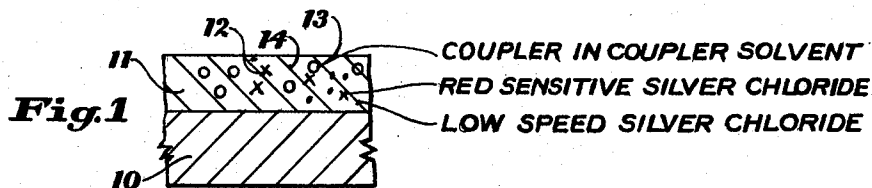
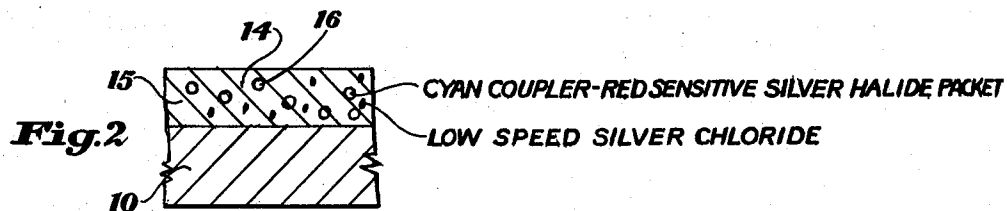
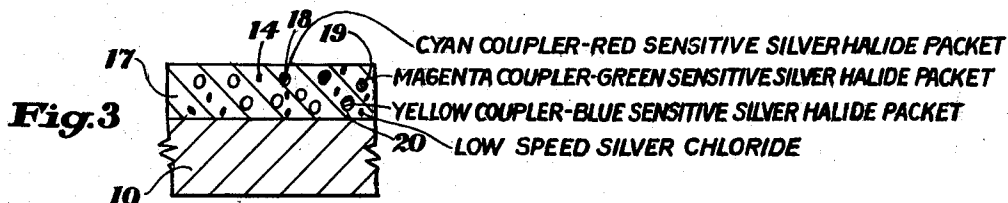
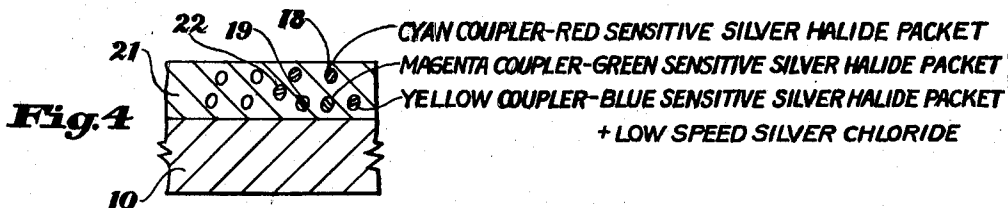


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METHOD FOR CONTROLLING SPEED AND CONTRAST
OF PHOTOGRAPHIC EMULSIONS
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3,152,907

METHOD FOR CONTROLLING SPEED AND CONTRAST OF PHOTOGRAPHIC EMULSIONS

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This invention relates to photography and particularly to a method for controlling the speed and contrast of silver halide emulsions.

When photographic emulsions sensitive to different spectral regions are coated on the same support for color photography either in superposed layers or mixed in the same layer, it is desirable to control the speed and contrast characteristics of the emulsions. For example, in the processes of Mannes and Godowsky, U.S. Patent 2,304,940, and Godowsky, U.S. Patent 2,698,794, the emulsions should have the same contrast and characteristic curve shape.

We have found that the speed, contrast and other characteristics of an optically sensitized silver chloride or silver bromide image-forming emulsion may be improved by mixing in the same layer as the optically sensitized emulsion, a silver chloride emulsion of sufficiently low speed that no visible image is produced therein by exposure and development of the optically sensitized emulsion. The admixed silver chloride emulsion should be present in an amount from 0.1 to 4 times, and preferably from $\frac{1}{2}$ to 2 times the amount of silver per mole of silver in the optically sensitized emulsion. The optically sensitized emulsion should be a surface image emulsion as defined in U.S. Patent 2,456,956 (Type II emulsion). Most silver halide emulsions are of this type.

The low-speed silver chloride emulsion may be mixed directly with the optically sensitized emulsion and coated with it in the same layer, and this type of coating is especially useful in color emulsions where a color-forming compound or coupler is to be incorporated in the emulsion in dispersion in a solvent for the coupler as described in Jelley and Vittum U.S. Patent 2,322,027, as a resin-coupler compound, directly in the emulsion in the case of a coupler containing a solubilizing group or in dispersion in the form of a low ratio coupler-to-coupler solvent dispersion as described in Fierke and Chechak U.S. Patent 2,801,171. The silver chloride emulsion should be of sufficiently low speed that no visible image is produced therein by exposure and development of the optically sensitized emulsion and should have a blue light sensitivity less than $\frac{1}{100}$ of the blue light sensitivity of the optically sensitized emulsion.

It is known that non-color sensitized emulsions can be added to color sensitized emulsions for the purpose of controlling image contrast by varying the color of the exposing light, or for other reasons. In the present case, the sensitive layer contains dispersed particles of color-forming compound and the image density increase of the resulting dye image comes solely from the greater amount of developed silver of the optically sensitized emulsion, no density being directly contributed by the low speed silver chloride emulsion.

In the accompanying drawing, FIGS. 1 to 4 are enlarged sectional views of film made according to our invention.

The degree of sensitivity of the low speed silver chloride emulsion is not important as long as it is not exposed sufficiently to form a visible image upon exposure and development of the optically sensitized emulsion. In general, the ratio of the speed of the optically sen-

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sitized emulsion to the speed of the low speed silver chloride emulsion should be at least 100:1 when measured in the optically-sensitized region.

Experiments with low speed emulsions other than predominately silver chloride indicate that other halides such as silver chlorobromide in which the ratio of chloride to bromide is 2:98 or 10:90, showed too little effect on speed and contrast to be useful. There has been no evidence in our work of sensitizer diffusion from the sensitized silver halide grains to the unsensitized silver chloride.

Our invention is useful with color emulsions, for example, of the type described in Jelley and Vittum U.S. Patent 2,322,027 and Godowsky U.S. Patent 2,698,794. These emulsions contain color-forming compounds dissolved in dispersed particles of water-permeable, water-insoluble material in the emulsion, and when the low speed silver chloride emulsion is used with such emulsions it can be either in the matrix surrounding the color-forming particle or in the particle containing the coupler and can be used either in single layer, multi-layer or in mixed packet single layer or multi-layer coatings.

In the incorporated coupler emulsions the speed and contrast increase is shown by the dye image after the silver has been bleached and fixed out. Inasmuch as the amount of dye density depends upon the amount of oxidized developer which is formed, we believe that the developability of the color sensitized emulsion has been increased by the presence of the low speed silver chloride emulsion. It is apparent that none of the low speed silver chloride is developed since there is no evidence of increased color contamination when differently color-sensitized packets are mixed in a single layer surrounded by the low speed silver chloride emulsion in the matrix. If the silver chloride in the matrix were developed to form oxidized developer outside the packets, then cyan and magenta colored dyes would be observed in the yellow image, for example, but this is not the case. The increase in dye density must therefore come from within the packets and from the sensitized silver halide only.

The added low speed silver chloride causes about the same dye increase, particularly of the cyan image, whether it is incorporated as free particles in the matrix, completely inside the packets, or in packets external to the sensitized packets. In one instance, yellow packets were prepared with unsensitized silver chloride included as part of the packets. These packets were then coated with cyan and magenta (red-sensitive and green-sensitive) packets in a single layer with no low speed silver chloride in the matrix. The cyan dye image showed a higher contrast in the developed image from this coating than in a similar coating made with yellow packets without the added low speed silver chloride. This indicates that the increase in developability is not dependent upon intimate contact of the sensitized and unsensitized low speed emulsions.

Several advantages are gained by the addition of low speed silver chloride to the emulsion-coupler combination. In the case of multi-layer coatings, this is a simple way to balance the differently sensitized emulsions. By the addition of the correct amount of unsensitized low speed silver chloride to each layer a controlled increase of contrast or speed can be made in the sensitized emulsions. In the case of mixed packets the primary increase occurs with the red-sensitive emulsion so that the control is less general than with multilayer coatings. However, in the case of mixed packets there is the advantage that the added low speed silver chloride serves as non-developable inert particle which tend to keep the packets separated from each other as they are laid down in drying. This can result in increased color separation by minimizing the area of contact of the differently sensitized pack-

ets. This together with the increased density which results may be construed as an increase in color separation of the coating.

The following examples illustrate the techniques which we employ.

Example 1

A pure silver chloride emulsion was made as follows:

Solutions were made of (a) 25 grams of gelatin in one liter of water at 40° C., (b) 100 grams of silver nitrate in 500 cc. of water at 20° C., and (c) 35 grams of sodium chloride in 500 cc. of water. Solutions (b) and (c) were run simultaneously into solution (a) at a uniform rate while stirring the latter over a period of about 10 minutes. Solution (b) is preferably not allowed to run in faster than (c). Thereafter, 150 grams of gelatin in 1500 cc. of water at 40° C. were added and the pH was adjusted to 5.0. The emulsion was sensitized to red light with an optical sensitizer and was then chilled and set. The final molar weight was 2020 grams and had a total gelatin content of 80 grams.

A dispersion of cyan coupler was prepared by dissolving 28 grams of 6- α -{4-[α -(2,4-di-tert. amylphenoxy) butyramido]-phenoxy}-acetamido-2,4-dichloro-3-methyl phenol in 28 grams of di-n-butyl phthalate at 120° C. and dispersing this in a solution of 130 grams of melted 10% phthalic anhydride gelatin solution and 30 cc. of 5% Alkanol B solution by repeated passages through a colloid mill. 7.1 grams of this coupler dispersion were mixed with 5.4 grams of the red sensitized silver chloride emulsion and stirred for 10 minutes at 40° C. 2.5 grams of this mixture were mixed with 1.58 grams of the unsensitized silver chloride emulsion, 15.5 grams of 20% gelatin solution, 18.5 cc. of water and 1 cc. of saponin and hardening agents. This melt was coated on one square foot of glass surface.

This coating is illustrated by FIGURE 1 of the drawing in which 10 is the support of glass, but which may also be cellulose ester, paper or similar suitable material coated with the emulsion layer 11 containing the red-sensitive silver chloride particles 12, dispersed coupler particles 13 and low speed unsensitized silver chloride particles 14.

Similar coating was also made of the red sensitized emulsion without the added unsensitized emulsion, both coatings were then exposed through a color test chart and developed for 12 minutes in the following developing solution:

2-amino-5-diethylaminotoluene HCl	-----grams--	2
Benzyl alcohol	-----cc--	10
Sodium sulfite	-----grams--	2
Ethylenediamine tetraacetic acid		
sodium salt	-----do--	2
Potassium bromide	-----do--	2
Sodium carbonate, monohydrate	-----do--	20
Sodium citrazinate	-----do--	11.5
Water to 1 liter.		

After bleaching and fixing to remove the silver and silver halide, the resulting dyes showed the following results for speed, gamma and fog, indicating that a speed increase was obtained with the coating containing the added silver chloride.

	Speed	Gamma	Fog
Check	-----	1.8	.02
AgCl added	+ .4 Log E	1.6	.06

Example 2

100 grams of 2-(α -di-tert. amylphenoxy-n-butyrylamino)-4,6-dichloro-5-methylphenol was dissolved in 350 cc. of ethyl acetate. This solution was poured into 1000

cc. of 10% phthalic anhydride gelatin solution containing 60 cc. of a 5% solution of Alkanol B. This mixture was passed through a colloid mill to form a finely-divided dispersion, chilled immediately, noodled and dried in air at room temperature. The auxiliary coupler solvent (ethyl acetate) dissolves the coupler readily at low temperature thus minimizing coupler decomposition and is itself quickly removed by evaporation from the set colloidal dispersion of the coupler.

5.2 grams of the coupler dispersion were soaked in 16 cc. of water, melted at 40° C., and mixed with 16 grams of 20% phthalic anhydride gelatin and 6 grams of bone gelatin at 40° C. and the mixture buffered with 7.5 cc. of a 10% sodium citrate solution. The red sensitized silver chloride emulsion of Example 1, 20 grams of the emulsion being used, was added and mixed with the coupler dispersion with stirring during 5 minutes. Packets were formed by adding 2.8 cc. of a 5% aqueous solution of the sodium salt of styrene-maleic anhydride resin and stirring for 15 minutes. The packets were then stabilized with 5 cc. of a 10% calcium acetate solution.

A quantity of these packets containing the equivalent of 0.0005 mole of silver was treated with a gelatin dispersion of di-n-butyl phthalate in such amount that equal quantites of cyan coupler and di-n-butyl phthalate resulted to make the coupler active to developer, as described in Godowsky and Duane U.S. Patent 2,787,544, then diluted with additional gelatin and water to raise the gelatin content to 8% for coating and setting. To one-half of this dispersion there was added the unsensitized silver chloride emulsion of Example 1 in an amount equal to 0.0005 mole of silver chloride. These two dispersions were coated equally on glass plates. The coating containing the low speed silver chloride is illustrated in FIGURE 2 of the drawings. As shown therein, the support 10 is coated with emulsion layer 15 containing the low speed silver chloride emulsion particles 14 and packet 16 of red-sensitive gelatino-silver halide emulsion containing the cyan coupler.

These coatings were exposed and processed as described in Example 1 and the coating containing the added silver chloride showed a speed and contrast increase as indicated by the following table:

	Speed	Gamma	Fog
Check	-----	1.46	.10
AgCl added	+ .16 log E	2.50	.10

Example 3

This example illustrates the use of our invention with a three-color mixed packet coating, the low speed silver chloride being in the matrix.

Cyan packets were made as described in Example 2 but using the coupler of Example 1 instead of that of Example 2. Magenta packets were made in the same way using a portion of the silver chloride emulsion which had been green sensitized and using 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxy acetamido)-benzamido]-5-pyrazolone as the coupler. Yellow packets were also made in the same way using a gelatino-silver chlorobromide emulsion containing 98 mol percent bromide instead of the silver chloride emulsion and using α -[3-[α -(2,4-di-tert. amylphenoxy)-acetamido]-benzoyl]-2-methoxyacetanilide as the coupler.

These three sets of packets were mixed in a silver molar ratio of 2:3:4 for the cyan, magenta and yellow respectively, then treated with a gelatin dispersion of di-n-butyl phthalate as in Example 2, in amount equal to the total weight of the couplers in the mixture. The final dispersion was divided into two portions and the unsensitized silver chloride emulsion of Example 1 was added to one portion in an amount equal to one molar equivalent. The coating addenda of Example 1 were added to each mixture and they were coated equally on supports.

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The mixture containing the added low-speed silver chloride is shown in FIGURE 3 of the drawing. As shown therein, the support 10 is coated with the emulsion layer 17 containing the unsensitized silver chloride particles 14, red-sensitive silver halide packets 18 containing cyan coupler, green-sensitive silver halide packets 19 containing magenta coupler and blue-sensitive silver halide packets 20 containing yellow coupler.

After exposure and processing as described in Example 1, the cyan dye image showed the following speed and contrast increase as compared with the coating not containing the low-speed silver chloride emulsion:

	Speed	Gamma	Fog
Check (cyan).....		.57	.05
AgCl added.....	+ .21 log E.....	1.83	.05

Example 4

This example illustrates our invention with a three-color mixed packet coating, the low-speed silver chloride being in the yellow dye forming packet.

Eight grams of the yellow coupler used in Example 3 were dissolved in a solution of 25 cc. of ethyl acetate at the reflux temperature of ethyl acetate. This solution was poured into a solution of 80 cc. of 10% phthalic anhydride gelatin solution and 8 cc. of 5% Alkanol B solution at 50° C., stirred for about one minute and run through a colloid mill five times after which the mill was rinsed with 25 cc. of water. The dispersion was set up on a chill plate at 40° F., noodled and air dried at 70° F. and 50% relative humidity. 1.45 grams of this dried dispersion containing 0.7 gram of coupler and 0.7 gram of phthalic anhydride gelatin was soaked in 7 cc. of cold water, then melted at 40° C. after the water had been completely taken up.

While stirring at 40° C. there were added in succession 2.5 cc. of a 1% solution of the antistain agent 5-octadecyl-2-(2-sulfo-tert-butyl)-hydroquinone (sodium salt), 12.5 cc. of a 20% solution of phthalic anhydride gelatin, 5 grams of the blue-sensitive silver chlorobromide emulsion used in Example 3 containing 0.0005 mole of silver and 10.1 grams of the unsensitized silver chloride emulsion described in Example 1, containing 0.005 mol of silver.

The temperature of the mixture was lowered to 32° C. while continuing to stir, and 1.6 cc. of a 5% aqueous solution of the ammonium salt of styrene-maleic anhydride resin was added. Stirring was continued for 5 minutes, the bath temperature was raised rapidly to 40° C. and stirring continued for 15 minutes more during which time the packets formed and hardened. The packets were then stabilized with 2 cc. of 10% aqueous calcium acetate monohydrate solution, and the final weight adjusted to 50 grams by the addition of water.

These packets were coated together in a single layer with magenta and cyan packets made as described in Example 3, and the coating thus made is shown in FIGURE 4 of the drawing. Layer 21 coated on support 10 has packets 18 of red-sensitive silver halide containing cyan coupler, packets 19 of green-sensitive silver halide containing magenta coupler, and packets 22 of blue-sensitive silver bromiodide and low-speed silver chloride containing yellow coupler.

This layer was exposed and processed as described in Example 1 together with similar coatings in which the molar ratio of silver chloride in the yellow packets was one-half the amount and twice the amount described in the example, and the results were recorded in the following table showing that in each case the silver chloride

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added to the yellow packets produced an increase in speed and contrast of the cyan image:

	Speed	Gamma	Fog
Check (cyan).....		.46	.03
1/2 mol AgCl.....	+ .28 log E.....	1.16	.03
1 mol AgCl.....	+ .35 log E.....	1.76	.04
2 moles AgCl.....	+ .41 log E.....	1.72	.04

Example 5

This example illustrates a coating in which the silver chloride emulsion is added to an emulsion containing a color former dispersed in the manner of Jelley and Vitum, U.S. Patent 2,322,027.

To a gelatino-silver bromiodide emulsion that had been digested to optimum sensitivity with a mixture of soluble gold salts and a sulfur compound, there was added an optical sensitizing dye which extended the light-sensitivity of the emulsion to 600-700 millimicrons. The treated emulsion was divided into two equal parts. To one part there was added 40 mol percent of a fine grain silver chlorobromide emulsion containing 80 mole percent chloride and 20 mole percent bromide. To both parts of the emulsion there was added the cyan coupler dispersion of Example 1.

These two emulsions were then separately coated on a suitable film support and dried. The dried films were exposed for 1/50 second to light of 3000° K. quality with an interposed density step tablet and a Wratten #29 filter. The two films were processed in a regular reversal process with the following results:

Coating	D _{max}	Relative Speed
Without AgClBr emulsion.....	2.84	100
With AgClBr.....	2.87	141

We have described developing our coatings in a developing solution containing benzyl alcohol. It is also possible to eliminate the benzyl alcohol from the developer and to treat the coatings just prior to development in a solution of a coupler solvent, for example, in a solution of di-n-butyl phthalate or diethyl lauramide in isopropyl alcohol and water, about a 1% solution of the coupler solvent being used.

In the specification and claims, where we refer to an unsensitized, low speed "chloride" emulsion, it will be understood that a small amount, up to about 20%, of bromide ion may be present.

The examples and modifications included herein are illustrative only, it being understood that our invention is to be taken as limited only by the scope of the appended claims.

What we claim is:

1. A light-sensitive photographic element including a support and a color-forming silver halide emulsion having increased speed and being capable of producing a dye image of increased contrast upon exposure and color development, comprising a photographic layer containing dispersed, discrete packets containing a silver halide selected from the class consisting of silver chloride and silver bromiodide and a color-forming compound capable of coupling with the oxidation products of an aromatic primary amine photographic color-developing agent to produce a colored image, the silver halide in said packets being sensitized to a wavelength longer than blue, said layer containing a spectrally unsensitized, unfogged silver chloride emulsion containing at least 80 mole percent of silver chloride and being of sufficiently low speed so that no visible image is produced therein upon exposure and color development of said spectrally sensitized silver halide emulsion, said unsensitized silver chloride emulsion being present in an amount of from 0.1 to 4

times the amount of silver per mole of silver in said spectrally sensitized silver halide emulsion and having a blue-light speed less than $\frac{1}{100}$ that of said spectrally sensitized silver halide emulsion.

2. A light-sensitive photographic element including a color-forming gelatino-silver-halide emulsion having increased speed and being capable of producing a dye image of increased contrast upon exposure and color development, comprising a gelatin layer containing dispersed packets of gelatin reacted with a water-soluble salt of an interpolymer of styrene and an α,β -unsaturated carboxylic acid, said packets containing a red-sensitive silver chloride emulsion producing a visible image upon exposure to red light and development in an aromatic primary amine color-developing agent, and a color-forming compound capable of coupling with the oxidation products of said aromatic primary amine color-developing agent to produce a cyan image, and said gelatin layer containing an unsensitized, unfogged silver chloride emulsion containing at least 80 mole percent silver chloride and being of sufficiently low speed in the red spectral region so that no visible image is produced therein by said exposure and said color-development, said unsensitized silver chloride emulsion being present in an amount of from 0.5 to 2 times the amount of silver per mole of silver in said red-sensitive silver chloride emulsion and having a blue-light speed less than $\frac{1}{100}$ that of said red-sensitive silver chloride emulsion.

3. A light-sensitive mixed packet photographic emulsion having dispersed therein three sets of discrete packets of gelatin reacted with a water-soluble salt of an interpolymer of styrene and an α,β -unsaturated carboxylic acid and containing, respectively, color-forming compounds capable of coupling with the oxidation products of an aromatic primary amine color-developing agent to

produce cyan, magenta and yellow images, said cyan color-forming packets containing an optically sensitized red-sensitive silver chloride emulsion, said magenta color-forming packets containing an optically sensitized green-sensitive silver chloride emulsion and said yellow color-forming packets containing a blue-sensitive silver chlorobromide emulsion, containing approximately 98 mole percent bromide and an approximately equimolar amount of an unsensitized, unfogged silver chloride emulsion containing at least 80 mole percent of silver chloride and having a blue-light speed less than $\frac{1}{100}$ that of said blue-sensitive silver chlorobromide emulsion.

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