United States Patent Office 3,128,185 Patented Apr. 7, 1964

3,128,185

ANTIFOGGANTS FOR FORMALDEHYDE-HARDENED PHOTOGRAPHIC LAYERS

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No Drawing. Filed Jan. 25, 1960, Ser. No. 4,186
13 Claims. (Cl. 96—108)

This invention relates to photographic layers, and more particularly, photographic silver halide emulsion layers which have been chemically sensitized and treated with formaldehyde as a hardener.

It is known that the sensitivity of photographic silver halide emulsions can be increased by several methods, including spectral sensitization and chemical sensitization. In spectral or optical sensitization, the optical range of sensitivity is increased, while this is generally not the case in chemical sensitization. The present invention is concerned primarily with chemical sensitization of photographic elements containing layers hardened by treatment with formaldehyde.

Chemical sensitization of silver halide emulsions results in an increase in sensitivity to visible light, generally with little or no change in grain-size distribution or in spectral sensitivity. Several different types of chemical sensitization are known. One of the more common types is sulfur sensitization, which involves treatment of silver halide emulsions with a labile sulfur compound and the possible formation of silver sulfide specks in or on the silver halide grain. Another type of chemical sensitization is gold sensitization, which involves treatment of silver halide emulsions with a gold compound or salt. Generally, gold sensitization and sulfur sensitization are additive, i.e., the sensitizing effects of one type of sensitization do not interfere with and can be added to the other type of sensitization.

While it is known that photographic silver halide emulsions can be simultaneously sensitized by sulfur sensitization and gold sensitization, difficulty frequently arises in applying this combined sensitization to photographic silver halide emulsions which have been treated with formaldehyde as a hardener. Formaldehyde is one of the more useful hardeners used in photography and offers considerable advantages over many other hardeners, including mucochloric acid, mucobromic acid, etc. However, when using formaldehyde hardening in conjunction with sulfur- and gold-sensitized emulsions, difficulty arises in that the fog levels of the emulsions frequently increase substantially.

The present invention makes possible the combination of gold sensitization and sulfur sensitization in photographic emulsions or layers which are hardened by treatment with formaldehyde.

It is, accordingly, an object of my invention to provide chemically sensitized photographic silver halide emulsions. Another object is to provide photographic silver halide emulsions and layers which have been hardened with formaldehyde. Still another object of my invention is to provide a means for using sulfur and gold sensitization where photographic emulsions or layers have been treated with formaldehyde as a hardener, without seriously increasing the fog levels of the emulsions. Other objects will become apparent from a consideration of the following description and examples.

According to my invention, I have found that the fog levels of photographic silver halide emulsions or layers, which have been chemically sensitized with a labile sulfur compound and a gold salt or compound, and hardened by treatment with formaldehyde, can be controlled by treatment with various aldehyde compounds. Aldehydes which have been found particularly useful according to my invention are aromatic aldehydes having a substituent on the 3- and/or 4-position with respect to the aldehyde group. Suitable substituents are hydroxyl, halogen (e.g., chlorine, bromine, etc.), alkyl (e.g., methyl, ethyl, etc.), alkoxyl (e.g., methoxyl, ethoxyl, etc.), etc. Such aromatic aldehydes can conveniently contain from about 7 to 10 carbon atoms. Other aldehydes useful in practicing my invention are halogen-substituted aldehyde-aliphatic carboxylic acids, including mucochloric acid, mucobromic acid, etc., as well as their water-soluble salts, including sodium, potassium, triethanol-ammonium, pyridinium, morpholinium, etc.

My invention is not confined to any particular sulfur sensitizer or group of sulfur sensitizers, although I have found that the following are particularly useful in practicing my invention: allylisothiourea, allylthiourea, allylisothiocyanate, phenylisothiocyanate, phenylthiourea, sodium thiosulfate, thiocarbanilide, thiourea, thiosemicarbazide, thioacetamide, thioformamide, thiobarbituric acid, etc. Such well known sensitizers have been previously described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926; Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927; Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946, etc.

Gold salts or compounds useful in practicing my invention are also well known to those skilled in the art and comprise auric trichloride, sodium chloroaurate, potassium chloroaurite, potassium bromaurite, potassium iodoaurite, potassium iodoaurate, potassium aurithiocyanate, potassium aurichloride, auric sulfate, sodium auric chloride, potassium auric bromide, sodium auric bromide, alkali metal aurous thiosulfate, alkali metal aurous sulfite, thioureaauric chloride complex, auric chloride - 3 - ethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]rhodanine addition product (e.g., Damschroder et al. U.S. Patent 2,642,361, issued June 16, 1953), etc. Typical gold sensitizers are described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946.

The formaldehyde can be incorporated directly in the photographic silver halide emulsion, or it can be incorporated in a contiguous hydrophilic colloid layer, such as an intermediate layer or an overcoating layer comprising gelatin, polyvinyl alcohol, hydrolyzed cellulose acetate, etc.

The concentration of sulfur sensitizer and gold sensitizer, as well as the concentration of the formaldehyde, used in my invention can be varied, depending upon the concentration of silver halide, concentration of gelatin, degree of ripening of the silver halide, etc. In general, I have found that from about 1.0 to 10 mg. per mole of silver halide of sulfur sensitizer is adequate for the purposes of my invention. The concentration of gold salt or compound can advantageously vary from about 0.5 to 10.0 mg. per mole of silver halide, although larger amounts can be employed, if desired. The amount of formaldehyde in the emulsion should generally be at least about 1 gram per pound of gelatin and the maximum amount can be as much as about 240 grams, depending upon the effect desired. The concentration of aldehyde antifoggant can likewise vary, although I have found that generally from about 1 to 240 grams per pound of gelatin is adequate for the purposes of my invention. The optimum amount of aldehyde antifoggant will vary for a given emulsion and can be determined by running a series of test coatings wherein the time of digestion with the aldehyde antifoggant and temperature of digestion are varied. The following examples will serve to illustrate our invention.

EXAMPLE 1

A fine-grain, gelatino-silver-chlorobromide emulsion containing approximately 120 grams of gelatin per mole of silver was sensitized by the addition of a sulfur sensitizer of the type shown in Sheppard U.S. Patent 1,623,499 (e.g., allylthiourea) and a water-soluble gold salt of the type shown in Waller et al. U.S. Patent 2,399,083 (e.g., sodium chloroaurate) and the emulsion was divided into two parts as follows:

(*a*) 2 g. of formaldehyde/mole of silver halide added.
- (1) No further addition.
- (2) No further addition plus dry overcoat No. 1.
- (3) No further addition plus dry overcoating No. 2.

(*b*) 11.4 g. of mucochloric acid/mole of silver halide added.
- (1) No further addition.
- (2) No further addition plus dry overcoat No. 1.
- (3) No further addition plus dry overcoat No. 2.

Dry overcoat No. 1 was coated from a gelatin solution with the addition of a coating aid, such as saponin, and formaldehyde hardened. The concentration of gelatin was 123 mg. per square foot and the concentration of formaldehyde was 3.25 mg. per square foot.

Dry overcoat No. 2 was coated as described for dry overcoat No. 1, except that the formaldehyde concentration was increased to 52 mg. per square foot.

Coatings were made on a cellulose acetate support and then dried. Exposure was made in an Eastman Type Ib Sensitometer to a step wedge and the coatings were developed for 2¾ minutes in a developer containing 17.5 grams of hydroquinone, 65 grams of sodium formaldehyde bisulfite, a buffer made up of sodium carbonate and sodium bicarbonate to adjust the pH to about 9.9 and sufficient water to make 1 liter (identified developer A below). After development, the coatings were then fixed, washed and dried in the usual manner. Separate strips of coatings were developed for 4 minutes in a developer having the following composition:

D–11 Developer

	Avoirdupois	Metric
Water, about 125° F. (50° C.)	16 ounces	500 cc.
p-N-methylaminophenol sulfate	15 grains	1.0 gram.
Sodium sulfite, desiccated	2½ ounces	75.0 grams.
Hydroquinone	130 grains	9.0 grams.
Sodium carbonate, desiccated	365 grains	25.0 grams.
Potassium bromide	73 grains	5.0 grams.
Cold water to make	32 ounces	1.0 liter.

These coatings were also fixed, washed and dried. Duplicate coatings were incubated for one week at 120° F. and 50% relative humidity and then processed in developer A for 2¾ minutes and separate strips developed for 4 minutes in developer D–11. The relative speed, contrast and fog for the coatings were then measured. The results are given in Table I below. The relative speed value is inversely proportional to the exposure required to give a density of about 0.3 above fog.

EXAMPLE 2

A fine-grain, gelatino-silver-chlorobromide emulsion, sulfur and gold sensitized as described in Example 1 and containing 120 grams gelatin per mole of silver, was divided into six batches and the batches treated as follows:

a–1.—2 g. formaldehyde/mole silver added.

a–2.—2 g. formaldehyde/mole silver plus 11.4 g. mucochloric acid added.

a–3.—2 g. formaldehyde/mole silver added, held 10 minutes at 40° C. then 11.4 g. mucochloric acid/mole silver was added.

b–1.—11.4 g. mucochloric acid added.

b–2.—11.4 g. mucochloric acid/mole silver plus 2 g. formaldehyde/mole silver added.

b–3.—11.4 g. mucochloric acid/mole silver added and held 10 minutes at 40° C. then 2 g. formaldehyde/mole silver added.

The coatings were then processed exactly as described in Example 1 together with a duplicate set of coatings which had been previously incubated for one week at about 120° F. and 50% relative humidity. The relative speed, contrast and fog for the coatings were then measured. The results are summarized in Table I.

TABLE I

Example No.	Fresh Coating				1 Week Incubation at 120° F./50% RH			
	2¾′ Developer A			4′ D–11	2¾′ Developer A			4′ D–11
	Relative Speed	Contrast	Fog	Fog	Relative Speed	Contrast	Fog	Fog
1*a*–1	100	3.3	0.01	0.10	80	0.70	0.01	1.25
1*a*–2	123	6.8	0.01	0.08	102	5.7	0.01	1.88
1*a*–3	200	5.2	0.01	0.08	151	4.9	0.01	1.31
1*b*–1	316	12.0	0.01	0.10	295	7.7	0.01	0.13
1*b*–2	316	10.2	0.01	0.08	229	8.8	0.01	0.12
1*b*–3	436		0.01	0.06	295	5.4	0.01	0.13
2*a*–1	617	9.2	0.01	0.10	813	5.3	0.29	2.46
2*a*–2	407	10.5	0.01	0.08	347	7.2	0.03	0.18
2*a*–3	398	9.1	0.01	0.10	363	7.2	0.02	0.17
2*b*–1	289	8.5	0.01	0.10	324	7.2	0.01	0.08
2*b*–2	427	9.5	0.01	0.08	380	7.3	0.02	0.16
2*b*–3	427	9.5	0.01	0.07	347	6.7	0.02	0.16

EXAMPLE 3

A fine-grain, gelatino-silver-chlorobromide emulsion was sulfur and gold sensitized as described in Example 1. This emulsion contained approximately 120 grams of gelatin per mole of silver halide. There were then added 2 grams of formaldehyde per mole of silver halide and the emulsion was divided into 5 portions. Aldehydes were then added, at the concentration shown below, to four of the coatings. The fifth coating served as a control and contained no aldehyde antifoggant. The emulsions were then coated on cellulose acetate supports and dried. The coatings were exposed on an intensity scale sensitometer and processed in Developer A of Example 1 for 2¾ minutes or in developer D–11 for four minutes. The coatings were then fixed, washed and dried. Duplicate coatings were processed after one weeks' incubation at 120° F. and 50% relative humidity. The relative speed, contrast and fog were then measured. The results are shown in the following table:

TABLE II

Coating No.	Aldehyde	Grams/Mole AgX	Fresh coating				One week incubation at 120° F./50% R.H.	
			Relative Speed	Contrast	Fog	D–11 Fog	Fog (Devel. A)	D–11 Fog
(a)	Control		109	9.5	.01	.10	0.29	2.46
(b)	Mucochloric acid	1	107	10.5	.01	.02	.01	.10
(c)	Vanillin	1	82	7.0	.01	.03	.01	.11
(d)	p-hydroxybenzaldehyde	1	63	10.5	.01	.04	.01	.10
(e)	m-hydroxybenzaldehyde	1	69	8.0	.01	.04	.01	.10

It has been found that certain aldehydes, such as benzaldehyde, o-hydroxybenzaldehyde, succinic dialdehyde, maleic dialdehyde, etc., do not function as antifoggants in my invention. It is important in the case of aromatic

aldehydes that they contain a substituent in either the 3- or 4-position with respect to the aldehyde group. The emulsions used in my invention can be either acidic or basic emulsions.

The photographic emulsions used in practicing my invention are of the developing-out type.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950; and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948, and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955, Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); or the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958; and the carboxymethylmercapto compounds of Murray, Reynolds and Van Allan U.S. Patent 2,819,965, issued January 14, 1958.

The emulsions may also contain speed increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955; or the thiopolymers of Graham and Sagal U.S. application Serial No. 779,839, filed December 12, 1958 (now U.S. Patent 3,046,129, issued July 24, 1962), or Dann and Chechak U.S. application Serial No. 779,874, filed December 12, 1958 (now U.S. Patent 3,046,134, issued July 24, 1962), or the quaternary ammonium salts and polyethylene glycols of Piper U.S. Patent 2,886,437, issued May 12, 1959.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956 (now U.S. Patent 2,960,404, issued November 16, 1960); an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957 (now U.S. Patent 2,904,434, issued September 15, 1959); bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956 (now U.S. Patent 2,940,854, issued June 14, 1960), or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may contain a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958, a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956 (now U.S. Patent 3,038,804, issued June 12, 1962); or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, filed October 21, 1957 (now U.S. Patent 2,992,108, issued July 11, 1961), or a sodium salt of an alkyl aryl polyether sulfonate of U.S. patent application Serial No. 753,642, filed August 7, 1958 (now U.S. Patent 3,026,202, issued March 20, 1962).

The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions, they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The agents may

be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,-250, issued April 8, 1952.

These may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,-014, issued June 20, 1944, and Land U.S. Patents 2,584,-029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,-705, filed May 23, 1956 (now U.S. Patent 3,020,155, issued February 6, 1962). They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,-933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, granted July 24, 1956, and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylimide content of 15–20% and a specific viscosity of 0.09–0.225 or an imidized polyacrylamide having a combined acrylimide content of 30–60%, a combined acrylic acid content of 4–12% and a specific viscosity of .25–1.5 as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,-474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,311, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,-382, of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with an aldehyde compound selected from the class consisting of mucochloric acid, a water-soluble salt of mucochloric acid, mucobromic acid, a water soluble salt of mucobromic acid and an aromatic aldehyde containing a substituent only in at least one of the positions: the 3-position with respect to the aldehyde group and the 4-position with respect to the aldehyde group, said substituent being selected from the class consisting of an hydroxyl group, a halogen atom, a lower alkyl group, and an alkoxyl group, said aromatic aldehyde containing from 7 to 10 carbon atoms.

2. A photographic element comprising a support and a photographic silver halide emulsion layer sensitized with a labile sulfur compound and a gold salt, and stabilized by the addition of a compound selected from the class consisting of mucochloric acid, a water-soluble salt of mucochloric acid, mucobromic acid, a water-soluble salt of mucobromic acid, and an aromatic aldehyde containing from 7 to 10 carbon atoms and containing a substituent only in at least one of the positions: the 3-position with respect to the aldehyde group and the 4-position with respect to the aldehyde group, said substituent being selected from the class consisting of an hydroxyl group, a halogen atom, a lower alkyl group and an alkoxyl group, and contiguous to said photographic silver halide emulsion layer a hydrophilic colloid layer, at least one of said layers containing formaldehyde, said emulsion layer being hardened substantially only by said formaldehyde.

3. A photographic material according to claim 1 wherein the photographic emulsion is a gelatino-silver halide photographic emulsion.

4. A photographic gelatino-silver-halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with an aldehyde compound selected from the class consisting of p-hydroxybenzaldehyde, m-hydroxybenzaldehyde and vanillin.

5. A photographic gelatino-silver-halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with mucochloric acid.

6. A photographic gelatino-silver-halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with p-hydroxybenzaldehyde.

7. A photographic gelatino-silver-halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with m-hydroxybenzaldehyde.

8. A photographic gelatino-silver-halide emulsion hardened substantially only with formaldehyde, sensitized with a labile sulfur compound and a gold salt, and stabilized with vanillin.

9. A photographic element comprising a photographic gelatino-silver-halide emulsion layer sensitized with a labile sulfur compound and a gold salt and stabilized with an aromatic aldehyde selected from the class consisting of p-hydroxybenzaldehyde, m-hydroxybenzaldehyde and vanillin, and contiguous to said photographic silver halide emulsion layer a hydrophilic colloid layer, at least one of said layers containing formaldehyde, said emulsion layer

being hardened substantially only by said formaldehyde.

10. A photographic element comprising a photographic gelatino-silver-halide emulsion layer sensitized with a labile sulfur compound and a gold salt and stabilized with mucochloric acid, and contiguous to said silver halide emulsion layer a gelatin layer, at least one of said layers containing formaldehyde, said emulsion layer being hardened substantially only by said formaldehyde.

11. A photographic element comprising a photographic gelatino-silver-halide emulsion layer sensitized with a labile sulfur compound and a gold salt and stabilized with p-hydroxybenzaldehyde, and contiguous to said silver halide emulsion layer a gelatin layer, at least one of said layers containing formaldehyde, said emulsion layer being hardened substantially only by said formaldehyde.

12. A photographic element comprising a photographic gelatino-silver-halide emulsion layer sensitized with a labile sulfur compound and a gold salt and stabilized with m-hydroxybenzaldehyde, and contiguous to said silver halide emulsion layer a gelatin layer, at least one of said layers containing formaldehyde, said emulsion layer being hardened substantially only by said formaldehyde.

13. A photographic element comprising a photographic gelatino-silver-halide emulsion layer sensitized with a labile sulfur compound and a gold salt and stabilized with vanillin, and contiguous to said silver halide emulsion layer a gelatin layer, at least one of said layers containing formaldehyde, said emulsion layer being hardened substantially only by said formaldehyde.

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