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3,384,485

SILVER HALIDE EMULSIONS PHOTOSOLUBILIZED WITH OPTICAL SENSITIZING DYES AND SILVER MERCAPTIDES

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This invention relates to photography and more particularly to new image-yielding photographic silver halide emulsion layers and to photographic elements embodying such layers and to image-forming processes using the elements.

The principal processes of photography are based on the use of colloid-silver halide emulsion layers. In the prior art processes a latent image is formed by image-wise exposure of a radiation-sensitive silver halide emulsion layer. Silver halide bearing a latent image has been developed to silver by selective reduction in these instances. In the prior processes of photography the unreduced silver remaining after development has been removed by silver halide solvents or rendered insensitive or transparent by treatment with complexing agents. Optional after-treatments include intensification, reduction, toning and tinting. However, the primary or first step in image formation always has been based on the selective reduction step.

An entirely different type of photographic process has been described in assignee's copending application of Blake, U.S. Ser. No. 236,420, filed Nov. 8, 1962 (U.S.P. 3,155,507, Nov. 3, 1964). The novel process of said application, which can be defined as "photo-solubilization," requires the use of a specially prepared silver halide emulsion layer containing an amount of an organic compound which modifies the silver halide solubility so that, under normal fixing conditions, said organic compound causes the silver halide grains to dissolve more slowly. Such an element is given an imagewise exposure and the exposed areas are then treated with a conventional fixing solution to form a positive, silver halide image (the silver halide remaining undissolved in the unexposed areas). As an optional additional processing step, the silver halide image may be intensified, e.g., by reduction, so as to convert it into a black, metallic silver image.

It is an object of this invention to provide new photographic silver halide compositions, photographic layers, and photographic elements bearing a layer of silver halide. Another object is to provide processes for making these products. A further object is to provide such products which are adapted to more versatile processes for forming silver and other images and which are simple, dependable and give results equal in quality to the prior conventional methods. A more particular object is to provide improved products for "photosolubilization" processing which have higher speeds, extended spectral sensitivity and improved insolubilization characteristics. Still further objects will be apparent from the following description of the invention.

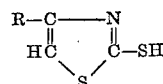
The above objects are realized by a photographic emulsion layer of this invention comprising, before exposure to actinic radiation, light-sensitive silver halide crystals having associated therewith,

(a) from 0.015 to 0.075 g. per mole of silver halide of a photographic optical sensitizing dye selected from the class consisting of cyanine, carbocyanine, and merocyanine dyes, and

(b) a silver mercaptide of an organic mercapto compound, said mercaptide being present in about 90% of the amount, in terms of the ratio of its weight to the sur-

face area of said silver halide crystals, that when admixed in such ratio with an aqueous silver chlorobromide (70/30 mole percent) gelatin dispersion containing 57 g. of gelatin per mole of Ag and .57 mg. of Ag per ml., and said silver chlorobromide dispersion is treated with 10%, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver and 100 mg. of sodium thiosulfate), at least three times the amount of silver chlorobromide remains undissolved as in a similar dispersion successively treated with 5%, by weight, aqueous sodium hypochlorite and 10%, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate), after vigorous agitation of the dispersions for 30 seconds at 25° C. In the preferred elements of the invention, any heavy metal salts present in the silver halide layer in more than trace or sensitizing amounts are noble metal salts.

In a particularly preferred embodiment, said organic mercaptan compound has the formula:



where R is a hydrocarbon nucleus of 4-12 carbon atoms. The silver mercaptides of the organic mercapto compound (including the mercapto compounds of the above, preferred structure), are of lower solubility in water than silver chloride. Also, the silver halide crystals associated with the silver mercaptide dissolve more slowly in 10% aqueous sodium thiosulfate than untreated silver halide crystals at a predetermined pH. Photosolubilizable elements containing silver mercaptides of the preferred mercapto compound of the above formula are disclosed and claimed in assignee's copending application of Blake, U.S. Ser. No. 317,824, filed Oct. 21, 1963, now U.S. Patent No. 3,155,519.

According to an important preferred aspect of the invention, R of the above formula is an unsubstituted hydrocarbon radical of 6-10 carbon atoms and has a cyclic hydrocarbon radical of 6 carbon atoms attached through a cyclic carbon of said radical to the 4-carbon atom of the thiazole ring. Suitable radicals of the latter type include cyclohexyl, methylcyclohexyl, phenyl, tolyl and alphanaphthyl.

The modified silver halide emulsions of this invention utilize a synergistic effect that has been found to occur when the silver mercaptide and a photographic optical sensitizing dye are co-adsorbed to the surface of the photographic silver halide crystal.

Preferably, the silver halide crystals are dispersed in a water-permeable organic colloid to form a light-sensitive photographic emulsion. The selected mercapto compound can be added to the silver halide emulsion while the latter is in the liquid state or the emulsion may be coated on a suitable support and the resulting element bathed or impregnated with a solution, e.g., an alcoholic solution of the organic compound. The desired amount of the mercaptan compound in the silver halide emulsion may vary with a number of factors such as the size of the silver halide crystal (and thus the surface of the crystal per mole of silver halide). Generally the organic mercaptan compound is used in a range of from 0.3 to 0.4 gram per mole of silver halide and preferably from 0.8 to 0.9 gram per mole of silver halide.

There are several factors which control the desired amount of sensitizing dye as well as the desired amount of organic mercaptan compound to be used in the photographic emulsion. Since both of these compounds are adsorbed to the silver halide crystal, the desired concentration of one compound is influenced by the concentra-

tion of the other, i.e., as the concentration of sensitizing dyes is increased, the concentration of the organic mercaptan compound may be decreased and vice versa. In general, the optimum concentration of organic mercaptan is reduced by about 5 to 10% when an optimum amount of sensitizing dye is adsorbed to the silver halide crystal. Other factors which influence the dye concentrations are the particular organic mercaptan compound, the particular optical sensitizing dye, and the size and nature of the silver halide crystals.

The gelatin-silver halide ratio is quite flexible and may vary from 3:1 to 1:20 depending on the particular organic compound and application.

The novel process of this invention which utilizes the foregoing emulsions comprises the following steps:

(1) exposing imagewise to actinic radiation a photosensitive layer comprising silver halide crystals treated with the organic compound and the optical sensitizing dye as described above,

(2) treating the exposed layer in a solution of a silver halide solvent to remove soluble silver halide in the exposed image areas, thus forming a positive silver halide image in the unexposed areas, and optionally,

(3) washing the resulting layer.

If desired, the silver halide image may be viewed directly, e.g., by projection (if on a transparent support) or it may be intensified by

(4) converting the residual silver halide to silver by treatment in a fogging developer, e.g., a high pH, 1-phenyl-4-methyl-3-pyrazolidone/hydroquinone developer containing iodide ion or by fogging the emulsion by exposure to light and then treating with a silver halide reducing agent, e.g., a conventional silver halide developer, and

(5) washing the developed layer to reveal a positive silver image in the original non-exposed areas.

The imagewise solution of the exposed silver halide/organic compound layer may be effected by the silver halide solvents commonly used as photographic fixing agents, e.g., sodium thiosulfate, sodium thiocyanate, concentrated solutions of potassium bromide, etc. In assignee's copending application, H. D. Hunt, Ser. No. 388,919 filed Aug. 11, 1964, it is disclosed that more efficient removal of the exposed silver halide crystals may be obtained when the fixing solution contains an inorganic cation selected from the class consisting of potassium, cesium, rubidium, thallium (I), strontium and lead (II). Reduction of the treated, residual silver halide may be accomplished by the use of any chemical reducing agent capable of reducing silver ion to silver metal, e.g., hydroquinone, metol, sodium hydrosulfite and stannous chloride. The function of the reducing agent may be enhanced by modifying the surface properties of the treated, residual silver halide crystals by means of alcohol, thiourea, potassium iodide, etc. The silver halide image may be toned, e.g., with sodium sulfide, sodium selenide, etc. In addition, color images may be obtained by developing the treated, residual silver halide with a primary aromatic amine color developing agent in the presence of a color coupling compound either in the developing bath or previously incorporated in the emulsion. The silver halide emulsion layers and process of this invention are not limited to utilization of a narrow class of organic mercaptan compounds with which the silver halide crystals are intimately associated or were treated in preparing the emulsion layers used in accordance with this invention. Instead, a large number of useful compounds can be used and their utility can be readily determined by a relatively simple test. Essentially, the test consists of two steps, Test A and Test B. In Test A, the candidate organic mercaptan compound must render a dispersion of silver halide crystals insoluble in a silver halide solvent, e.g., an aqueous solution of sodium thiosulfate, at some pH between 1 and 13. If the candidate compound meets the insolubility requirements of Test A, it must also meet

the requirements of Test B by forming with said dispersion of silver halide crystals a reaction product which, upon treatment with an aqueous solution of sodium hypochlorite, becomes soluble when subsequently treated with aqueous sodium thiosulfate. The following practical tests are provided in further exemplification of the invention and include specific concentrations of solutions, times, etc., so that suitable organic compounds may be readily and positively identified.

Test A

A solution nearly saturated at 25° C. with a candidate organic compound is prepared using ethanol, acetone, dimethyl formamide, water or other suitable solvent. Depending on the solubility, a solution concentration from 0.01 to 10 percent by weight is obtained. Twenty-five ml. of a gelatin silver chlorobromide dispersion containing 25 mg. of silver halide (calculated as silver bromide), prepared as described below, is treated with small increments (i.e., about 0.1 to 0.2 ml. at a time) of the said candidate solution under safelight conditions (Wratten 1A filter or equivalent) until the silver halide dispersion either is rendered insoluble in 10% aqueous sodium thiosulfate or the candidate is found not to cause insolubilization. Generally insolubilization will occur upon the addition of 0.05 g. or less of said candidate compound, calculated as the pure compound. Compounds which must be used in substantially greater quantities than this, e.g., 1-2 g. to effect insolubilization are considered less preferred compounds. The silver halide dispersion insolubility is determined by taking a 0.5 ml. portion of the silver halide dispersion (after each incremental addition of the candidate organic compound), adding about 0.1 to 0.2 ml. of 10% aqueous sodium thiosulfate solution and observing the turbidity after 30 seconds.

As a control, one should use 25 ml. of water to which small increments of the candidate solution are added. Half-milliliter portions of the control are treated in the same manner with the sodium thiosulfate solution. The presence of visual turbidity relative to the control solution is sufficient to satisfy the definition of insolubility in this test.

This test may be repeated for various pH increments from 1 to 13. Although there is some optimum pH value at which the test is most sensitive, this is not a sharp maximum which must be precisely attained. Rather, it has been found that there is a fairly broad range of pH values (e.g., 2.0 to 3.0 pH units) over which the test has a satisfactory sensitivity. In practice, the silver halide dispersion might be tested without adjustment (e.g., at pH 5.0 to 7.0) and if insolubilization occurs here, Test A is completed. If there is no insolubilization, the test is repeated at a higher pH (e.g., from 10-13). If there is still no insolubilization, the test is conducted with emulsion adjusted to a lower pH (e.g., about pH 1-3). Thus three different pH values represent a practical maximum number which must be investigated to determine whether or not insolubilization will occur.

Test B

An organic compound capable of insolubilizing a silver halide dispersion according to Test A is now ready for the next test, which again will be conducted under safelight conditions. To the above silver halide dispersion, there is added the minimum amount of a solution of the candidate organic compound found necessary for insolubilization. Half-milliliter samples of the dispersion containing 0.5 mg. AgBr or 0.29 mg. are placed in two test tubes. To one sample is added 0.5 ml. of water; to the other is added 0.5 ml. of a 5% by weight aqueous solution of sodium hypochlorite (25 mg. NaOCl). Next, there is added to both samples, 1.0 ml. of an aqueous 10% by weight solution of sodium thiosulfate (100 mg. thiosul-

fate). If, after standing for up to thirty seconds, the sample treated with sodium hydrochlorite clarifies (or becomes less turbid) relative to the control sample, the candidate organic compound meets the requirements of Test B and is satisfactory for use in accordance with this invention. The chemical testing for selecting suitable compounds has been found to give absolute correlation, i.e., organic compounds which have been subjected to Tests A and B have produced without exception when tested in actual photographic emulsion, the very effects predictable by said tests.

The silver chlorobromide dispersion referred to in the above test is a lithographic emulsion having a silver halide composition of 30 mole percent AgBr and 70 mole percent AgCl and having 20 grams of gelatin present per mole of silver halide for the steps of precipitation and ripening. This emulsion was freed of unwanted, soluble, by-product salt by a coagulation and wash procedure as taught in Waller et al., U.S. Patent 2,489,341, wherein the silver halide and most of the gelatin were coagulated by an anionic wetting agent, sodium lauryl sulfate, using an acid coagulation environment. Following the washing step, the emulsion coagulate was redispersed in water together with 47 grams of additional bulking gelatin. For use in the above tests, the dispersion was diluted to the extent that one milliliter of dispersion contained one mg. of silver halide (calculated as AgBr, or 0.58 mg. of Ag).

Dispersed crystals of silver halide, treated with an appropriate amount of a suitable organic mercaptan are affected by exposure of a portion of said crystals to actinic radiation, e.g., ultraviolet, visible, infrared, X-radiation, etc., to such an extent that at least 20% of the less soluble crystals remain when 90% of the more soluble crystals dissolve when treated in 10% by weight aqueous sodium thiosulfate solution.

Suitable elements for this invention can be prepared by bathing a photographic film in a solution of an appropriate organic mercapto compound including, but not limited to, those described in the applications that are identified above. In this embodiment, the silver halide crystals near the surface of the coated emulsion stratum are in contact with a higher concentration of the mercaptan. Crystals farther from the surface are treated with less of the organic compound and, if the rate of diffusion is sufficiently slow, there may be considerably less of the mercaptan (even approaching zero) reacting with the lower than with the surface silver halide crystals. In such elements, satisfactory results might be obtained with only a fraction, e.g., from 1/2 of the amount of the organic mercapto compound theoretically calculated as required to just cover the surface of a mole of the silver halide crystals up to 0.90 g. per mole of silver. As discussed earlier, it has also been found that the concentration of the mercaptan compound may be lower in the presence of another compound with which it must compete for adsorption sites on the silver halide crystals, i.e., the optical sensitizing dye.

The invention will be further illustrated by, but is not intended to be limited to, the following examples.

EXAMPLE I

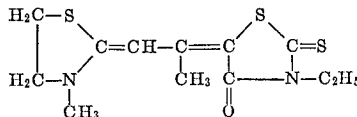
A lithographic-type, gelatino-silver halide emulsion (70 mole percent silver chloride and 30 mole percent silver bromide) was prepared according to the conventional procedures of precipitation, Ostwald ripening and coagulation washing to remove soluble salts. An amount of the coagulate remaining after washing which contained one mole of silver halide was redispersed with 2220 g. H₂O and 67 g.

photographic gelatin, then divided into 4 equal portions. The 4 portions were treated as follows:

	Portion		
	1	2	3
Add mercaptan ¹ (g. per mole of silver).....	0.400	0.533	0.533
Add optical sensitizing dye ² (g. per mole)....	0.023	0.023	None
Digestion time at 160° F., min.....	20	20	20

¹ 2-mercapto-4-cyclohexylthiazole.

² Merocyanine dye of the structure:



Chrome alum hardener was added and each portion was brought up to a weight of 2800 g./mole of silver by addition of water. The emulsions were coated at a coating weight of 60 mg./dm.² (calculated as silver bromide) on a vinylidene chloride copolymer subbed film base prepared as described in Example IV of Alles, U.S. Patent 2,779,-684.

Samples of the dried coatings were exposed through a square-root-of-two photographic step wedge in conjunction with a yellow filter (Wratten® No. 4) which transmits essentially no light at wave lengths up to 450 mμ. The exposure was to a 500-watt incandescent lamp (#2 photoflood) at six inches distance for one second. Positive silver halide images were obtained by treating the exposed samples for 30 seconds with constant agitation in a solution of silver halide solvent at 68° F. having the composition:

Na ₂ S ₂ O ₃ , anhydrous	g--	76.5
Na ₂ SO ₃ , anhydrous	g--	7.5
Na ₂ B ₄ O ₇ ·10H ₂ O	g--	9.0
CH ₃ COOH (glacial)	ml--	6.0
KAl(SO ₄) ₂ ·12H ₂ O	g--	10.0
CH ₃ COOK	g--	10.0
H ₂ O, up to 1 liter.		
pH		4.8

After a 30-second water rinse the images were intensified by flashing to white light (500-watt lamp, 1 second at 6 inches) and then reducing the silver halide to metallic silver images by treatment in a conventional hydroquinone/1-phenyl-3 - pyrazolidone photographic developer solution. Transmission densities were measured using a densitometer (Eastman Kodak Model B) to give the following results:

OPTICAL DENSITY			
Coating from Emulsion Portion.....	1	2	3
Base	0.13	0.13	0.13
Step 1	0.97	1.66	1.57
Step 8	0.98	1.65	1.57
Step 10	0.99	1.64	1.57
Step 12	0.98	1.57	1.57
Step 14	0.99	1.37	1.57
Step 16	0.85	1.06	1.57
Step 18	0.78	0.49	1.57
Step 20	0.76	0.30	1.57
Step 21	0.77	0.28	1.57

In the foregoing example and tables, coating 3 (no dye present) had no sensitivity to yellow light. Coatings No. 1 and 2, differing only in the concentration of mercaptan, both exhibited sensitivity to yellow light, with the mercaptan concentration obviously being closer to optimum in Coating No. 2.

In addition to effecting optical sensitization, the dye also improves the insolubilization by acting synergistically with the mercaptan. Thus Coating No. 2 (containing the dye) has a higher maximum optical density than Coating No. 3 (digested identically but free from dye). Similar results were obtained by substituting for the mercaptan equivalent amounts of 1-phenyl-5-mercaptotetrazole.

EXAMPLE II

One mole of a washed gelatino-silver halide emulsion coagulate as in Example I was redispersed with 87 g. of gelatin and 1860 g. of water by stirring for 10 minutes at 110° F. After adding 0.375 g. of 2-mercapto-4-phenylthiazole (from a 1% by weight ethanol solution), the emulsion was divided into 4 equal portions. Varying amounts of the merocyanine optical sensitizing dye of Example I were added to each portion as indicated below. Each portion was then heated and stirred (digested) for 20 minutes at 160° F., cooled to 95° F., treated with chrome alum hardener, brought up to a total weight of 2700 g. per mole of silver halide by the addition of water, and coated on the film base of Example I at a coating weight of 100 mg./dm.² of silver halide (calculated as silver bromide). After drying, samples of the coatings were exposed to yellow light as in Example I and positive silver halide images were obtained by treating for 60 seconds with constant agitation in a solution of silver halide solvent at 68° F. having the composition:

Na ₂ S ₂ O ₃ , anhydrous	g--	153
Na ₂ SO ₄ , anhydrous	g--	15
Na ₂ B ₄ O ₇ ·10H ₂ O	g--	18
CH ₃ COOH (glacial)	ml--	12
KAl(SO ₄) ₂ ·12H ₂ O	g--	20
CH ₃ COOK	g--	10
H ₂ O, up to 1 liter.		
pH		5.2

After a 30 second water rinse, the images were intensified by flashing to white light and treating in a photographic developer solution as in Example I. Transmission densities, obtained as in Example I, were as follows:

OPTICAL DENSITY

Coating from Emulsion Portion	1	2	3	4
Optical sensitizing dye (g. per mole of silver)	none	0.042	0.063	0.084
Base	0.13	0.13	0.13	0.13
Step 1	1.21	1.77	2.31	2.05
Step 7	1.21	1.78	2.14	2.01
Step 9	1.21	1.37	2.00	1.85
Step 11	1.21	0.62	1.24	1.13
Step 13	1.21	0.26	0.44	0.49
Step 15	1.21	0.14	0.23	0.21
Step 17	1.21	0.15	0.21	0.19
Step 19	1.21	0.17	0.14	0.17
Step 21	1.21	0.15	0.16	0.12

It can be seen that maximum optical density (in areas receiving no exposure to light) is almost twice as high in Coating No. 3, which has close to optimum dye sensitization, as in non-optically-sensitized Coating No. 1. This synergistic effect of the dye and the mercaptan in improving the insolubilization of unexposed silver halide is in addition to the dye's expected effect of sensitizing the film to longer wave length (yellow) light.

EXAMPLE III

One mole of a washed gelatino-silver halide emulsion coagulate as in Example I was redispersed with 33 g. of gelatin and 1250 g. of water by stirring for 10 minutes at 110° F. After adding 0.415 g. of 2-mercapto-4-phenylthiazole (from a 1% by weight ethanol solution), the emulsion was divided into 4 equal portions. No dye was added to the 1st (control) portion but to each of the remaining portions there was added a different optical sensitizing dye as indicated below. Each portion was heated and stirred (digested) for 20 minutes at 160° F., cooled to 95° F., treated with chrome alum hardener,

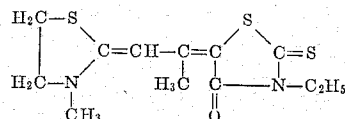
brought up to a total weight of 1670 g. per mole of silver halide by addition of water, and coated on the film base of Example I at a coating weight of 100 mg./dm.² of silver halide (calculated as silver bromide).

Samples of the dried coating were exposed through a square-root-of-two photographic step wedge from a 500-watt lamp (#2 photoflood) at 6 inches distance for 1 second. Positive silver halide images were obtained by treating the exposed samples for 50 seconds at 68° F. in a silver halide solvent solution as described in Example I. The images were intensified and their transmission densities were obtained as in Example I, giving the following results:

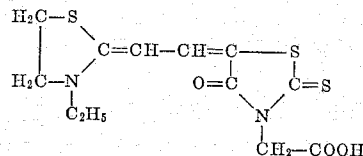
Coating from Emulsion Portion	1	2	3	4
Optical sensitizing dye	None	A	B	C
Dye concentration (g. per mole of silver halide)	0	0.025	0.025	0.027
Optical density in unexposed area (D _{max})	1.04	2.73	2.68	1.79

Dye structure

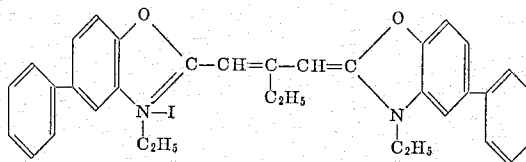
Dye A is neutral merocyanine:



Dye B is a merocyanine containing a carboxyl group:



Dye C is a carbocyanine:



All three of the dyes, it can be seen, acted in conjunction with the mercaptan to decrease the rate of solubility of unexposed silver halide crystals in the solvent solution. The differences in effect among the three dyes may be correlated with their water solubility, the least water-soluble dye (and the one which absorbs most efficiently to the silver halide crystal) being the one which is most useful in improving the insolubilization of the silver halide. The three coatings which contained sensitizing dyes were all sensitive to both blue and yellow light while the non-dye-sensitized coating was sensitive only to blue light.

EXAMPLE IV

A gelatino-silver chloride emulsion was prepared, starting with a solution of 67 g. of photographic gelatin in 1330 g. of water. Eighty-three g. of NH₄Cl were added to the solution and stirred until dissolved. One mole of 0.6 N AgNO₃ was added over a period of 30 seconds and the resulting precipitate was ripened for 15 minutes at 110° F. After adding 4000 ml. of water, the emulsion was adjusted to a pH of 3.5 by the addition of H₂SO₄ and coagulated by the addition of an aqueous solution of a partial acetal of polyvinyl alcohol and o-sulfobenzaldehyde as disclosed in U.S. 2,772,165. The coagulate was then washed with water and redispersed with 2370 g. of water, NaOH to raise the pH to 6.3, and sufficient gelatin to give a total of 188 g. The emulsion was stirred for 30 minutes at 110° F. to insure adequate redispersion, then divided into 2 equal portions. To each portion there was added 0.67 g. per mole of silver halide of 2-mercapto-4-phenylthiazole while to only one portion there was added 0.030 g. per mole of silver halide of the neutral mero-

cyanine optical sensitizing dye identified as "Dye A" of Example III. Both emulsion portions were digested for 20 minutes at 160° F., cooled to 95° F., treated with chrome alum hardener, brought up to a total weight of 3600 g. per mole of silver halide by addition of water, and coated on the film base of Example I at a coating weight of 61 mg./dm.² of AgCl.

Samples of the dried coatings were exposed through a square-root-of-two photographic step wedge from a 500-watt lamp (#2 photoflood) at 12 inches distance for 4 seconds. Positive silver chloride images were obtained by treating the exposed samples for 75 seconds at 68° F. in a silver halide solvent solution as described in Example I. The images were then washed for 30 seconds and intensified by flashing to white light (500-watt lamp, 4 seconds at 12 inches) and reducing the silver chloride to metallic silver images as in Example I. Their optical densities, determined as in Example I, were as follows:

	Optical Density	
	Dye Sensitized	Non-Dye Sensitized
Base.....	0.13	0.13
Step 1.....	3.20	2.65
Step 3.....	3.20	2.65
Step 5.....	3.12	2.65
Step 7.....	2.70	2.65
Step 9.....	2.09	2.65
Step 11.....	1.48	2.64
Step 13.....	0.91	2.06
Step 15.....	0.49	1.78
Step 17.....	0.30	0.69
Step 19.....	0.21	0.27
Step 21.....	0.21	0.19

The presence of optical sensitizing dye not only improves the $D_{\max}$ but also increases the sensitivity to white light in the photosolubilization process.

EXAMPLE V

Example I, Portions 2 and 4, were essentially repeated in a number of experiments except that other mercaptans were used in place of 2-mercapto-4-cyclohexylthiazole. Just as in Example I, 0.023 g. of the merocyanine dye were added per mole of silver halide to Portion 2 but no dye was added to Portion 4. Various mercaptans, as identified in the table below, were added to each portion in a concentration of 0.533 g. per mole and the emulsions were digested at 160° F. for 20 minutes. The emulsions were coated, dried, processed and evaluated as described in Example I and maximum densities (densities corresponding to no exposure) were recorded as follows:

Set No.	Mercaptan	Maximum Optical Densities	
		Portion 2 (dye sensitized)	Portion 4 (non-dye sensitized)
1.....	2-mercapto-4-(p-bromophenyl)-thiazole.....	1.76	1.68
2.....	2-mercapto-4-undecylthiazole.....	.75	.66
3.....	2-mercapto-4-octanoylthiazole.....	.31	.25
4.....	2-mercapto-4-(p-nitrophenyl)-thiazole.....	1.85	1.33
5.....	2-mercatop-5-phenylthiazole.....	.61	.40
6.....	2-mercapto-4-isobutylthiazole.....	.53	.10
7.....	2-mercapto-4-naphthylthiazole.....	1.11	1.06

EXAMPLE VI

A photographic element was prepared by coating an aqueous gelatin dispersion of silver chlorobromide (70 mole percent silver chloride and 30 mole percent silver bromide) on a film base prepared as described in Example IV of Alles, U.S. Patent 2,779,684. The dispersion had a ratio of silver halide to gelatin of 19:1 by weight and was coated at a pH of 6 at a rate of 116 mg. of silver halide per sq. dec. A sample of this dried film was overcoated at room temperature at 25 feet per minute, under red safelights, with a solution containing 12.5 ml. of a 1.2% by weight ethanol solution of 2-mercapto-4-phenylthiazole, 12.5 ml. of a 0.06% by weight acetone solution of the merocyanine dye of Example I,

5 ml. of 0.1 molar NaOH, 120 ml. of ethanol and 50 ml. of water. Another sample of the dried film was overcoated in a similar manner except that the merocyanine dye was omitted from the overcoating solution.

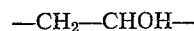
Small areas of both of the overcoated films were exposed to a high intensity incandescent lamp (a No. 2 photoflood lamp) for 10 seconds at a distance of about 6 inches through a blue filter. Other areas of both films were given a similar exposure but through a yellow filter which transmits essentially no light of a wave length below 450 millimicrons. Still other areas of both films were masked so that they received no exposure.

After exposure, the films were treated for 30 seconds at 68° F. in an aqueous solution containing 128 g. of Na₂S₂O₃ per liter and having a pH of 9.4. After a 30-second water-wash, the films were intensified by flashing to white light and treating for 30 seconds in a hydroquinone/4-methyl-1-phenyl-3-hydrazolidone photographic developer solution which contained 2.5 g. of KI per liter. By visual observation it was evident that the dye-sensitized film had a high transmission optical density in the unexposed areas and considerably lower optical densities (caused by photosolubilization) in the areas exposed through the blue and yellow filters. The non-dye-sensitized film had relatively high and essentially equal optical densities in the areas which received no exposure and in the areas which were exposed through the yellow filter. The exposure through the blue filter caused a substantial lowering of optical density. Thus, both films were sensitive to blue light while dye sensitization was shown to extend the spectral sensitivity of one of the films to longer wave lengths.

While the invention is useful with undigested emulsions, in preferred embodiments of the invention the emulsions of the invention are digested at a temperature of at least 140° F. (e.g., 140° F. to about 212° F. for about 1.0 to about 40 minutes).

The silver halide need not be a combination of silver chloride and silver bromide, but may be silver chloride, silver bromide and other mixed halide systems conventional in photographic practice, e.g., silver bromiodide. While, for rapid processing, a high silver halide to binder ratio is desirable, more conventional ratios can also be used.

In place of part of the gelatin, other natural or synthetic water-permeable organic colloid binding agents can be used and in some cases such binders can be used alone. Such agents include water-permeable or water-soluble polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers and acetals containing a large number of intralinear



groups, hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid esters and styrene. Suitable such colloids of the last-mentioned type were disclosed in U.S. Patents 2,276,322; 2,276,323 and 2,397,866. The useful polyvinyl acetals include polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloid binding agents which can be used include the poly-N-vinylactams of Bolton U.S. Patent 2,495,918, various polysaccharides, e.g., dextran, dextrin, etc., the hydrophilic copolymers in Shacklett U.S. Patent 2,833,650, hydrophilic cellulose ethers and esters, and polymers of acrylic and methacrylic esters and amides. Also, it has been found practical to treat silver halide layers on a base material in the essential absence of a binder, e.g., by chemical or vacuum deposition.

The emulsions may optionally contain any of the usual adjuvants customarily employed in silver halide systems so long as they do not interfere with the adsorption and complexing action of the essential ingredients of the invention.

The emulsions can be coated on any suitable support, e.g., cellulose esters, cellulose mixed esters; superpolymers, e.g., poly(vinyl chloride *co* vinyl acetate); polyvinyl acetals, butyrals; polystyrene; polyamides, e.g., polyhexamethylene adipamide; polyesters, e.g. polycarbonates, polyethylene terephthalate/isophthalate, esters formed by condensing terephthalic acid and its derivatives, e.g., dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol, cyclohexane-1,4-dimethanol (hexahydro-p-xylene dialcohol); paper, metal, glass, etc.

The novel photographic compositions of this invention have numerous advantages. A primary advantage is the simplicity of their preparation. They can be exposed and processed to form images under ordinary room light conditions. The photographic processes applicable to the compositions of the invention likewise have advantages over previously known systems based on selective reduction of exposed silver halide for forming either direct positive or negative images without resorting to the special effects and sensitizing procedures previously used for preparing such images. In addition, since direct positive image formation does not require selective reduction, this process is not limited to the use of certain photographic developing agents but may be accomplished by using a wide range of reducing agents. Many such compounds are of very low cost and can be used to form images of much higher covering power than customary, thus effecting important economies in processing, as well as greatly increasing the efficiency of the silver image.

The improved photosolubilization elements of this invention have the particular advantages of higher photosolubilization speeds, extended spectral sensitivity and improved insolubilization (i.e., higher maximum densities). As compared with photosolubilization elements claimed in earlier applications, the organic mercaptan compounds and the optical sensitizing dyes present in the elements of this invention exert a synergistic effect upon one another to bring about the above advantages of greater speed and improved insolubilization.

Another advantage of this invention is that it provides new elements for forming silver images that do not require special equipment but instead can be used with conventional equipment and apparatus. A further advantage is that the elements can be used successfully by photographic technicians and photographers of ordinary skill. A still further advantage is that the elements can be processed with conventional reducing agents, e.g., developers and fixing agents. Still additional advantages will be apparent from the above description of the invention.

I claim:

1. A photographic silver halide emulsion layer comprising before imagewise exposure to actinic radiation, silver halide crystals having associated therewith

(a) from 0.015 g. to 0.075 g. per mole of silver of an optical sensitizing dye selected from the group consisting of cyanine, carbocyanine and merocyanine dyes, and

(b) a silver mercaptide of an organic mercapto compound, said mercaptide being present in about 90% of the amount, in terms of the ratio of its weight to the surface area of said silver halide crystals, that when admixed in such ratio with an aqueous silver chlorobromide (70/30 mole percent) gelatin dispersion containing 57 g. of gelatin per mole of Ag and .57 mg. of Ag per ml., and said silver chlorobromide dispersion is treated with 10%, by weight, aqueous sodium thiosulfate (so that when the resulting mixture contains 0.29 mg. of silver and 100 mg. of sodium thiosulfate), at least three times the amount of silver chlorobromide remains undissolved as in a similar dispersion successively treated with 5%, by weight, aqueous sodium hypochlorite and 10%, by weight, aqueous sodium thiosulfate (so that

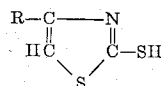
the resulting mixture contains 0.29 mg. of silver, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate), after vigorous agitation of the dispersions for 30 seconds at 25° C.

2. An emulsion layer according to claim 1 containing gelatin as the binding agent for the silver halide crystals.

3. An emulsion layer according to claim 1 wherein any heavy metal salt present is a noble metal salt.

4. An emulsion layer according to claim 1 wherein the silver halide emulsion is a digested emulsion.

5. An emulsion layer according to claim 1 wherein said silver mercaptide is of a mercapto compound of the formula



where R is a hydrocarbon nucleus of 4-12 carbon atoms.

6. An emulsion layer according to claim 1 wherein said silver mercaptide is of 2-mercapto-4-phenylthiazole.

7. An emulsion layer according to claim 1 wherein said silver mercaptide is of 2-mercapto-4-cyclohexylthiazole.

8. An emulsion layer according to claim 1 wherein said silver mercaptide is of 2-mercapto-4-(p-bromophenyl)thiazole.

9. A process for the formation of images which comprises, in the order stated, the sequential steps of

(1) exposing, imagewise, to actinic radiation, a photosolubilizable silver halide emulsion layer of silver halide crystals having associated therewith

(a) from 0.015 g. to 0.075 g. per mole of silver of an optical sensitizing dye selected from the group consisting of cyanine, carbocyanine and merocyanine dyes, and

(b) a silver mercaptide of an organic mercapto compound, said mercaptide being present in about 90% of the amount, in terms of the ratio of its weight to the surface area of said silver halide crystals, that when admixed in such ratio with an aqueous silver chlorobromide (70/30 mole percent) gelatin dispersion containing 57 g. of gelatin per mole of Ag and .57 mg. of Ag per ml., and said silver chlorobromide dispersion is treated with 10%, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver and 100 mg. of sodium thiosulfate) at least three times the amount of silver chlorobromide remains undissolved as in a similar dispersion successively treated with 5%, by weight, aqueous sodium hypochlorite and 10%, by weight, aqueous sodium thiosulfate (so that the resulting mixture contains 0.29 mg. of silver, 25 mg. of sodium hypochlorite and 100 mg. of sodium thiosulfate), after vigorous agitation of the dispersions for 30 seconds at 25° C.,

(2) treating the exposed layer in a solution of a silver halide solvent to remove soluble silver halide in the exposed image areas, thus forming a positive silver halide image in the unexposed areas.

10. A process according to claim 9 embodying the additional step of

(3) washing the resulting layer containing a positive silver halide image.

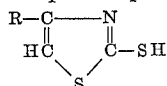
11. A process according to claim 9 embodying the additional steps

(3) washing the resulting layer containing a positive silver halide image, and

(4) reducing said silver halide image to a silver image.

13

12. A process according to claim 9 wherein said silver mercaptide is of a mercapto compound of the formula



where R is a hydrocarbon nucleus of 4-12 carbon atoms.

13. A process according to claim 9 wherein said silver mercaptide is of 2-mercapto-4-phenylthiazole.

14. A process according to claim 9 wherein said silver mercaptide is of 2-mercapto-4-cyclohexylthiazole. 10

14

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