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3,368,899

EMULSION LAYERS AND ELEMENTS

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No Drawing. Filed Oct. 13, 1964, Ser. No. 403,660
8 Claims. (Cl. 96—107)

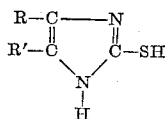
This invention relates to photography and more particularly to new image-yielding photographic silver halide emulsion layers and to photographic elements embodying such layers.

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 further 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 Blake, U.S. Patent 3,155,507, Nov. 3, 1964. The novel process of said application, characterized as "photosolubilization," requires the use of a specially prepared silver halide emulsion layer containing a stipulated amount of an organic compound which modifies the silver halide solubility so that, in conventional silver halide solvents, said organic compound causes the silver halide grains to dissolve more slowly than normal. Such an element is given an imagewise exposure and the exposed areas can then be treated in a solution of a silver halide solvent to yield 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, 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 new compositions and elements for "photosolubilization" processing embodying a class of organic compounds which provide a new combination for the required alteration of the silver halide crystals. Still further objects will be apparent from the following description of the invention.

The above objects are realized in a photographic emulsion layer comprising, before exposure to actinic radiation, light-sensitive silver halide crystals having associated therewith a silver mercaptide of a substituted mercapto compound of the formula:



where R and R', which may be the same or different, are hydrogen, hydrocarbon or substituted hydrocarbon nuclei

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of 1-14 carbon atoms connected through carbon to the imidazole nucleus, i.e., alkyl, aryl, alkaryl, aralkyl radicals, and such radicals containing substituent groups such as nitro, halogen, e.g., chlorine and bromine, and alkoxy of 1-6 carbon atoms. Useful alkyls include ethyl, propyl, butyl and n-pentyl, and useful alkoxy radicals include the corresponding alkoxy radicals. When separate, at least one of the radicals R and R' is a hydrocarbon nucleus of 3-14 carbon atoms. When R and R' are taken together, they form an aromatic or alicyclic ring. The silver mercaptide is of lower solubility in water than silver chloride and the silver halide crystals so associated with the silver mercaptide dissolve more slowly in 10% aqueous sodium thiosulfate solution, at a predetermined pH, than untreated silver halide crystals.

It is preferred that the silver mercaptide be present in such 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 10 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 both dispersions for 30 seconds at 25° C.

According to a particularly preferred aspect of the invention, R' of the above formula is hydrogen and R 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 imidazole ring. Suitable radicals of the latter type include cyclohexyl, phenyl, and alpha-naphthyl.

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 mercapto compound in the silver halide emulsion may vary with a number of factors such as the nature of the mercapto compound and the size of the silver halide crystal (and thus the surface area of the crystal per mole of silver halide).

When the mercaptan is added to the emulsion in the liquid state it is most efficiently adsorbed to the silver halide crystal by "digesting" the emulsion, e.g., heating the emulsion between 140° and 180° F. The organic mercapto compound is used in greater than fog-inhibiting amounts, e.g., in a range of from 0.3 to 1.5 grams per mole of silver halide and, more preferably from 0.4 to 1.2 grams per mole of silver halide. The optimum concentration of mercaptan is decreased somewhat, e.g., about 10%, when the emulsion is sensitized with a photographic optical sensitizing dye as disclosed in assignee's copending application of Blake, Ser. No. 390,460, filed Aug. 18, 1964.

The gelatin-silver halide ratio is not critical and may vary from 3:1 to 1:20 depending on the particular organic compound and silver halide crystals.

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 photo-sensitive layer comprising silver halide crystals treated with the mercaptan 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 optionally,

(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/mercaptan 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. In assignee's copending application Hunt, Ser. No. 388,919, filed Aug. 8, 1964, it is disclosed that more efficient removal of exposed silver halide crystals (insolubilized by mercapto compounds) 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). These cations are also effective as additives for fixing solutions used in treating the elements of the present invention.

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. Additionally, the silver halide image may be intensified by dye mordanting.

The present invention is not limited to a narrow class of mercaptans 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 as defined above can be employed and their utility can be determined readily by a relatively simple test. Essentially, the test consists of two steps, Test A and Test B. In Test A, the candidate mercapto 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 mercaptans may be readily and positively identified.

TEST A

A solution nearly saturated at 25° C. with a candidate mercaptan, 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 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 mercaptan, 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 mercaptan), 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 the 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

A mercaptan 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 mercaptan found necessary for insolubilization. Half-milliliter samples of the dispersion containing 0.5 mg. of AgBr or 0.29 mg. of 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 (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. 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 mercaptan 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 emulsions, the very effects predicted 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 coagulant was redispersed in water. Assuming a loss of 10 grams of gelatin per mole of silver halide during washing the final gelatin concentration was about 10 grams per mole of silver halide. For use in the above test, 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 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 (unexposed) crystals remain when 90% of the more soluble (exposed) crystals dissolve when treated in 10% by weight aqueous sodium thiosulfate solution.

Suitable elements in this invention can be prepared by bathing a photographic film in a solution of an appropriate mercaptan. 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 mercaptan 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., one-half of the amount of the mercaptan 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.—4,5-diphenyl-2-mercaptoimidazole

Benzoin (21.2 g., 0.1 mole) and ammonium thiocyanate (22.8 g., 0.1 m.) were heated to reflux in dioxane (200 ml.) for 6 hours. After cooling, the precipitate was collected and recrystallized from acetic acid. Yield=21 g. (83% of theoretical) with M.P. 299–300° C.

A lithographic emulsion containing about 57 g. of gelatin per mole of silver halide (prepared as described following Test B) was diluted with water and brought to a temperature of 110° F. The 4,5-diphenyl-2-mercaptoimidazole, prepared as described above, was added to the emulsion from a 1% ethanol solution in the amount of 0.65 g. per mole of silver halide. After digesting for 20 minutes, chrome alum hardener and other emulsion adjuncts were added. The emulsion was applied at a coating weight of 85 mg./dm.² (calculated as AgBr) on 0.004-inch thick polyester photographic film base as described in Example IV of Alles, U.S. 2,779,684. The coating, after imagewise exposure, showed a greater rate of fixing in a 1.0 N (0.5 molar) aqueous sodium thiosulfate solution 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 an intensified positive image of metallic silver.

Example II.—4-phenyl-2-mercaptoimidazole

Omega-aminoacetophenone hydrochloride (5 g., 0.029 m.) and potassium thiocyanate (3.15 g., 0.033 m.) were heated to reflux for 3.5 hours in 25 ml. of ethanol. After cooling, the precipitate was collected and recrystallized from benzene-ethanol; M.P. 261°.

A sample of the 4-phenyl-2-mercaptoimidazole was found to produce the required insolubilization of silver

halide crystals when tested according to the above-described Test A. Chemical solubilization also occurred according to Test B as described above. More quantitative results were obtained by applying Test C, a simulated photographic test as described below:

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. heat-resistant glass test tube 3 inches from a high-intensity, tungsten filament lamp (General Electric reflector Photoflood lamp ASA No. PH/RFL2). This dispersion is exposed 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 which are compared under safelight conditions. Any reduction in turbidity of the dispersion exposed to the Photoflood lamp compared to the unexposed control, after treatment with aqueous sodium thiosulfate solution, shows that photosolubilization occurs.

In this more quantitative test, it was determined that the approximate minimum quantity of 4-phenyl-2-mercaptoimidazole required to insolubilize 25 milligrams of silver halide was 0.0002 g. (The pH was adjusted to 9.5 using 5% sodium bicarbonate.)

Example III.—4-(p-nitrophenyl)-2-mercaptoimidazole

4-(p-nitrophenyl)-2-mercaptoimidazole was prepared according to the procedure described in Example II, using omega-amino-4-nitroacetophenone hydrochloride as a starting material.

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 milligrams of silver halide per square decimeter. After drying, the element was bathed for about 30 seconds in an ethanol-water solution of 4-(p-nitrophenyl)-2-mercaptoimidazole and dried. The solution of 4-(p-nitrophenyl)-2-mercaptoimidazole was prepared by diluting 5 ml. of a stock solution (1 gram of the compound made up to 100 ml. in ethanol) with an additional 20 ml. of ethanol and 10 ml. of water. The dried element was then exposed behind a photographic transparency for 5 seconds to the radiation from a high-intensity, tungsten filament, incandescent lamp (reflector photolamp ASA No. PH/RFL2) at a distance of about 6 inches. The exposed element was then immersed in a solution containing, on a liter basis, 77 g. Na₂S₂O₃, 7.5 g. Na₂SO₃, 9 g. Na₂B₄O₇·10H₂O, 6 ml. glacial acetic acid, 10 g. KAl(SO₄)₂·2H₂O and 10 g. CH₃COOK. A 30-second treatment in this solution resulted in the removal of the silver salt in the exposed areas to form a positive silver halide image. Subsequently, the fixed film was then rinsed briefly in water and bathed in a rapid-acting fogging photographic developer solution comprising 1-phenyl-4-methyl-3-pyrazolidone and hydroquinone as reducing agents to which there had been added potassium iodide. This treatment caused the intensification of the positive image by converting the silver halide to a black metallic silver image. All of the above operations were carried out in ordinary red safelight illumination.

Example IV.—5-nitro-2-mercaptobenzimidazole

The commercially available compound above was employed in a treating solution for a photographic element as described in Example III and a similar positive image was obtained.

This mercaptan also caused the required insolubilization of silver halide crystals of Test A and the required

chemical solubilization of Test B. In the more quantitative Test C of Example II, it was determined that approximately 0.0012 g. of 5-nitro-2-mercaptobenzimidazole was required to insolubilize 25 mg. of silver halide.

Example V.—4-(p-methoxyphenyl)-2-mercaptoimidazole

This compound, with a melting point of 240° C. after recrystallization from ethanol, was prepared according to the procedure of A. Lawson and H. V. Morley, J. Chem. Soc., 1957, 566-568. The recrystallized compound was employed as a treating solution for a photographic element as described in Example III and a similar positive image was obtained.

Example VI.—2-mercaptanaphth(2,3-d)imidazole

2,3-diaminonaphthalene (10 g.) and thiourea (10 g.) were heated at 195° C. for 15 min. The reaction mixture was extracted with 0.5 N NaOH at 50° C. Adjustment to pH 4 with acetic acid gave 2-mercaptanaphth(2,3-d)imidazole which, upon recrystallization from ethanol, had a melting point of 305° C.

This compound was employed in a treating solution for a photographic element as described in Example III and a similar positive image was obtained.

Example VII.—2-mercaptobenzimidazole

Commercially available 2-mercaptobenzimidazole was employed in a treating solution for a photographic element as described in Example III and a similar positive image was obtained. This compound was also found to produce the required insolubilization of silver halide crystals of Test A as well as the required chemical solubilization of Test B.

In the more quantitative Test C of Example II, it was determined that approximately 0.0012 g. of 2-mercaptobenzimidazole was required to insolubilize 25 mg. of silver halide.

Example VIII.—5-amino-2-mercaptobenzimidazole

Commercially available 5-amino-2-mercaptobenzimidazole was employed in a treating solution for a photographic element as described in Example III and a similar positive image was obtained. This compound was also found to produce the required insolubilization of silver halide crystals of Test A as well as the required chemical solubilization of Test B.

In the more quantitative Test C of Example II, it was determined that approximately 0.006 g. of 5-amino-2-mercaptobenzimidazole was required to insolubilize 25 mg. of silver halide.

Example IX.—4-cyclopentyl-2-mercaptoimidazole

This compound with a melting point of 218-220° C. after recrystallization from ethanol-water, was prepared according to M. Jackman, N. Klenk, B. Fishburn, B. F. Tullar and S. Archer, J. Amer. Chem. Soc. 70, 2884-2886 (1948). When this compound was employed in a treating solution for a photographic element as described in Example III, a similar positive image was obtained.

Example X.—4-(n-hexyl)-2-mercaptoimidazole

This compound was prepared in a manner very similar to that disclosed in the Jackman et al. reference of Example IX. When this compound was employed in a treating solution for a photographic element as described in Example III, a similar positive image was obtained.

Example XI

A silver bromide emulsion of the medical X-ray type was prepared by adding ammonia converted silver nitrate to a mixture of ammonium bromide and potassium iodide in an aqueous gelatin solution. After ripening, the emulsion was coagulated and washed. The washed curds were redispersed with additional gelatin and digested in the presence of sensitizing materials. The finished emulsion, with about 200 g. of gelatin per mole of silver halide,

contained 1.2 mole per cent silver iodide and 98.8 mole percent silver bromide. The emulsion was applied to both sides of an appropriately subbed cellulose acetate photographic film base having a thickness of 0.008 inch, the total coating weight being 206 mg./dm.² calculated as silver bromide.

After drying, a sample of the element was bathed for about 30 seconds in an ethanol-water solution of 4,5-diphenyl-2-mercaptoimidazole (prepared as described in Example I) and dried. The solution was prepared by diluting 5 ml. of a stock solution (1 gram of the compound made up to 100 ml. in ethanol) with an additional 20 ml. of ethanol and 10 ml. of water. The dried element was exposed and processed as described in Example III to give a direct positive image.

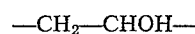
Example XII

A gelatino-silver chloride emulsion was prepared in a conventional manner through the steps of precipitation, Oswald ripening, coagulation and washing. A quantity of washed coagulum containing 1 mole of silver chloride was redispersed in an aqueous solution containing 117 g. gelatin. There was then added 1.28 g. of 4,5-diphenyl-2-mercaptoimidazole prepared according to Example I from a 0.25%, by weight, ethanol solution. The emulsion was digested for 20 minutes at 170° F. and, after the addition of the usual post-digestion adjuvants, was applied at a coating weight of 54 mg./dm.² of AgCl to the film base of Example I.

After drying, the element was exposed at a distance of 6 inches through a square-root of two photographic step wedge for 10 seconds to the radiation from a high-intensity, tungsten filament lamp (General Electric reflector Photoflood lamp ASA No. PH/RFL2). The exposed element was then immersed in a solution containing, on a one-liter basis 77 g. Na₂S₂O₃, 7.5 g. Na₂SO₃, 9 g. Na₂B₄O₇·10H₂O, 6 ml. glacial acetic acid, 10 g. KAl(SO₄)₂·12H₂O and 10 g. CH₃COOK. A 30-second treatment in this solution resulted in the removal of the silver halide in the exposed areas. Subsequently, the film was rinsed briefly in water, re-exposed by flashing for 5 seconds at a distance of 6 inches from the above-described lamp, and bathed in a rapid-acting photographic developer solution comprising 1-phenyl-3-methyl-3-pyrazolidone and hydroquinone as reducing agents. A direct-positive image of the step wedge was formed.

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 or 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., those made by chemical or vacuum deposition.

The emulsion 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 organic mercaptans of the invention.

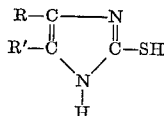
The emulsions can be coated on any suitable support, e.g., cellulose esters, cellulose mixed esters; superpolymers, e.g., poly(vinyl chloride covinyl acetate); polyvinyl acetals, butyrals; polystyrene; polyamides, e.g., polyhexamethylene adipamide, polyesters, e.g., polycarbonates, polyethylene terephthalate/isophthalate,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

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.

We claim:

1. A photographic emulsion layer comprising, before exposure to actinic radiation, light-sensitive silver halide crystals having associated therewith in greater than fog-inhibiting amounts of silver mercaptide of a substituted compound of the formula



wherein R and R' are members selected from the group consisting of hydrogen and hydrocarbon nuclei of 1-14 carbon atoms connected through carbon to the imidazole ring, at least one of R and R' when separate being a hydrocarbon nucleus of 3-14 carbon atoms and when taken together constituting the atoms necessary to complete with the two carbon atoms of the imidazole ring a cyclic radical; 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, the mercapto compound of said formula being present in such 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 10 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 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 both dispersions for 30 seconds at 25° C.

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

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

4. An emulsion layer according to claim 1 wherein said substituted compound is 4,5-diphenyl-2-mercaptoimidazole.

5. An emulsion layer according to claim 1 wherein R' is hydrogen and R 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 imidazole ring.

6. An emulsion layer according to claim 5 wherein said substituted compound is 4-phenyl-2-mercaptoimidazole.

7. A process according to claim 1 wherein said silver halide is silver chloride.

8. A process according to claim 1 wherein said silver halide is silver bromiodide.

References Cited

UNITED STATES PATENTS

3,155,514	11/1964	Blake	96-107
3,155,515	11/1964	Celeste	96-107
3,155,519	11/1964	Blake	96-107

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