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3,155,514

PHOTOGRAPHIC COMPOSITIONS AND ELEMENTS

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This invention relates to photography, and more particularly to new photographic products useful therein.

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 and reduction, toning and tinting. However, the primary or first step in image formation always has been based on the selective reduction step.

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. Still further objects will be apparent from the following description of the invention.

The objects of this invention are realized by new silver halide compositions in which an image may be formed, after exposure to actinic radiation, by imagewise solution of the silver halide. The residual silver halide image may then be converted to silver, dyed or toned images.

The novel photographic emulsion layers and elements of this invention comprise, before exposure to actinic light, silver halide crystals having associated therewith, in substantially greater than fog-inhibiting amounts, a silver mercaptide of a substituted thiourea having at least one —SH group in one of its tautomeric forms, the latter compound being characterized in that when admixed with an aqueous silver halide dispersion it protects the silver halide crystals to such an extent that when a silver halide dispersion protected by said compound is treated with 10%, by weight, aqueous sodium thiosulfate at least three times the amount of silver halide remains undissolved as in a similar dispersion successively treated with 5% aqueous sodium hypochlorite and 10% sodium thiosulfate, after vigorous agitation of the dispersions for 30 seconds at 25° C.

Preferably, the silver halide crystals are dispersed in a water-permeable organic colloid to form a light-sensitive photographic emulsion. The selected substituted thiourea 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. In the working examples below, the amount of organic compound in the silver halide emulsion is from about 0.4 to 63 g. per mole of silver halide but wider ranges of concentration can be useful, depending upon the particular organic compound, the size and nature of the silver halide crystals, the presence of other materials which may partially cover the

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surface of the silver halide crystal, and upon various other factors.

The gelatin:silver halide ratio is quite flexible and may vary from 3:1 to 1:30 depending on the particular organic compound and application.

In one commercially practical aspect of the invention, the silver halide is present in much higher concentration than in conventional emulsions and emulsion layers.

In an important use of the products of the invention, direct positive images are formed by a process which comprises

(a) Exposing imagewise to actinic radiation a photosensitive layer comprising silver halide crystals treated with the organic compound as described above.

(b) 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, and

(c) Washing the resulting layers.

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

(d) 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

(e) 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 stratum 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. Reduction of the treated, residual silver halide may be accomplished by use of any chemical reducing agent capable of reducing silver ion to silver metal, e.g., hydroquinone, metal 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 present invention embodies a broad new photographic principle and is not limited to a narrow class of thiourea compounds with which the silver halide crystals are intimately associated or may be treated in preparing the novel compositions of 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 thiourea compound must render a dispersion of silver halide crystals insoluble in a silver halide solvent, i.e., 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 solvents. Depending on the solubility, a solution concentration from 0.01 to 10 percent by weight is obtained. Twenty-five ml. of a 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 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 pH 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 represents 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 2.29 mg. Ag 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 (containing 25 mg. sodium hypochlorite). Next, there is added to both samples, 1.0 ml. of an aqueous 10% by weight solution of sodium thiosulfate (containing 100 mg. sodium thiosulfate). If, after standing for up to thirty seconds, the sample treated with sodium hypochlorite 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.

Silver Halide Dispersion Preparation—Dispersion I

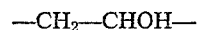
A silver halide dispersion useful for Tests A and B is prepared according to the following specifications. In red light, 30 g. of photographic grade gelatin is soaked in 1100 ml. of distilled water for 10 minutes. The tempera-

ture is then raised to 120° F. and 100 g. of solid ammonium chloride added. The mixture is stirred at 120° F. and after the ammonium chloride is completely dissolved, a solution made by diluting 500 ml. of 3 N silver nitrate with 2000 ml. of distilled water is added while stirring the solution for 5 seconds. This mixture is held at 120° F. for 4 minutes with stirring, and then 150 ml. of 3 N ammonium bromide added (30 mole percent) in 10 seconds. The mixture is held an additional 15 minutes at 120° F. with stirring and then cooled to 100° F. A mixture of 75 g. of the sodium salt of technical lauryl alcohol sulfate (a white powder) and 7 ml. of 3 N sulfuric acid is added in 10 seconds to the silver chlorobromide, stirring continued for one minute and then the mixture allowed to settle. The supernatant liquid is decanted and replaced by 2000 ml. of distilled water containing 4 g. of sodium chloride. This mixture is stirred for 5 minutes at 100° F., allowed to settle and decanted again. Two hundred ml. of distilled water is added to the silver halide curds and the temperature adjusted to 95° F. This mixture is vigorously stirred for 10 minutes at 95° F. and then the pH adjusted to 6.1±0.1 with aqueous sodium hydroxide solution. The redispersed emulsion is then analyzed for silver halide content calculated as silver bromide and a dispersion made by diluting the appropriate amount with distilled water such that the dispersion contains 1 mg. calculated silver bromide per ml.

Dispersed crystals of silver halide, treated with an appropriate amount of a suitable organic compound 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. Generally, the presence of solubilizing groups should be avoided in order that reaction products with silver halide will be formed which will significantly reduce the solubility of silver halide grains in silver halide solvents. There are exceptions to this rule, particularly in the case of suitable compounds containing solubilizing groups which are compensated for by the presence of insolubilizing groups, e.g., long chain alkyl groups. 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 emulsions, the very effects predicted by said tests. Combinations of the compounds with various basic dyes, including various cyanine dyes, and Methylene Blue (Colour Index No. 922), Crystal Violet AO (Colour Index No. 681) and Rhodamine 6 GDN Extra (Colour Index No. 752) have proven useful additions.

The silver halide need not be combination of silver chloride and silver bromide, but may be silver chloride, silver bromide and other mixed systems conventional in photographic practice, e.g., silver bromoiodide. While, for rapid processing, a high silver halide to binder ratio is preferred as described in several of the examples, 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 system so long as they do not interfere with the adsorption and complexing action of the essential ingredient of the invention.

The emulsions can be coated on any suitable support, e.g., cellulose esters, cellulose mixed esters; superpolymers, e.g., polyvinyl chloride (co) vinyl acetate, polyvinyl acetals, butyral; polystyrene; polyamides, e.g., polyhexamethylene adipamide, polyesters, e.g., polycarbonates, polyethylene terephthalate, 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.

As disclosed earlier, the desirable concentration of the selected organic compound depends on many factors such as the size and solubility of the organic compound, the nature of its reaction with silver halide, the size and nature of the silver halide crystals, the presence of other materials which may react with or be adsorbed to the surface of the silver halide, etc. In Example I below, a large number of organic compounds are disclosed which were tested in a dispersion of silver halide crystals wherein the average grain size was 0.35μ (micron) in diameter therefore about $0.43\mu^3$ in volume, assuming cubic grains. The silver halide comprised 70 mole percent silver chloride and 30 mole percent silver bromide, with a specific density of about 5.7 g./cc. or 5.7×10^{-12} g./ μ^3 . The weight per individual crystal or grain is $0.043\mu^3 \times 5.7 \times 10^{-12}$ g./ $\mu^3 = 0.25 \times 10^{-12}$. Assuming a molecular weight of 157 for the mixed AgCl-AgBr crystals, and dividing this number by the weight per grain, gives $157 \text{ g./mole} \div 0.25 \times 10^{-12} \text{ g.} = 6.3 \times 10^{14}$ grains/mole. The area of a cubic grain of 0.35μ diameter $= 6 \times .35^2 = .74\mu^2$ which multiplied by the 6.3×10^{14} grains per mole, gives a molar surface area of $4.6 \times 10^{14}\mu^2$ or 4.6×10^{22} square angstroms.

A particularly preferred organic compound is 2-mercapto-4-phenylthiazole (hereinafter to be referred to as "MPT"). This compound is disclosed and claimed in my copending application Ser. No. 317,824, filed October 21, 1963, entitled "Photographic Compositions, Layers and Elements" which is a continuation-in-part of this application. Assuming that a single molecule of MPT could occupy an area of 28 square angstroms, it would require 1.5×10^{21} molecules to occupy a molar surface area of silver halide. With a molecular weight of 193, this would require

$$193 \times \frac{1.5 \times 10^{21}}{6 \times 10^{23}} = 0.48 \text{ g.}$$

to just cover the surface of one mole of the silver halide crystals. In Example I it required 1.2×10^{-4} g. of MPT to insolubilize 2.5×10^{-2} of silver halide of average molecular weight 157. Therefore according to experimental data (test tube results) it would require

$$1.2 \times 10^{-4} \times \frac{157}{2.5 \times 10^{-2}} = 0.75 \text{ g.}$$

of MPT to insolubilize one mole of the silver halide.

More significantly, as disclosed in Procedure A in a photographic emulsion coated on a film base support, it was found that 0.4 g. of MPT per mole of silver halide gave optimum results. This compares more closely with the theoretically determined amount of MPT required to cover the silver halide surface.

As shown in various examples below, e.g. Example I, elements suitable for this novel process can be prepared by treatment with an appropriate substituted thiourea compound. In this embodiment, the silver halide crystals near the surface of the coated emulsion stratum are in contact with a higher concentration of the organic compound. 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 organic compound (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., one-half, of the amount of the organic compound theoretically calculated as required to just cover the surface of a mole of the silver halide crystals.

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

EXAMPLE I

Tests A and B have been described earlier as procedures whereby one can determine whether or not a given organic compound is suitable for use according to the process of this invention. Many of the compounds which were indicated as suitable according to the screening procedures of both tests, have been incorporated into actual photographic coatings and good results have been obtained. Below there are listed a number of thiourea organic compounds which were tested in this manner including one such compound which has been found to be inoperable. Of the unsuitable compounds shown, most failed to produce the insolubility required of Test A and were therefore not subjected to further testing. Since it was impracticable to perform complete photographic experiments with each and every compound screened according to Tests A and B, a simulated photographic test was devised and will be designated as Test C. It is noted that there is complete testing correlation in that any compound which was found suitable according to the photographic test to be described in the next paragraph was also found suitable according to Tests A and B.

TEST C

A 0.5 ml. portion of the insolubilized dispersion prepared in Test A under safelight conditions is placed in a 12 x 75 mm. Pyrex test tube three inches from a No. 2 reflectoflood lamp. This insolubilized dispersion is exposed to the lamp for up to 10 minutes. A control consisting of another 0.5 ml. portion of the insolubilized silver halide dispersion from Test A is taken under safelight conditions. Two-tenths of a milliliter of 10% aqueous sodium thiosulfate is added to each of the dispersion samples taken and compared under safelight conditions. Any reduction in turbidity of the dispersion exposed to the reflectoflood lamp compared to the unexposed control after treatment with aqueous sodium thiosulfate solution shows that photosolubilization occurs.

Tests A, B and C were all conducted using Silver Halide Dispersion I, the preparation of which was given immediately following the description of the procedure for Test B. To determine and approximate minimum concentration of the organic compound required to effect insolubilization of silver halide in the presence of an aqueous solution of sodium thiosulfate, the qualitative procedure of Test A was repeated in a more quantitative manner, using a ripened, washed and redispersed (but not chemically sensitized) gelatino-silver chlorobromide emulsion as described in Example I of assignee's copending application, Nottorf, U.S. Serial No. 94,989, filed March 13,

1961. This emulsion is designated in the table below as Dispersion II, and was made as follows:

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 was freed of unwanted, soluble, by-product salts 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.

Thiourea Derivatives

Compound	Test Results with Dispersion I			Gms. Compound to Insolubilize Dispersion II Containing 25 mg. Silver Halide
	Insolubilization Test A	Chemical Solubilization Test B	Photosolubilization Test C	
1. Thioacetanilide	Insoluble	Soluble	Soluble	0.0025
2. Thiobenzanilide	do	do	do	0.002
3. Thiourea	Soluble	do	do	0.002
4. N-phenylthiourea	Insoluble	Soluble	Soluble	0.002
5. 1-(1-naphthyl)-2-thiourea	do	do	do	0.0005
6. 1,1-diphenyl-2-thiourea	do	do	do	0.001
7. 1-ethyl-1-(1-naphthyl)-2-thiourea	do	do	do	0.0006
8. 1,3-di-n-butyl-2-thiourea	do	do	do	0.0072
9. 1-ethyl-3-phenyl-2-thiourea	do	do	do	0.0035
10. Thiocarbaniide	do	do	do	0.0009
11. 2,2'-diethylthiocarbaniide	do	do	do	0.0006
12. 1,3-dibenzyl-2-thiourea	do	do	do	0.0002
13. 1,3-di-(1-naphthyl)-2-thiourea	do	do	do	0.0035
14. Thiosemicarbazide	do	do	do	0.01
15. 4-phenyl-3-thiosemicarbazide	do	do	do	0.0002
16. 1,5-diphenyl-3-thiocarbohydrazide	do	do	do	0.0009
17. Diphenylthiocarbazone	do	do	do	0.003
18. α-Mercapto acetanilide	do	do	do	0.001
19. 1,3-diallyl-2-thiourea	do	do	do	0.005
20. 1-allyl-3-phenyl-2-thiourea	do	do	do	0.005
21. 1,3-di-n-octyl-2-thiourea	do	do	do	0.004
22. Thioacetamide	Soluble	do	do	do
23. 1-acetyl-2-thiourea	do	do	do	do

Procedure A.—An emulsion, as described in Dispersion II, Example I was brought to 2320 g. by addition of water and the temperature adjusted to 120° F. Four-tenths of a gram of MPT (2-mercapto-4-phenylthiazole) was added per mole of silver halide from a 1% by weight ethanol solution. Chrome alum hardener was added and the emulsion was diluted with water to a total weight of 2334 g. per mole of silver halide. This emulsion was applied at a coating weight of 46 mg. of silver per square decimeter on 0.004 inch thick polyester photographic film base as described in Example I. The coating, after imagewise exposure, showed a greater rate of fixing in a 1.0 N (0.5 molar) aqueous sodium thiosulfate in exposed areas than in the unexposed areas so as to form a positive silver halide image. Subsequent flashing to white light, followed by treatment with a reducing agent (a conventional photographic developing solution containing 1-phenyl-4-methyl-3-pyrazolidone and hydroquinone), resulted in the formation of a positive image of metallic silver.

EXAMPLE II

Example I was repeated except that other thiourea compounds, in the same amounts by weight, were examined in place of MPT. After photographic processing as described in Procedure A, the optical densities of completely unexposed areas and heavily exposed areas of the film were determined using a Western Electric RA-100-C Densitometer.

Compound	Optical Unexposed	Density Exposed
2-Mercapto-4-phenylthiazole	1.80	0.05
Dibenzylthiourea	0.79	0.70
1,3-Dibenzylthiourea	0.85	0.24

The silver halide photosoluble elements of this invention differ from conventional silver halide emulsions containing antifogging agents in that the insolubilizing compounds used in the photosoluble elements are present in substantially greater than fog-inhibiting amounts, the latter amounts being the maximum quantity which provides low fog without serious loss in speed and photographic quality. For this reason it is not practical to use photosoluble elements in place of ordinary silver halide photographic materials. When photosoluble elements are exposed and processed normally, development proceeds slowly and incompletely to give a negative silver image having much less speed and lower density. In addition, fixing is slower and may be incomplete for practical fixing

times. Thus, photosoluble elements require longer conventional processing times and give slower speed, inferior quality images when compared to ordinary silver halide photographic elements.

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 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 image formation does not require selective reduction, this present 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 with a resultant increase in sensitivity.

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. A still further advantage is that the new elements can be used to produce images without selective

reduction. Still additional advantages will be apparent from the above description of the invention.

This application is a continuation-in-part of my application Ser. No. 158,132, now abandoned, filed December 8, 1961 for Photographic Compositions and Processes.

I claim:

1. A photographic silver halide emulsion layer comprising, before exposure to actinic light, silver halide crystals and associated therewith in substantially greater than fog-inhibiting amounts a silver mercaptide of a substituted thiourea compound containing at least one —SH group, the silver mercaptide being of lower solubility in water than silver chloride, the silver halide crystals so associated with the silver mercaptide being less soluble in 10% aqueous sodium thiosulfate than untreated silver halide crystals at a predetermined pH and the substituted thiourea compound being present in such an 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 emulsion containing 57 g. of gelatin per mole 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 compared with similar dispersion successively treated with a 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. A photographic layer according to claim 1 wherein said emulsion layer is a gelatino-silver chlorobromide emulsion.

3. A photographic layer according to claim 1 wherein said emulsion layer is a gelatino-silver chlorobromide emulsion and the gelatin/silver halide ratio is from 3:1 to 1:30 by weight.

4. A photographic silver halide emulsion layer according to claim 1, wherein said compound is N-phenylthiourea.

5. A photographic silver halide emulsion layer according to claim 1, wherein said compound is 1,3-dibenzylthiourea.

6. A photographic element comprising a support bearing a photographic silver halide emulsion layer as defined in claim 1.

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