

1

2

3,155,518 SILVER HALIDE COMPOSITIONS, LAYERS AND ELEMENTS

Ralph Kingsley Blake, Westfield, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Oct. 21, 1963, Ser. No. 317,817
6 Claims. (Cl. 96—107)

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 imagewise 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, unreduced silver halide 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, layers and elements 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, or simply used as a silver halide image.

The present application is a continuation-in-part of my copending application Ser. No. 236,412, filed November 8, 1962.

The photographic compositions, layers and elements of this invention comprise, before exposure to actinic radiation, e.g., imagewise exposure to visible light, light-sensitive silver halide crystals, preferably having at least 10% by weight of silver chloride, having associated therewith, in greater than fog-inhibiting amounts, a silver mercaptide of an aromatic mercaptan having a single mercapto group attached to an aromatic hydrocarbon nucleus of 6-10 carbon atoms, i.e., benzene or naphthalene.

The aromatic hydrocarbon nucleus may have a hydrogen atom thereof substituted by a monovalent radical, e.g., Cl, Br, NH₂, COOH, or an alkyl radical of 1-18 carbons, for example —CH₃ and —C₉H₁₉. The mercapto compounds which form the silver mercaptides can be associated initially with the silver halide grains as a free —SH compound or as the sodium, potassium or ammonium salt of the —SH compound.

The amount of the silver mercaptide present in the photographic silver halide layer should be sufficient to protect the silver halide crystals so that the unexposed layer cannot be fixed by conventional fixing conditions, i.e., at normal times, temperatures and concentrations of silver halide solvent.

The silver mercaptide, which is less soluble in water than silver chloride, is further characterized in that when such silver mercaptide is formed by addition of an organic

mercaptan or ion thereof to an aqueous dispersion of silver halide, said silver mercaptide protects the silver halide from solution to the extent that at least three times the amount of silver halide remains undissolved as compared to (a) the untreated silver halide dispersion or (b) the mercaptan-treated silver halide dispersion which has subsequently been treated with 5% aqueous sodium hypochlorite, when all three of said dispersions are treated individually with equal amounts of 10% aqueous sodium thiosulfate and agitated identically for 30 seconds at 25° C.

To be more specific, it can be readily determined that the aromatic mercaptan of this invention should be 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 dispersion containing 57 g. gelatin per mole Ag and .57 mg. of silver 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 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.

The invention is useful with silver halide layers free from or containing a water-permeable colloid binding agent.

The compounds can be added to the silver halide coating solutions, e.g., aqueous gelatin silver halide solutions or the coated layers can be bathed with an aqueous or an organic solvent solution, e.g., ethanol solution containing the requisite amount of the aromatic mercaptan.

Preferably, the silver halide crystals are dispersed in a water-permeable organic colloid to form a light-sensitive photographic silver halide emulsion. The aromatic mercaptan or salt thereof 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 63.0 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 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 intended use for the emulsion layer.

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 constituting the subject matter of my application Ser. No. 236,420, filed Nov. 8, 1962, which process comprises:

(a) Exposing imagewise to actinic radiation a photosensitive layer comprising silver halide crystals treated with an 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 preferably

(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, alkali metal thiocyanate (e.g., sodium, potassium), 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, metol, sodium hydrosulfate 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 is not limited to a class of organic compounds with which the silver halide crystals are intimately associated or may be treated in preparing the novel compositions of this invention. The utility of a specific aromatic mercaptan compound or salt thereof 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 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 (i.e., 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 safe-light 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. 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. of 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 it is satisfactory for use as disclosed in this invention.

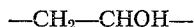
Silver Halide Dispersion Preparation

Dispersion I.—The silver halide dispersion disclosed in 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 temperature 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 is 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.

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-vinyl lactams 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 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, butyrals; 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 $0.043\mu^3$ 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

$$0.043\mu^3 \times 5.7 \times 10^{-12} \text{ g./}\mu^3 = 0.25 \times 10^{-12} \text{ g.}$$

Assuming a molecular weight of 157 for the mixed AgCl-AgBr crystals, and dividing this number by the

weight per grain, gives $157 \text{ g./mole} \div 0.25 \times 10^{-12} \text{ g.} = 6.3 \times 10^{14} \text{ grains/mole}$. 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.

According to my application Ser. No. 236,412 filed Nov. 8, 1962, a preferred mercapto compound is 2-mercapto-4-phenylthiazole (hereinafter to be referred to as "MPT"). 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 VI of Ser. No. 236,420 it required 1.2×10^{-4} g. of MPT to insolubilize 2.5×10^{-2} g. 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 Example VII of Ser. No. 236,420, 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 application Ser. No. 236,420, Example I, elements suitable for this novel process can be prepared by bathing a photographic film in a solution of an appropriate organic 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 aromatic mercaptans that were tested. In addition, of the unsuitable compounds tested, 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 note that there is complete testing correlation in that any thiophenol of this application that 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 pre-

pared 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 an 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. Ser. No. 94,989, filed Mar. 13, 1961. 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 by adding an aqueous solution containing 47 g. of gelatin per mole of silver halide, adjusting the pH to about 6.0 and vigorously agitating for 65 minutes at 100° F. By testing, the following results were obtained:

AROMATIC MERCAPTANS

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. Thiophenol.....	Insoluble..	Soluble..	Soluble..	0.00014
2. β -Naphthothiol.....	do.....	do.....	do.....	0.00019
3. p-Chlorothiophenol.....	do.....	do.....	do.....	0.001
4. 2-Aminothiophenol.....	do.....	do.....	do.....	0.0011
5. 4-Aminothiophenol.....	do.....	do.....	do.....	0.004
6. p-Bromothiophenol.....	do.....	do.....	do.....	0.0015
7. p-Nitrothiophenol.....	do.....	do.....	do.....	0.01
8. Thioalicyclic acid.....	do.....	do.....	do.....	0.01
9. o-Toluenethiol.....	do.....	do.....	do.....	0.0091
10. m-Toluenethiol.....	do.....	do.....	do.....	0.0091
11. p-Toluenethiol.....	do.....	do.....	do.....	0.0091
12. 4-t-Butylthiophenol.....	do.....	do.....	do.....	0.0002
13. 4-Nonylthiophenol.....	do.....	do.....	do.....	0.002
14. 4-t-Butyl-o-thiocresol.....	do.....	do.....	do.....	0.001

Example II

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 by adding an aqueous solution containing 53 g. of gelatin per mole of silver halide, adjusting the pH to about 6.0 and vigorously agitating for 65 minutes at 110° F.

To a quantity of this redispersed emulsion containing 0.15 mole of silver halide there was added 40 ml. of an aqueous solution of the sodium salt of p-bromothiophenol obtained by dissolving 0.19 g. p-bromothiophenol in 2 ml. of 1-molar NaOH and diluting with water to 100 ml. The emulsion was stirred for 20 minutes at 160° F., cooled to 95° F., the usual coating adjuvants added and the emulsion was coated on the film base described in Example I, at a silver coating weight of 35 mg./dm.². The coating, after imagewise exposure, showed a greater rate of fixing in an aqueous solution containing 75 g. of sodium thiosulfate per liter in exposed areas than in the unexposed areas so as to form a positive silver halide image. Similar results were obtained by using 60 ml. of an aqueous solution of the sodium salt of p-bromothiophenol, or 0.4 g. of the free mercaptan per mole of silver halide.

When the sodium, potassium or ammonium salt is used, in place of the free mercaptan, there are advantages as these salts can be added from aqueous solution instead of from an ethanol solution.

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 products 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 new products 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.

I claim:

1. A photographic silver halide emulsion layer wherein any heavy metal salt present is a silver halide comprising, before exposure to actinic radiation, light-sensitive silver halide crystals having associated therewith in substantially greater than fog-inhibiting amounts, a silver mercaptide of an aromatic mercaptan having a single mercapto group

attached to an aromatic hydrocarbon radical of 6-10 carbon atoms, said silver mercaptide being of lower solubility in water than silver chloride, the silver halide crystals so associated with the silver mercaptide dissolving more slowly in 10% aqueous sodium thiosulfate than untreated silver halide crystals at a predetermined pH, said mercaptan 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 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 compared with a similar dispersion successively treated with 5%, by weight, aqueous sodium hypochlorite and 10%, by weight, aqueous sodium thio-

sodium thiosulfate), after vigorous agitation of the dispersions for 30 seconds at 25° C.

2. An emulsion layer according to claim 1 containing at least 10% by weight of silver chloride.

3. An emulsion layer according to claim 1 wherein the silver halide is silver chlorobromide.

4. An emulsion layer according to claim 1 wherein the layer contains gelatin as the binding agent for the crystals.

5. An emulsion layer according to claim 1 wherein said aromatic mercaptan is thiophenol.

6. An emulsion layer according to claim 1 wherein said mercaptan is a toluenethiol.

References Cited in the file of this patent

- 15 Mees: "The Theory of the Photographic Process," Macmillan, 1942, pages 306-309 of interest.
- Faerman et al.: "The Photographic Action of 2-Mercaptobenzoxazde," Uspekhi Nauchnoi Fotografii, Akademiya Nauk, S.S.S.R., Otdelenie Khimicheskikh Nauk 5, 107-113 (1957).
- 20 Van Veelen et al.: Phot Korr 99, No. 9, September 1963, pages 139-145 of interest.