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# ANTIFOGGANTS FOR GOLD SENSITIZED EMULSIONS IN THE PRESENCE OF REDUCTION SENSITIZERS

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This invention relates to photographic silver halide emulsions, and more particularly, to chemical sensitizers and antifoggants therefor.

It is known that the sensitivity of silver halide emulsions can be increased by several methods, including spectral sensitization and chemical sensitization. In spectral sensitizaiton, the optical range of sensitivity is increased, while this is generally not the case in chemical sensitization. The present invention is concerned primarily with the latter type of sensitizaiton.

Chemical sensitization of silver halide emulsions results in an increase in sensitivity to light, generally with little or no change in grain-size distribution or in spectral sensitivity. Several types of chemical sensitization are known. One of the more common types of chemical sensitization is that known as sulfur sensitization, which involves treatment of the silver halide emulsion 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 known as gold sensitization which involves treatment of the silver halide emulsions with a gold salt or compound. Generally, gold sensitization and sulfur sensitization are additive, i.e., the sensitizing effects of one type of sensitization can be added to the other type of sensitization.

Still another type of chemical sensitization is that known as reduction sensitizing by compounds having a sufficiently strong reducing action to reduce silver halide to metallic silver or to nucleate silver halide. Reduction sensitization is quite useful since it is frequently additive to sulfur sensitization. These types of chemical sensitization (gold, sulfur and reduction) are well known and have been previously described by Lowe et al., "Fundamental Mechanism of Photographic Sensitivity," 1951, pages 112–125. The present invention is concerned with all three types of sensitization.

While the effects of reduction sensitization are frequently additive to gold sensitization, the utility of such combinations is sometimes limited by the fact that certain reduction sensitizers cause marked increases in the fog levels of the silver halide emulsions. While treatment of the emulsions with antifoggants may, in some instances, control the fog levels, certain antifoggants reduce rather severely the speed levels of the silver halide emulsions. It is sometimes true then that marked increases in speed can be obtained by combining reduction sensitization, gold sensitization and sulfur sensitization with concomitant increases in fog levels. In some instances this fog level can be controlled by careful handling and finishing of the silver halide emulsions, but frequently this undesirable fog becomes uncontrollable and results in overall fogging of the silver halide emulsions.

The present invention makes possible the combination of reduction sensitization, gold sensitization and sulfur sensitization, while maintaining within controllable limits the fog levels of the emulsions, and without causing any serious loss of speed in the emulsions.

It is, accordingly, an object of our invention to provide chemically sensitized photographic silver halide emulsions. Another object is to provide photographic silver halide emulsions which have been simultaneously sensitized with gold salts or compounds, sulfur sensitizers and



reduction sensitizers. Still another object of our invention is to provide photographic silver halide emulsions which have been chemically sensitized with gold salts or compounds, sulfur sensitizers and reduction sensitizers, which have low levels of fog and improved stability on keeping.

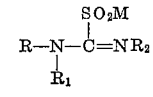
According to our invention, we have found that the fog levels of chemically sensitized emulsions can be controlled by treatment with various aldehyde compounds. These aldehyde compounds can be added before, during or after chemical sensitization. Especially useful results have been obtained where these aldehyde compounds are added before reduction sensitizing (e.g., where chemical fogging is a problem), although they can be added during or after chemical sensitization where the primary problem is one of keeping and chemical fogging has been avoided by means known to those skilled in the art, as described, for example, in Lowe et al. U.S. Patent 2,743,183, issued April 24, 1956. For example, these aldehydes can be added to photographic silver halide emulsions which have been previously gold-sensitized (and generally sulfur-sensitized) and the emulsions digested at elevated temperatures for varying lengths of time, depending upon the amounts of chemical sensitizers added, type of silver halide, etc. Aldehydes which have been found particularly useful according to our invention are aromatic aldehydes having a substituent in 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 our invention are halogen-substituted aldehyde-aliphatic carboxylic acids, such as mucochloric acid, mucobromic acid, etc., as well as their water-soluble salts, including sodium, potassium, pyridinium, triethanolammonium, morpholinium, etc.

Our invention is not confined to any particular sulfur sensitizer or group of sulfur sensitizers, although we have found that the following are particularly useful in practicing our 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 our 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, thiourea-auric 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.

Reduction sensitizers useful in our invention include those which have been previously described in the prior art. Especially useful are those reduction sensitizers represented by the following general formula:

(I)



wherein R, $R_1$ and $R_2$ each represents a hydrogen atom, an alkyl group, such as methyl, ethyl, propyl, etc,, or an aryl group, such as phenyl, tolyl, etc., and M represents a water-solubilizing cation, such as hydrogen, sodium, potassium, ammonium, triethanolammonium, etc.

Another group of useful reduction sensitizers is that represented by the following general formula:

(II) $$H_2N(R_3NH)_nR_3NH_2$$

wherein $R_3$ represents an alkylene group containing from 2 to 4 carbon atoms, such as ethylene, propylene, etc., and *n* represents a positive integer of from 1 to 5. Typical compounds embraced by Formula II include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tetrapropylenepentamine, etc., as well as their water-soluble salts of non-desensitizing acids, such as acetates, carbonates, sulfates, hydrochlorides, etc.

Still another useful group of reduction sensitizers are silane compounds having a silicon-hydrogen bond, e.g., those represented by the following general formula:

(III) $$(R_4)_dSiH_{4-d}$$

or their hydrolysis products:

(III*a*) $$(R_4)_dSiOH_{4-d}$$

wherein $R_4$ represents a hydrogen atom, a halogen atom (e.g., chlorine, bromine, fluorine, etc.), an alkyl group containing from 1 to 30 carbon atoms (e.g., methyl, ethyl, etc.), an aryl group containing from 6 to 10 carbon atoms (e.g., phenyl, tolyl, naphthyl, etc.), an aryloxy group containing from 6 to 10 carbon atoms (e.g., phenoxy, naphthoxy, etc.), siloxy, or combinations thereof, and *d* represents a positive integer of from 1 to 3. Typical compounds embraced by Formula III above include methylsilane, dimethylsilane, trimethylsilane, ethylsilane, diethylsilane, triethylsilane, butylsilane, n-propylsilane, alkyl halogenosilanes, dimethylchlorosilane, ethyldichlorosilane, diethylchlorosilane, propyldichlorosilane, diphenylsilane, triphenylsilane, ethyldiphenylsilane, methylphenylsilane, dihexylphenylsilane, etc., and their hydrolysis products. Typical silane compounds useful in practicing our invention are described in the Gray U.S. Patent 2,694,637, issued November 16, 1954.

Other reduction sensitizers useful in practicing our invention includes stannous chloride, spermine, sodium formaldehyde sulfoxalate, etc.

The concentration of the chemical sensitizers and antifoggants used in our invention can be varied, depending upon the concentration of silver halide, concentration of gelatin, degree of ripening of the silver halide, molecular weight of sensitizer, efficiency of sensitizer, etc., and the amounts given below are merely illustrative. In general, we have found that from 1 to 10 mg. per mole of silver halide of sulfur sensitizer is adequate for the purposes of our invention. In like manner, the concentration of gold salt or compound can advantageously vary from about 0.5 to 10 mg. per mole of silver halide, although larger amounts can be employed. The amount of reduction sensitizer can likewise vary, although we have found that generally from about 0.05 to 100 mg. per mole of silver halide is quite adequate. The concentration of aldehyde antifoggant can likewise vary, depending upon the desired time of digestion with the aldehyde, temperature of digestion, amount of gold sensitizer employed, etc. In general, we have found that from about 0.5 to 15 g. per mole of silver halide is adequate for the purposes of our invention. The optimum amount of aldehyde antifoggant and chemical sensitizer 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, or chemical sensitizer, and temperature of digestion are varied. This technique is illustrated in the following examples.

The following examples will serve to illustrate our invention:

A fine-grain, low gelatin, positive speed silver bromiodide emulsion was prepared and washed by the acid coagulation described in Yutzy and Frame U.S. Patent 2,614,928, issued October 21, 1952. The pH of the emulsion was adjusted to 6.0 and the emulsion was then sensitized by the addition of 3.5 mg./mole of silver halide of a sulfur sensitizer of the type shown in Sheppard U.S. Patent 1,623,499 (e.g., allylthiourea), 2 mg./mole of silver halide of a water-soluble gold salt of the type shown in Waller et al. U.S. Patent 2,399,083 (e.g., sodium chloroaurate), and 50 mg./mole of silver halide of a water-soluble thiocyanate, followed by heating for 30 minutes at 60° C. Samples of this emulsion were then cooled to 40° C. and reduction sensitized by treatment with from 0.25 to 0.50 mg./mole of silver halide, of stannous chloride and heated further at 60° C. The fog levels obtained after these finishes were compared with those of other samples of the same emulsion which were digested with m-hydroxybenzaldehyde (amount given in table below) before the stannous chloride treatment. The emulsions were then exposed on an intensity scale sensitometer (Eastman Type I*b*) and developed in a developer having the following composition for 6 minutes at 68° F.:



D–16

| | Grams |
|---|---|
| N-methyl-p-aminophenol sulfate | 0.3 |
| Hydroquinone | 6.0 |
| Sodium sulfite (dry) | 38.0 |
| Sodium bisulfite | 1.5 |
| Sodium carbonate monohydrate | 22.0 |
| Sodium bromide | 0.78 |
| Citric acid | 0.7 |

Water to make 1 liter.

The emulsions were then fixed, washed and dried in the usual manner and the relative speed values, gamma and fogs were measured. The relative speed value is inversely proportional to the exposure required to give a density of about 0.3 above fog. The data obtained are given in Table I below.

*Table I*

| Coating No. | Coating Description | Relative Speed | Gamma | Fog |
|---|---|---|---|---|
| (*a*) | Control, sulfur and gold sensitized | 100 | 2.96 | 0.10 |
| (*b*) | Control + sulfur and gold, then + stannous chloride and heat at 60° C. | ---- | fogged | 1.45 |
| (*c*) | (*a*) plus 5 g./m. m-hydroxybenzaldehyde 15 min. at 40° C., then stannous chloride and then reheated at 60° C. | 120 | 2.24 | 0.41 |
| (*d*) | (*a*) plus 5 g./m. m-hydroxybenzaldehyde 30 min. at 40° C., then stannous chloride and then reheated at 60° C. | 141 | 2.50 | 0.30 |
| (*e*) | (*a*) plus 5 g./m. m-hydroxybenzaldehyde 4 hours at 40° C., then stannous chloride and then reheated at 60° C. | 145 | 2.38 | 0.15 |

The following data were obtained in the same manner as those of Table I and illustrate the effect of other aldehyde compounds.

*Table II*

| Coating No. | Coating Description (g./mol. AgX) | Relative Speed | Gamma | Fog |
|---|---|---|---|---|
| (*a*) | Control (sulfur and gold sensitized) | 100 | 2.80 | 0.10 |
| (*b*) | Control plus stannous chloride and heated at 60° C. | ---- | ---- | 2.02 |
| (*c*) | Control + 5 g./m. p-hydroxybenzaldehyde held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 316 | 2.34 | 0.52 |
| (*d*) | Control + 5 g./m. p-hydroxybenzaldehyde held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 331 | 2.60 | 0.47 |
| (*e*) | Control + 5 g./m. p-hydroxybenzaldehyde held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 389 | 2.78 | 0.40 |

*Table II*—Continued

| Coating No. | Coating Description (g./mol. AgX) | Relative Speed | Gamma | Fog |
|---|---|---|---|---|
| (*f*) | Control + 10 g./m. p-hydroxybenzaldehyde held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 263 | 2.84 | 0.20 |
| (*g*) | Control + 10 g./m. p-hydroxybenzaldehyde held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 276 | 2.68 | 0.16 |
| (*h*) | Control + 10 g./m. p-hydroxybenzaldehyde held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 331 | 2.66 | 0.14 |
| (*i*) | Control (sulfur and gold sensitized) | 100 | 2.60 | 0.10 |
| (*j*) | Control + stannous chloride and then reheated at 60° C. | | | 1.20 |
| (*k*) | Control + 1 g./m. vanillin held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 490 | 3.08 | 0.28 |
| (*l*) | Control + 1 g./m. vanillin held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 457 | 2.98 | 0.29 |
| (*m*) | Control + 1 g./m. vanillin held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 447 | 2.14 | 0.22 |
| (*n*) | Control (sulfur and gold sensitized) | 100 | 3.46 | 0.10 |
| (*o*) | Control + stannous chloride and then reheated at 60° C. | | | 0.80 |
| (*p*) | Control + 1 g./m. mucochloric acid held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 246 | 1.71 | 0.50 |
| (*q*) | Control + 1 g./m. mucochloric acid held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 251 | 1.69 | 0.47 |
| (*r*) | Control + 1 g./m. mucochloric acid held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 219 | 1.87 | 0.39 |
| (*s*) | Control + 5 g./m. mucochloric acid held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 174 | 1.93 | 0.23 |
| (*t*) | Control + 5 g./m. mucochloric acid held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 159 | 1.49 | 0.20 |
| (*u*) | Control + 5 g./m. mucochloric acid held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 138 | 1.59 | 0.22 |
| (*v*) | Control + 10 g./m. mucochloric acid held 15′ at 40° C. then + stannous chloride and then reheated at 60° C. | 276 | 2.52 | 0.23 |
| (*w*) | Control + 10 g./m. mucochloric acid held 30′ at 40° C. then + stannous chloride and then reheated at 60° C. | 162 | 2.04 | 0.13 |
| (*x*) | Control + 10 g./m. mucochloric acid held 4 hrs. at 40° C. then + stannous chloride and then reheated at 60° C. | 209 | 1.93 | 0.17 |

The data in the following table were obtained in the same manner as those of Tables I and II and illustrate the effect of another reduction sensitizer.

*Table III*

| Coating No. | Coating Description | Relative Speed | Gamma | Fog |
|---|---|---|---|---|
| (*a*) | Control (sulfur and gold sensitized emulsion). | 100 | 3.32 | 0.07 |
| (*b*) | Control + .25 mg. formamidine sulfinic acid per Ag mole held for 30 minutes at 60° C. | 37 | 3.26 | 0.47 |
| (*c*) | Control + .50 mg. formamidine sulfinic acid per Ag mole held for 30 minutes at 60° C. | | | 1.09 |
| (*d*) | Control + 5 gm. vanillin per Ag mole held for 60 minutes at 40° C. | 80 | 3.02 | 0.06 |
| (*e*) | As in (*d*) above + .25 mg. formamidine sulfinic acid per Ag mole held for 30 minutes at 60° C. | 112 | 3.36 | 0.10 |
| (*f*) | As in (*d*) above + .50 mg. formamidine sulfinic acid per Ag mole held for 30 minutes at 60° C. | 162 | 3.42 | 0.13 |

It has been found that certain aldehydes, such as benzaldehyde, o-hydroxybenzaldehyde, succinic dialdehyde, maleic dialdehyde, etc., do not function as antifoggants in our invention. It is important in the case of aromatic aldehydes that they contain a substitutent in either the 3- or 4-position with respect to the aldehyde group. The emulsions used in our invention can be either acidic or basic emulsions, depending upon the type of reduction sensitizer used. Some types of reduction sensitizing, such as with silane compounds, are most effective in alkaline emulsions. Other types of reduction sensitizing operate in either acidic or basic emulsions.

The photographic emulsions used in practicing our 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 stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952.

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 1,943,854, 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 Novem-

ber 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 15, 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, 1950), 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 be hardened with any suitable hardener for gelatin, such as formaldehyde; a compound having a plurality of acid anhydride groups such as 7,8-diphenyl-bicyclo (2,2,2)-7-octene-2,3,5,6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride, such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone, such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness Canadian Patent 588,451, issued December 8, 1959; a bis-aziridine carboxamide such as trimethylene bis((1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956 (now U.S. Patent 2,950,197, issued August 23, 1960); 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959, or the bisiocyanate of Henn et al. U.S. patent application Serial No. 805,357, filed April 10, 1959.

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 7, 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 July 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 Knox and Wright 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 crystals 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.

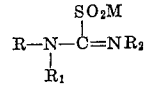
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt, and a reduction sensitizer, said photographic silver halide emulsion having been digested subsequent to sensitization with said gold salt, but prior to sensitization with said reduction sensitizer, in the presence of a compound selected from the class consisting of p-hydroxybenzaldehyde, m-hydroxybenzaldehyde and vanillin.

2. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt, and a reduction sensitizer, said photographic silver halide emulsion having been digested in the presence of a compound selected from the class consisting of mucochloric acid, a water-soluble salt of mucochloric acid, mucobromic acid and a water-soluble salt of mucobromic acid subsequent to sensitization with said gold salt, but prior to sensitization with said reduction sensitizer.

3. A photographic silver halide emulsion as defined in claim 2 wherein said reduction sensitizer is stannous chloride.

4. A photographic silver halide emulsion as defined in claim 2 wherein said reduction sensitizer is a compound selected from those represented by the following general formula:

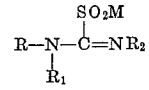


wherein R, $R_1$ and $R_2$ each represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group.

5. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt and stannous chloride, said photographic silver halide emulsion having been digested subsequent to sensitization with said gold salt, but prior to sensitization with said stannous chloride in the presence of mucochloric acid.

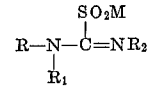


6. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt and a reduction sensitizer selected from those represented by the following general formula:



wherein R, $R_1$ and $R_2$ each represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group, said photographic silver halide emulsion having been digested subsequent to sensitization with said gold salt but prior to sensitization with said reduction sensitizer in the presence of an aldehyde selected from the class consisting of p-hydroxybenzaldehyde, m-hydroxybenzaldehyde and vanillin.

7. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt and a reduction sensitizer selected from those represented by the following general formula:



wherein R, $R_1$ and $R_2$ each represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group, said photographic silver halide emulsion having been digested subsequent to sensitization with said gold salt but prior to sensitization with said reduction sensitizer in the presence of mucochloric acid.

8. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt and formamidine sulfinic acid, said photographic silver halide emulsion having been digested subsequent to sensitization with said gold salt and prior to sensitization with said formamidine sulfinic acid in the presence of mucochloric acid.

9. A photographic silver halide emulsion sensitized with a labile sulfur compound, a gold salt and a reduction sensitizer comprising a silane compound containing at least one silicon-hydrogen bond, such photographic silver halide emulsion having been digested prior to sensitization with said gold salt in the presence 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 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 a hydroxyl group, a hydrogen atom, a lower alkyl group and an alkoxyl group.


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