacolflav. Other useful dyes are described in Brooker U.S. Patents 1,846,301, issued Feb. 23, 1932; 1,846,302, issued Feb. 23, 1932; and 1,942,854, issued Jan. 9, 1934; White U.S. Patent 1,990,507, issued Feb. 12, 1935; Brooker and White U.S. Patents 2,112,140, issued Mar. 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued Jan. 10, 1950, and 2,739,964, issued Mar. 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued Jan. 10, 1950; Sprague U.S. Patents 2,503,776, issued Apr. 11, 1950, and 2,519,001, issued Aug. 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued Jan. 19, 1954; Heseltine U.S. Patent 2,734,900, issued Feb. 14, 1956; Van Lare U.S. Patent 2,739,149, issued Mar. 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

Photosensitive materials which can be spectrally sensitized include silver halide, such as silver bromide, silver chloride, silver iodide, and mixed silver halides such as silver chloroiodide and silver bromoiodide. Other photosensitive materials may be spectrally sensitized by this invention, such as TiO₂ or ZnO. The photosensitive material to be sensitized may be dispersed or suspended in a hydrophilic colloid binder solution, or the dispersions of this invention may be applied over binder-free deposits of

the photosensitive material, such as supports having vacuum deposited thereon a light sensitive silver halide layer.

Any suitable solvents may be used for dissolving the dyes, the cyanines generally being soluble in lower alcohols such as methanol and the merocyanines generally having good solubility in ketones such as acetone. The organic solvents which may be used may be water-miscible, water-immiscible or partially water-miscible. In one embodiment of the invention, the solvent used has a sufficiently high vapor pressure to volatilize from the hydrophilic colloid, thereby providing compositions which may be entirely free of organic solvent, or compositions which contain such a small quantity of organic solvent that coating problems are avoided.

Especially useful are the partially water-miscible solvents, such as organic solvents having a solubility between 1 and 8 percent at room temperature (20° C. or 68° F.) and a boiling point above 175° F. Typical preferred solvents of this type are:

Pentanol-2
n-Butanol
2-methyl propanol-1
Butyl carbitol acetate
Cyclohexanol
Cyclohexanone
Ethyl acetate
Methyl n-propyl ketone
Methyl isobutyl ketone
Methyl phenyl carbitol
2-ethyl-1,3-ketone diol
Diethyl acetal

It has been found that such solvents when employed in the process of preparing dispersions of sensitizing dye and hydrophilic colloid results in desirable small particle size. The high boiling point, such as over 175° F., is desirable to enable preparation of more concentrated solutions of sensitizing dye in the solvent, sensitizing dyes having greater solubility at elevated temperatures.

In order to obtain good spectral sensitized speed, it is desirable that the particle size of the dye crystals in the hydrophilic colloid have an average diameter of less than about 1 micron. Dispersions of dyes having large particle size do not effectively sensitize photographic materials.

The process of spectrally sensitizing hydrophilic photosensitive systems in accordance with this invention is particularly useful when the system is being coated at high speeds, such as over 150 feet per minute. The dispersions of sensitizing dye provided by this invention may be incorporated in warm solutions of the hydrophilic photosensitive system shortly before coating. The photosensitive system in which the dispersions are being incorporated may be concentrated; for example, gelatin silver halide emulsions in which more than $\frac{1}{20}$, such as $\frac{1}{3}$ or more, of the gelatin emulsion is silver halide, and the emulsion viscosity is at least 50 cps., such as 500 cps. or more. The small amount of organic solvent employed in the processes and dispersions in accordance with this invention allows high speed coating with such concentrated emulsions since only small quantities of organic solvent are present. Large quantities of organic solvents cause coating defects in various ways, such as by causing local dehydration of the hydrophilic colloid which results in particulate matter which cannot readily be redispersed. This particulate matter remains in the composition causing coating defects such as streaks or spots. The process of sensitizing as described herein is highly useful in wet-on-wet coatings, and high speed coatings such as the coating techniques described in British Patents 855,216; 925,179; U.S. Patents 2,620,285 and 2,681,294. The coating may be applied simultaneously with at least one other layer such as by using the procedures described in U.S. Patents 2,941,898 of N. R. Wynn or in 2,761,791 of T. A. Russell. The coating operation is conveniently carried out using an emulsion having a viscosity of 50-

150 centipoises and a coating speed of 150-500 feet per minute.

The dispersions of sensitizing dye and hydrophilic colloid provided herein are highly stable. However, prior art solutions of spectral sensitizing dye in organic solvent remain stable for a very short time. This feature of the novel dispersions of the dye is highly useful in commercial operations, since dispersions of the dye can be formed and stored for relatively long periods of time until required in the course of manufacturing sensitized materials.

A wide variety of hydrophilic, water-permeable organic colloids can be suitably utilized in preparing the dispersions of sensitizing dyes of this invention. Gelatin is preferably utilized although other colloidal material such as colloidal albumin, cellulose derivatives, synthetic resins or the like can be utilized. Suitable colloids that can be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe, U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19 to 26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued Aug. 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30 to 60% and a specific viscosity of 0.25 to 1.5, or an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued Feb. 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued Aug. 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued Oct. 23, 1956; or containing cyanoacetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued Oct. 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann and Gates U.S. Patent 2,852,382, issued Sept. 19, 1958.

A still further advantage of the processes and compositions of this invention is the reduction in hazard in employing smaller quantities of organic solvents and less flammable solvents, thereby reducing hazards of fire, explosion or toxicity.

It was surprising to find that the dispersions of sensitizing dye in hydrophilic colloid could be used to spectrally sensitize photosensitive materials dispersed in a hydrophilic colloid. It would not be expected that the sensitizing dye would diffuse through an aqueous solution of hydrophilic colloid in which the dye is relatively insoluble and become adsorbed to a photosensitive material such as silver halide crystals.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. The process of spectrally sensitizing photosensitive silver halide which comprises:

(a) forming a dispersion of a substantially water-insoluble spectral sensitizing dye in a hydrophilic colloid, said hydrophilic colloid being essentially free from silver halide; and,

(b) incorporating said dispersion in a light sensitive system comprising photosensitive silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.

2. The process of spectrally sensitizing photosensitive silver halide which comprises:

(a) dissolving a substantially water-insoluble spectral sensitizing dye in an organic solvent;

- (b) adding the solution of dissolved dye to a hydrophilic colloid in which the dye is substantially insoluble to provide a dispersion of the sensitizing dye in the colloid, said hydrophilic colloid being essentially free from silver halide; and,
- (c) incorporating said dispersion in a light sensitive system comprising photosensitive silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.
3. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a substantially water-immiscible organic solvent which has a sufficiently high vapor pressure to volatilize from a hydrophilic colloid;
- (b) adding the solution of dissolved dye to said hydrophilic colloid to provide a dispersion of the sensitizing dye in the colloid, said hydrophilic colloid being essentially free from silver halide;
- (c) drying said colloid to remove essentially all of the organic solvent; and,
- (d) incorporating said dispersion in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid to spectrally sensitize the silver halide photosensitive material.
4. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a heated, high-boiling, partially water-miscible organic solvent to provide a concentrated dye solution;
- (b) adding the concentrated dye solution to a hydrophilic colloid to provide an oil-in-water emulsion wherein the colloid contains small globules of solvent containing dye, said hydrophilic colloid being essentially free from silver halide; and,
- (c) incorporating said dispersion in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid to spectrally sensitize the silver halide photosensitive material.
5. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a volatile, water-miscible organic solvent;
- (b) adding the solution of dissolved dye to a heated, aqueous hydrophilic colloid solution;
- (c) chilling said heated solution obtained in (b) to form a fine dispersion of dye crystals in the colloid, and to vaporize the solvent out of the colloid, said hydrophilic colloid being essentially free from silver halide; and,
- (d) incorporating said dispersion formed in (c) in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.
6. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) forming a dispersion of a substantially water-insoluble spectral sensitizing dye in a hydrophilic colloid selected from the group consisting of gelatin; polyvinyl alcohol; cellulose acetate hydrolyzed to an acetyl content of from 19 to 26%; water-soluble ethanalamine cellulose acetate; polyacrylamide having a combined acrylamide content of 30 to 60% and a viscosity of 0.25 to 1.5; an imidized polyacrylamide having a combined acrylamide content of 30 to 60% and a viscosity of 0.25 to 1.5; zein; and, the polymeric material which results from polymerizing a protein with a monomer having a vinyl group, said hydrophilic colloid being essentially free from silver halide; and,
- (b) incorporating said dispersion in a light sensitive system comprising photosensitive silver halide dis-

- persed in a hydrophilic colloid, to spectrally sensitize the silver halide.
7. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in an organic solvent;
- (b) adding the solution of dissolved dye to gelatin to provide a dispersion of the sensitizing dye in the gelatin, said gelatin being essentially free from silver halide; and,
- (c) incorporating said dispersion in a light sensitive system comprising photosensitive silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.
8. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) forming a dispersion of a substantially water-insoluble spectral sensitizing dye in gelatin, said gelatin being substantially free from silver halide; and,
- (b) incorporating said dispersion in a light sensitive system comprising photosensitive silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.
9. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a substantially water-immiscible organic solvent which has a sufficiently high vapor pressure to volatilize from a hydrophilic colloid;
- (b) adding the solution of dissolved dye to gelatin to provide a dispersion of the sensitizing dye in the gelatin, said gelatin being essentially free from silver halide;
- (c) drying said gelatin to remove essentially all of the organic solvent; and,
- (d) incorporating said dispersion in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid to spectrally sensitize the silver halide photosensitive material.
10. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a heated, high-boiling, partially water-miscible organic solvent to provide a concentrated dye solution;
- (b) adding the concentrated dye solution to gelatin to provide an oil-in-water emulsion wherein the gelatin contains small globules of solvent containing dye, said gelatin being essentially free from silver halide; and,
- (c) incorporating said dispersion in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid to spectrally sensitize the silver halide photosensitive material.
11. The process of spectrally sensitizing photosensitive silver halide which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in a volatile, water-miscible organic solvent;
- (b) adding the solution of dissolved dye to a heated, aqueous gelatin solution;
- (c) chilling said heated solution obtained in (b) to form a fine dispersion of dye crystals in the gelatin, and to vaporize the solvent out of the gelatin, said gelatin being essentially free from silver halide; and,
- (d) incorporating said dispersion formed in (c) in a light sensitive system comprising silver halide dispersed in a hydrophilic colloid, to spectrally sensitize the silver halide.
12. The process of spectrally sensitizing a photographic gelatin silver halide emulsion which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in an organic solvent;
- (b) adding the solution of dissolved dye to gelatin, which is essentially free from silver halide, to pro-

- vide a dispersion of the sensitizing dye in the gelatin; and,
- (c) incorporating said dispersion in the gelatin photographic emulsion to spectrally sensitize the silver halide.
13. The process of spectrally sensitizing a photographic gelatin silver halide emulsion which comprises:
- (a) dissolving a substantially water-insoluble spectral sensitizing dye in an organic solvent, said solvent having a boiling point higher than 175° F. and a solubility in water of from 1-8% at about 68° F.;
- (b) adding a concentrated, heated solution of dissolved dye to a gelatin which is essentially free from silver halide, to provide a dispersion of the sensitizing dye in gelatin; and,
- (c) incorporating said dispersion in the gelatin photographic emulsion to spectrally sensitize the silver halide.
14. The process of spectrally sensitizing a photographic gelatin silver halide emulsion which comprises:
- (a) dissolving a substantially water insoluble spectral sensitizing thiocyanine dye in phenoxyethanol at 220° F.;
- (b) mixing the solution of dye in solvent and an aqueous gelatin solution essentially free from silver halide and containing a surfactant;
- (c) milling the composition obtained in (b) to obtain an average particle size of dye in gelatin of less than about 1 micron in diameter;
- (d) cooling and setting the dispersion of dye in gelatin; and,
- (e) adding the dispersion of dye in gelatin to a warm, fluid photographic gelatin silver halide emulsion to spectrally sensitize the silver halide.
15. The process of spectrally sensitizing photographic gelatin silver halide emulsion which comprises:
- (a) providing a concentrated solution heated to over

- 175° F. of a substantially water insoluble spectral sensitizing dye selected from the class consisting of cyanine, merocyanine, styryl and oxanol spectral sensitizing dyes in an organic solvent having a boiling point higher than 175° F. and a solubility in water of from 1 to 8% at about 68° F.;
- (b) adding said heated solution of dye and solvent to an aqueous gelatin solution which is essentially free from silver halide;
- (c) milling the composition obtained in (b) to obtain an average particle size of dye crystals in gelatin of less than about one micron in diameter;
- (d) cooling and setting said dispersion of dye in gelatin; and,
- (e) adding said dispersion obtained in (d) to a warm, fluid photographic gelatin silver halide emulsion to spectrally sensitize the silver halide.

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