

1

3,061,437

SULFONE BIS-QUATERNARY SALTS AS SENSITIZERS FOR PHOTOGRAPHIC EMULSIONS

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16 Claims. (Cl. 96—108)

This invention relates to photographic silver halide emulsions, and more particularly, to an improved means for sensitizing such photographic silver halide emulsions.

A number of methods have been previously described for increasing the sensitivity of photographic silver halide emulsions, other than methods of optical or spectral sensitization which involve the incorporation of certain colored compounds or dyes in the emulsions. The incorporation of such dyes in the emulsions increases the optical range of sensitivity, and for this reason such dyes are commonly referred to as optical or spectral sensitizing dyes. It is also well known to increase the sensitivity of photographic emulsions by addition of sulfur compounds capable of reacting with silver salts to form silver sulfide, or with reducing agents (compounds of these types are also naturally present in gelatin), or with salts of gold or other noble metals, or with combinations of two or more of the aforementioned compounds generally known as chemical sensitizers. Such chemical sensitizers are believed to react with the silver halide to form, on the surface of the silver halide, minute amounts of silver sulfide or of silver or of other noble metals, and these processes are capable of increasing the sensitivity of developing-out emulsions by very large factors. The process of chemical sensitization, however, reaches a definite limit beyond which further addition of sensitizer, or of further digestion with the sensitizer present, merely increases the fog of the photographic emulsion with constant or decreasing speed.

We have now found a means of further increasing the sensitivity of photographic emulsions which may be applied even though the ordinary processes of chemical sensitization have been carried to the effective limit of the photographic emulsion in question. Our process is to be distinguished from hypersensitization, which is produced by bathing a finished coating with water or with solutions of ammonia, amines or silver salts. Such processes act primarily on optically sensitized photographic emulsions and tend to increase the free silver ion concentration of the emulsion and greatly diminish its stability. Our process is also to be distinguished from hypersensitization by mercury vapor, which gives a transitory effect which is lost on storage of the film. The compounds used in our invention do not appear to be chemical sensitizers in the usual sense, since they increase speed by their presence during exposure and processing and require no digestion with the photographic emulsion to produce an increase in speed, nor does their chemistry indicate that they are likely to react with silver halide under normal emulsion conditions.

The novel sensitizers of our invention are quite unique in that the effects produced are additive in photographic emulsions which have already been sensitized to their optimum, or near-optimum, with conventional chemical sensitizers, such as labile sulfur compounds. The novel sensitizers of our invention, however, can be used to sensitize photographic silver halide emulsions containing no other sensitizers, if desired. The novel sensitizers of our invention are not strictly chemical sensitizers, since chemical sensitizers do not generally provide the additive effects of the type mentioned.

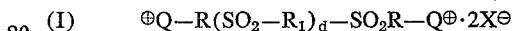
It is, therefore, an object of our invention to provide

2

photographic silver halide emulsions which have been sensitized with various non-polymeric compounds containing sulfone groups and quaternary ammonium groups. Another object of our invention is to increase the sensitivity of ordinary photographic silver halide emulsions which have been sensitized with chemical sensitizers, such as compounds containing labile sulfur atoms, and/or gold-containing compounds. Other objects will become apparent from a consideration of the following description and examples.

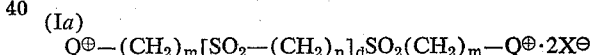
According to our invention, we have found that the sensitivity of an ordinary photographic silver halide emulsion can be materially increased by incorporating therein non-polymeric compounds which can be characterized as sulfone bis-quaternary salts.

The sensitizing compounds useful in practicing our invention include compounds represented by the following general formula:



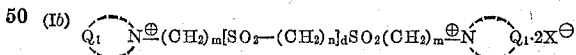
wherein R and R₁ each represents an alkylene group, such as ethylene, trimethylene, tetramethylene (butylene), methyl-substituted ethylene, methyl-substituted trimethylene, pentamethylene, ethyl-substituted tetramethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, etc. (e.g., a hydrocarbon alkylene group containing from about 2 to 10 carbon atoms), d represents a positive integer of from about 1 to 3, Q[⊕] represents an organic quaternary ammonium group, such as pyridinium, picolinium, collidinium, N-methylpiperidinium, N-ethylpiperidinium, triethyl ammonium, diethylmethyl ammonium, tripropyl ammonium, diethylbutyl ammonium, N-methylmorpholinium, etc., and X represents an acid anion or radical, such as perchlorate, p-toluenesulfonate, benzenesulfonate, methylsulfate, ethylsulfate, bromide, etc.

An especially useful group of sensitizing compounds embraced by Formula I above is that represented by the following general formula:



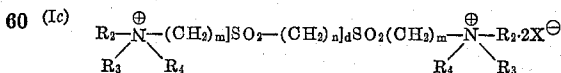
wherein Q[⊕], X and d each have the values given above, and m and n each represents a positive integer of from about 2 to 10.

A useful group of compounds according to our invention containing heterocyclic quaternary ammonium groups is the group represented by the following general formula:



wherein d, m, n and X each have the values given above, and Q₁ represents the non-metallic atoms necessary to complete a heterocyclic monoazine ring, such as pyridine, picoline, collidine, etc.

Another group of useful sensitizers embraced by Formula Ia is that represented by the following general formula:

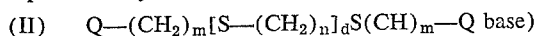


wherein d, m, n and X each have the values given above, and R₂, R₃ and R₄ each represents a lower alkyl group, such as methyl, ethyl, propyl, butyl, etc.

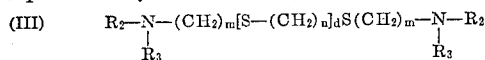
The compounds of Formulas I-Ic above can advantageously be prepared according to methods which have been previously described in the prior art. For example, the compounds of Formula Ib can be prepared by condensing the hydroxy compounds of Williams and Cossar U.S. application Serial No. 843,638, filed October 1, 1959, with an organic sulfonyl chloride, followed by condensa-

3

tion of the resulting organic sulfonic ester with a heterocyclic amine, such as pyridine, picolines, collidines, etc. The resulting thioether compound can then be oxidized to the desired sulfone by treatment with hydrogen peroxide in acetic acid solution, or by other oxidizing agents, such as hypochlorous acid, and the like. The compounds of Formula Ia, wherein Q represents the non-metallic atoms necessary to complete a piperidine ring, or the like, can be prepared by quaternating a compound selected from those represented by the following general formula:

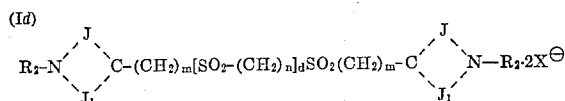


wherein Q, d, m and n each have the values given above with an organic sulfonic ester; such as dimethyl sulfate, diethyl sulfate, methyl benzenesulfonate, methyl p-toluenesulfonate, etc. The resulting thioether compound can then be oxidized to the desired sulfone by treatment with hydrogen peroxide in acetic acid solution, or by other oxidizing agents, such as hypochlorous acid, and the like. In like manner, the compounds of Formula Ic can be prepared by quaternating a compound selected from those represented by the following general formula:

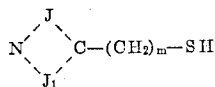


wherein R₂, R₃, d, m, and n each have the values given above with an organic sulfonic ester, such as dimethyl sulfate, diethyl sulfate, methyl benzenesulfonate, methyl p-toluenesulfonate, etc. The resulting thioether compound can then be oxidized to the desired sulfone by treatment with hydrogen peroxide in acetic acid solution, or by other oxidizing agents, such as hypochlorous acid, and the like.

Still another useful group of sensitizers embraced by our invention include those represented by the following general formula:



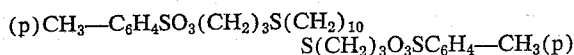
wherein R₂, d, m, n and X each have the values given above, and J and J₁ together represent the non-metallic atoms necessary to complete a pyridine ring, which may contain conventional substituents, such as methyl, ethyl, chlorine, etc. In the compounds of Formula Id, it will be noted that the quaternary nitrogen atom is not attached to the terminal carbon atoms of the intercycle chain, as contrasted with the nitrogen atoms of Formula Ib, which are attached to these carbon atoms. The compounds of Formula Id can be prepared in a manner similar to that outlined above. For example, these compounds can be prepared by condensing together a dihalogenated alkane, or thiaalkane, with a pyridylalkanethiol of the following general formula:



wherein J, J₁, and m have the values given above. The resulting thioether compound can then be quaternated with an organic sulfonic ester, such as those illustrated above, followed by oxidation with an aqueous solution containing hydrogen peroxide and acetic acid or another oxidizing bath, such as is illustrated above.

The preparation of the compounds useful in practicing our invention and the necessary intermediates are described in the following examples.

Example 1.—1,18-Di-p-Toluenesulfonyl-4,15-Dithiaoctadecane

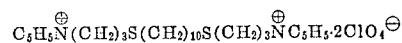


A mixture of 31.2 g. (0.1 mole) of 4,15-dithiaoctadecane-1,18-diol and 100 ml. of pyridine was treated with

4

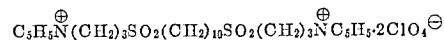
39.4 g. (0.23 mole) of p-toluenesulfonyl chloride. After one hour below 20° C., there were added 150 ml. of concentrated hydrochloric acid in one liter of water. The oil was extracted with chloroform, washed with dilute acid, and saturated brine, and dried over magnesium sulfate. Removal of the solvent at reduced pressure yielded 41 g. of a light brown oil.

Example 2.—4,15-Dithiaoctadecane-1,18-Bis(Pyridinium Perchlorate)



A solution of 21 g. of the product from Example 1 and 10 g. of pyridine was heated at the boiling point for 10 minutes, cooled, and poured into ether. The solid was filtered, washed with ether, dissolved in water, and treated with an excess of sodium perchlorate. The yield of colorless solid was 13 g. (the intermediate p-toluenesulfonate salt may be used directly in the next step).

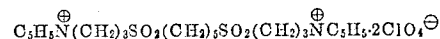
Example 3.—4,4,15,15-Tetroxo-4,15-Dithiaoctadecane-1,18-Bis(Pyridinium Perchlorate)



The 13 g. of product from Example 2 were dissolved in 500 ml. of acetic acid, heated to 60° C., and 15 g. of 30 percent hydrogen peroxide added. After 24 hours at 60° C., the solvent was removed at reduced pressure and the product recrystallized from acetone; yield, 4 g.; M.P. 86° C.

Analysis.—Calcd. for C₂₆H₄₂Cl₂N₂O₁₂S₂: C, 44.0; H, 5.9; N, 3.9. Found: C, 44.4; H, 6.0; N, 3.8.

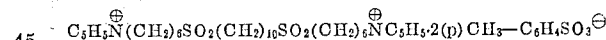
Example 4.—4,4,10,10-Tetroxo-4,10-Dithiatridecane-1,13-Bis(Pyridinium Perchlorate)



By a procedure similar to that of Examples 1–3, the title compound having M.P. 235° C. (dec.) was prepared.

Analysis.—Calcd. for C₂₁H₃₂Cl₂N₂O₁₂S₂: C, 39.4; H, 5.0; N, 4.4. Found: C, 38.5; H, 5.1; N, 3.6.

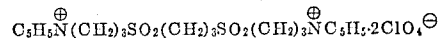
Example 5.—7,7,18,18-Tetroxo-7,18-Dithiatetradecane-1,24-Bis(Pyridinium p-Tosylate)



By the method of Examples 1–3, this compound having melting point 125–130° C. was prepared.

Analysis.—Calcd. for C₄₆H₆₁N₂O₁₀S₄: C, 60.0; H, 7.3; N, 3.0; S, 13.7. Found: C, 58.4; H, 7.6; N, 3.1; S, 13.5.

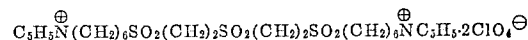
Example 6.—4,4,8,8-Tetroxo-4,8-Dithiaundecane-1,11-Bis(Pyridinium Perchlorate)



This compound, prepared according to Examples 1–3 and recrystallized from nitromethane, melted at 203–205° C.

Analysis.—Calcd. for C₁₉H₂₈Cl₂N₂O₁₂S₂: C, 37.4; H, 4.6; N, 4.6. Found: C, 38.1; H, 4.9; N, 4.6.

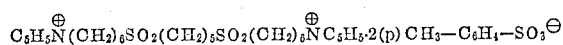
Example 7.—7,7,10,10,13,13-Hexoxo-7,10,13-Tri-thianonadecane-1,19-Bis(Pyridinium Perchlorate)



This compound, prepared in the usual manner, melted with decomposition at ca. 160° C.

Analysis.—Calcd. for C₂₆H₄₂Cl₂N₂O₁₄S₃: C, 40.3; H, 5.4; N, 3.6; S, 12.4. Found: C, 39.2; H, 5.6; N, 3.0; S, 12.0.

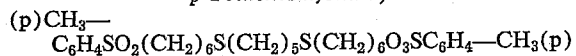
Example 8.—7,7,13,13-Tetroxo-7,13-Dithianonadecane-1,19-Bis(Pyridinium p-Toluenesulfonate)



This compound, prepared as in Examples 1–3, melted at 187–190° C.

Analysis.—Calcd. for $C_{41}H_{58}N_2O_{10}S_4$: C, 56.7; H, 6.7; N, 3.2; S, 14.7. Found: C, 56.0; H, 6.7; N, 3.4; S, 15.1.

Example 9.—7,13-Dithianonadecane-1,19-Bis(Pyridinium *p*-Toluenesulfonate)

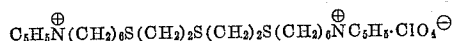


(Intermediate for Example 8.) A solution of 34 g. of 7,13-dithia-1,19-nonadecanediol in 100 ml. of pyridine was treated with 50 g. of *p*-toluenesulfonyl chloride at

−20° C., and kept cold overnight. The mixture was worked up as in Example 1 and the resulting oil boiled for 15 minutes in excess pyridine. The solution was cooled and poured into ether to give a colorless, hygroscopic solid of M.P. 130–132° C., after drying in vacuo.

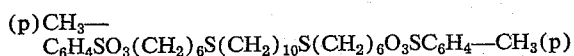
Analysis.—Calcd. for $C_{41}H_{58}N_2S_4O_6$: C, 61.3; H, 7.3; N, 3.5; S, 15.9. Found: C, 61.0; H, 7.3; N, 3.2; S, 15.6.

Example 10.—7,10,13-Trithianonadecanebis(Pyridinium Perchlorate)



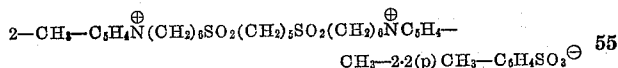
(Intermediate for Example 7.) The *p*-toluenesulfonate salt, obtained from 7,10,13-trithia-1,19-nonadecanediol as in Example 9, was treated in aqueous solution with excess sodium perchlorate. Removal of the solvent and recrystallization from ethanol gave a crystalline solid of M.P. >235° C. (dec.)

Example 11.—7,18-Dithiatetracosane-1,24-Bis(Pyridinium *p*-Toluenesulfonate)



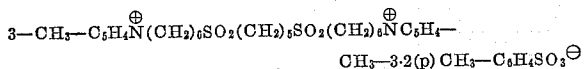
(Intermediate for Example 5.) Prepared as in Example 9 this compound, recrystallized from ether-ethanol, melted at 143–145° C.

Example 12.—7,7,13,13-Tetroxo-7,13-Dithianonadecane-1,19-Bis(2-Picolinium *p*-Toluenesulfonate)



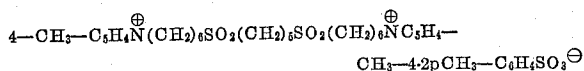
By a procedure similar to that of Examples 9 and 3 and using 2-picoline in place of pyridine, this compound of M.P. 85–90° C. was prepared.

Example 13.—7,7,13,13-Tetroxo-7,13-Dithianonadecane-1,19-Bis(3-Picolinium *p*-Toluenesulfonate)



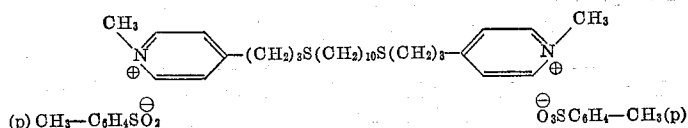
This was obtained as in Examples 9 and 3 by use of 3-picoline as an uncrystallizable oil.

Example 14.—7,7,13,13-Tetroxo-7,13-Dithianonadecane-1,19-Bis(4-Picolinium *p*-Toluenesulfonate)



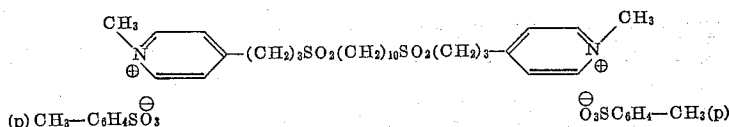
This compound, obtained as in Examples 9 and 3 from 4-picoline, melted at 79–80° C.

Example 15.—1,18-Di- γ -Pyridyl-4,15-Dithiaoctadecane Bismetho-*p*-Toluenesulfonate



A solution of 44.4 g. of 1,18-di- γ -pyridyl-4,15-dithiaoctadecane and 37.2 g. of methyl *p*-toluenesulfonate in 200 ml. of ethanol was refluxed for 4 hours. Evaporation of the solvent and recrystallization from acetone produced colorless crystals of M.P. 100–102° C.

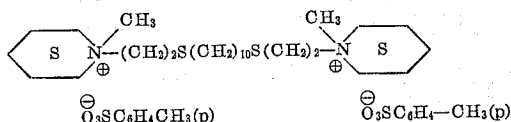
Example 16.—1,18-Di- γ -Pyridyl-4,4,15,15-Tetroxo-4,15-Dithiaoctadecane Bismetho-*p*-Toluenesulfonate



A solution of 15 g. of the sulfide from Example 15 and 5 g. of 30 percent hydrogen peroxide in glacial acetic acid was heated at 60° C. for 24 hours. The solvent was removed at reduced pressure, the residue dissolved in methanol, decolorized with activated carbon and the solvent removed to give the light amber, oily sulfone.

Analysis.—Calcd. for $C_{42}H_{60}N_2S_4O_{10}$: C, 57.3; H, 6.8; N, 3.2; S, 14.5. Found: C, 56.4; H, 7.0; N, 3.1; S, 14.3.

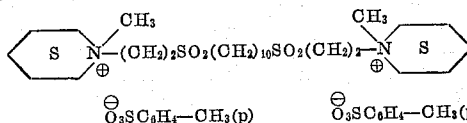
Example 17.—3,14-Dithiahexadecane-1,16-Bis(*N*-Methylpiperidinium *p*-Toluenesulfonate)



A solution of 48.7 g. of 1,16-bis(1-piperidyl)-3,14-dithiahexadecane and 53 g. of methyl *p*-toluenesulfonate in methanol was refluxed for 16 hours, the solvent removed and the residue dissolved in ethanol. Precipitation with ether produced 86 g. of crystalline solid of M.P. 155–157° C.

Analysis.—Calcd. for $C_{40}H_{68}N_2S_4O_6$: C, 60.0; H, 8.5; N, 3.5; S, 16.0. Found: C, 59.0; H, 8.5; N, 3.1; S, 16.3.

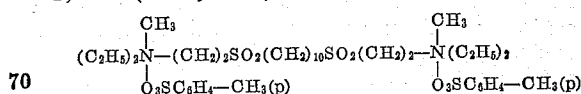
Example 18.—3,14-Dithia-3,3,14,14-Tetroxohexadecane-1,16-Bis(*N*-Methylpiperidinium *p*-Toluenesulfonate)



A solution of 60 g. of the sulfide of Example 17 and 36 ml. of 30 percent hydrogen peroxide in acetic acid was heated at 50–60° C. for 16 hours. The solvent was removed at reduced pressure, the residue dissolved in ethanol and precipitated with ether, then recrystallized from ethanol; M.P. 175–178° C.

Analysis.—Calcd. for $C_{40}H_{68}N_2S_4O_{10}$: C, 55.7; H, 7.9; N, 3.2; S, 14.8. Found: C, 54.7; H, 7.9; N, 2.9; S, 14.4.

Example 19.—3,14-Dithia-3,3,14,14-Tetroxohexadecane-1,16-Bis(Diethylmethylammonium *p*-Toluenesulfonate)

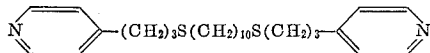


This compound, a viscous oil, was obtained by the procedures described in Examples 17, 18 and 20 from β -diethylaminoethanethiol.

The following examples will serve to illustrate the

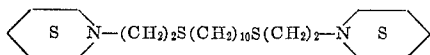
method of preparing the two intermediates required for Examples 15 and 17 above.

Example 20.—1,18-Di-γ-Pyridyl-4,15-Dithiaoctadecane



To a solution of 9.2 g. of sodium in 500 ml. of absolute methanol were added 16.6 of γ-3-mercaptopyrpyridine, followed by 60.2 g. of 1,10-dibromodecane. After a 2-3 hour reflux period, one liter of water was added, the mixture extracted with chloroform, the extracts decolorized with carbon, dried over magnesium sulfate and evaporated to a yellow crystalline mass.

Example 21.—1,16-Bis(1-Piperidyl)-3,14-Dithiahexadecane



This was prepared by the procedure of Example 20, using 9.2 g. of sodium, 500 ml. of methanol, 58 g. of β-1-piperidinoethanethiol and 60 g. of 1,10-dibromodecane. The product, an oil, weighed 62 g.

The sensitizing compounds of our invention can be added to ordinary photographic silver halide emulsions for the purpose of increasing the sensitivity thereof, as has been indicated above.

The preparation of photographic silver halide emulsions involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, usually by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The sensitizers of our invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating. Our new photographic sensitizers require no special final digestion or after-ripening.

The particular quantity of sensitizer used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. The amount used is also dependent upon the particular stage at which the sensitizer was added during the preparation of the emulsion. We have found that generally from about 50 mg. to about 5 g. of sensitizer per mole of silver halide are quite adequate to accomplish the desired sensitization.

The sensitizers of our invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the sensitizers can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. As indicated above, the solvent should be selected so that it has no harmful effect upon the emulsion, and generally solvents or diluents which are miscible with water are to be preferred. Water is a dispersing medium for many of the sensitizers of the invention. In a preferred embodiment, the sensitizer can be dissolved in a solvent, such as water, ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form. If desired, certain of the sensitizers can be prepared in finely-divided form and dispersed in water alone, or in the presence of a suitable dispersing agent (such as alkali metal salts of aromatic or aliphatic sulfonic acids) and added to the emulsion in this form. It is quite apparent that the sensitizers of our invention should have sufficient water-dispersibility so that they can be adsorbed to or associated with the grains of the silver halide present in the emulsion

in sufficient amount to sensitize the emulsion. It is apparent that the optimum amount for each of the sensitizers will vary somewhat from emulsion to emulsion and from compound to compound. The optimum amount of any given sensitizers can be determined for any particular emulsion by running a series of tests in which the quantity of sensitizer is varied over a given range. Exposure of the treated emulsion in conventional photographic testing apparatus, such as an intensity scale sensitometer, will reveal the most advantageous concentrations for that sensitizer in that particular emulsion. Such matters are well understood by those skilled in the art.

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

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those 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, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

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 chloropalladate, 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 anti-foggants 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 gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or 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. Suitable compounds are potassium chloraurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurisulfobenzothiazole methochloride.

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, or Dann and Chechak U.S. application Serial No. 779,874, filed December 12, 1958, or the quaternary ammonium salts and PEG's 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, 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 be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; 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(methane-sulfonyl)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxy-methylbenzimidazol-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 glutaralde-

hyde bis-sodium bisulfite as described in Allen and Burness U.S. patent application Serial No. 556,031, filed December 29, 1955 (now abandoned); 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); or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 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 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 mono-ester 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. octylphenoxy-pentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; 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).

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 bromiodide. 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. 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 acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 or an imidized polyacrylamide of like acrylamide content and viscosity 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 2,808,331, 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 sensitizing compounds of our invention can be used both in emulsions intended for black-and-white photography, or emulsions intended for color photography. When used for this latter purpose, they can be used in emulsions containing color-forming compounds or couplers, or they can be used in emulsions which are to be color-developed in developers containing the color-forming compounds or couplers. In either type of color photography, the particular color-forming compounds or couplers react with the oxidation products of color developers (particularly phenylenediamine developers) to provide subtractively-colored images. The color-forming compounds can be of the customary types employed in color photography, such as pyrazolone couplers for formation of the magenta image, phenolic couplers for formation of the cyan image and open-chain compounds containing a reactive methylene group for formation of the yellow image. Such couplers can be of the type which can be dispersed in a high-boiling, crystalloidal compound, which can be used as a vehicle for incorporating the color-forming compound in the photographic emulsion, or such couplers can be of the "fat-tail" varieties (see, for example, F.I.A.T., Final Report, No. 721, for examples thereof) which can be dispersed in the photographic silver halide emulsions. Both of these types of couplers are characterized by non-diffusing properties from the particular silver halide emulsions in which they are incorporated. The couplers or color-forming compounds can be incorporated

in the silver halide emulsions by any of the common methods known to those skilled in the art.

Typical color-forming compounds or couplers which are useful in color photography, according to our invention, include the following:

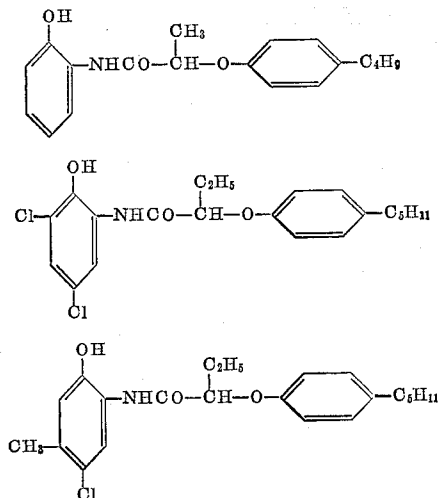
Couplers Producing Cyan Images

5-(p-amyphenoxybenzenesulfonamino)-1-naphthol
5-(N-benzyl-N-naphthalenesulfonamino)-1-naphthol
5-(n-benzyl-N-n-valeryl-amino)-1-naphthol
5-caproylamino-1-naphthol
2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
2,4-dichloro-5-(p-nitrobenzoyl-β-o-hydroxyethylamino)-1-naphthol
2,4-dichloro-5-palmitylamino-1-naphthol
2,2'-dihydroxy-5,5'-dibromostilbene
5-diphenylethersulfonamido-1-naphthol
1-hydroxy-2-(N-isoamyl-N-phenyl)naphthamide
1-hydroxy-2-(N-p-sec. amylphenyl)naphthamide
8-hydroxy-1-α-naphthoyl-1,2,3,4-tetrahydroquinoline
2-lauryl-4-chlorophenol
1-naphthol-2-(N-carboxylic-α-naphthalide
1-naphthol-5-sulfo-cyclohexylamide
5-phenoxyacetamino-1-naphthol
5-β-phenylpropionylamino-1-naphthol
Monochlor-5-(N-γ-phenylpropyl-N-p-sec.-amylbenzoylamino)-1-naphthol
2-acetyl-amino-5-methylphenol
2-benzoylamino-3,5-dimethylphenol
2-α(p-tert. amylphenoxy)n-butrylamino-5-methylphenol
6-{γ-[4-(γ-(2,4-di-tert. amylphenoxy)butyramido]phenoxy}acetamido-2,4-dichloro-3-methylphenol
1-hydroxy-2-[δ-(2,4-di-tert. amylphenoxy)-n-butyl]naphthamide
2-α(p-tert. amylphenoxy)-n-butrylamino-4-chloro-5-methylphenol
2-(p'-tert. amylphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
2-phenylacetyl-amino-4-chloro-5-methylphenol
2-benzoylamino-4-chloro-5-methylphenol
2-anilinoacetyl-amino-4-chloro-5-methylphenol
2-{4-[α-(4''-tert. amylphenoxy)-n-butrylamino]benzoylamino}-4-chloro-5-methylphenol
2-[4',3''-(4'''-tert. amylphenoxy)benzoylamino]benzoylamino-4-chloro-5-methylphenol
2-p-nitrobenzoylamino-4-chloro-5-methylphenol
2-m-aminobenzoyl-4-chloro-5-methylphenol
2-acetamino-4-chloro-5-methylphenol
2(4'-sec. amylbenzamino)-4-chloro-5-methylphenol
2(4'-n-amyloxybenzamino)-4-chloro-5-methylphenol
2(4'-phenoxybenzoylamino)phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
2-[α-(4'-tert. butylphenoxy)propionylamino]phenol
2-[α-(4'-tert. amyl)phenoxypropionylamino]phenol
2-[N-methyl-N-(4''-tert. amyl-3'-phenoxybenzoylamino)]phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-methyl-1-phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-6-methyl-1-phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,6-dimethyl-phenol
2-6-di(4''-tert. amyl-3'-phenoxybenzoylamino)-1-phenol
2-α-(4'-tert. amylphenoxy)butrylamino-1-phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
2-[α-(4'-tert. amylphenoxy)-n-butrylamino]-5-methyl-1-phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)-4-chloro-1-phenol
3-[α-(4'-tert. amylphenoxy)-n-butrylamino]-6-chloro-phenol

13

- 2-(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
- 2-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-6-chlorophenol
- 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-4-chlorophenol
- 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-5-chlorophenol
- 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-2-chlorophenol
- 2- α -(4'-tert. amylphenoxybutyrylamino)-5-chlorophenol
- 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-chlorophenol
- 5-benzene sulfonamino-1-naphthol
- 2,4-dichloro-5-benzenesulfonamino-1-naphthol
- 2,4-dichloro-5-(p-toluenesulfonamino)-1-naphthol
- 5-(1,2,3,4-tetrahydronaphthalene-6-sulfamino)-1-naphthol
- 2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
- 5-(quinoline-5-sulfamino)-1-naphthol

Any of the acylaminophenol couplers disclosed in Salminen and Weissberger U.S. Patent 2,423,730, dated July 8, 1947, can be used as couplers for the cyan image, e.g.



etc.

Couplers Producing Magenta Images

- 1-p-sec. amylphenyl-3-n-amyl-5-pyrazolone
- 2-cyanoacetyl-5-(p-sec. amylbenzoylamino)coumarone
- 2-cyanoacetylcoumarone-5-(n-amyl-p-sec. amylsulfanilide)
- 2-cyanoacetylcoumarone-5-(N-n-amyl-p-tert. amylsulfanilide)
- 2-cyanoacetylcoumarone-5-sulfon-N-n-butyranilide
- 2-cyanoacetyl-5-benzoylamino-coumarone
- 2-cyanoacetylcoumarone-5-sulfondimethylamide
- 2-cyanoacetylcoumarone-5-sulfon-N-methylanilide
- 2-cyanoacetylnaphthalene sulfon-N-methylanilide
- 2-cyanoacetylcoumarone-5-(N- γ -phenylpropyl)-p-tert. amylsulfonanilide
- 1-p-laurylphenyl-3-methyl-5-pyrazolone
- 1- β -naphthyl-3-amyl-5-pyrazolone
- 1-p-nitrophenyl-3-n-amyl-5-pyrazolone
- 1-p-phenoxyphenyl-3-n-amyl-5-pyrazolone
- 1-phenyl-3-n-amyl-5-pyrazolone
- 1,4-phenylene bis-3-(1-phenyl-5-pyrazolone)
- 1-phenyl-3-acetyl-amino-5-pyrazolone
- 1-phenyl-3-propionyl-amino-5-pyrazolone
- 1-phenyl-3-n-valeryl-amino-5-pyrazolone
- 1-phenyl-3-chloroacetyl-amino-5-pyrazolone
- 1-phenyl-3-dichloroacetyl-amino-5-pyrazolone
- 1-phenyl-3-benzoyl-amino-5-pyrazolone
- 1-phenyl-3-(m-aminobenzoyl)-amino-5-pyrazolone
- 1-phenyl-3-(p-sec. amylbenzoylamino)-5-pyrazolone
- 1-phenyl-3-diamylbenzoylamino-5-pyrazolone

14

- 1-phenyl-3- β -naphthoylamino-5-pyrazolone
- 1-phenyl-3-phenylcarbamyloamino-5-pyrazolone
- 1-phenyl-3-palmitoylamino-5-pyrazolone
- 1-phenyl-3-benzenesulfonylamino-5-pyrazolone
- 5 1-(p-phenoxyphenyl)-3-(p-tert. amyloxybenzoyl)-amino-5-pyrazolone
- 1-(2',4',6'-tribromophenyl)-3-benzamido-5-pyrazolone
- 1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone
- 1-(2',4',6'-trichlorophenyl)-3-phenylacetamido-5-pyrazolone
- 10 1-(2',4',6'-tribromophenyl)-3-phenylacetamido-5-pyrazolone
- 1-(2',4'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
- 15 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
- 1-(2',4',6'-tribromophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
- 1-(2',4',6'-trichlorophenyl)-3-[β -(2''',4'''-di-tert. amylphenoxy)propionamido]-5-pyrazolone
- 20 1-(2',4',6'-tribromophenyl)-3-[β -(2''',4'''-di-tert. amylphenoxy)propionamido]-5-pyrazolone
- 1-(2',5'-dichloro)-3-[3''-(4'''-tert. amylphenoxy)benzamido]-5-pyrazolone
- 25 1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert. amylphenoxy)benzamido]-5-pyrazolone
- 1-(2',5'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone

Couplers Producing Yellow Images

- 30 N-amyl-p-benzoylacetaminobenzenesulfonate
- N-(4-anisoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
- N-(4-benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
- 35 N-(4-benzoylacetaminobenzenesulfonyl)-N-n-amyl-p-toluidine
- N-(4-benzoylacetaminobenzenesulfonyl)-N-benzylaniline
- ω -(p-Benzoylbenzoyl)acetanilide
- 40 ω -Benzoylacet-2,5-dichloroanilide
- ω -Benzoyl-p-sec. amylacetanilide
- N,N'-di(ω -benzoylacetyl)-p-phenylenediamine
- N,N'-di(acetoacetamino)diphenyl
- α -[3-(α -(2,4-di-tert.-amylphenoxy)butyramido)benzoyl]-2-methoxyacetanilide
- 45 α -[3-(α -(2,4-di-tert.-amylphenoxy)acetamido)benzoyl]-2-methoxyacetanilide
- 4,4'-di(acetoacetamino)-3,3'-dimethyldiphenyl
- p,p'-di(acetoacetamino)diphenylmethane
- 50 Ethyl-p-benzoylacetaminobenzenesulfonate
- Nonyl-p-benzoylacetaminobenzenesulfonate
- N-phenyl-N'-(p-acetoacetaminophenyl)urea
- n-Propyl-p-benzoylacetaminobenzenesulfonate
- acetoacetpiperidine
- 55 ω -Benzoylacetpiperidide
- N-(ω -benzoylacetyl)-1,2,3,4-tetrahydroquinoline
- N-(ω -benzoylacetyl)morpholine

The above color-forming compounds produce colored images upon development of the exposed emulsions with color developers, such as the phenylenediamine color developers. Especially useful color developers are those derived from p-phenylenediamines containing at least one primary amino group, such as

- 60 N,N-dimethyl-p-phenylenediamine,
- 65 N,N-diethyl-p-phenylenediamine,
- N-carbamidomethyl-N-methyl-p-phenylenediamine,
- N⁴-carbamidomethyl-N⁴-tetrahydrofurfuryl-2-methyl-p-phenylenediamine,
- 70 N⁴-ethyl-N⁴-carboxymethyl-2-methyl-p-phenylenediamine,
- N⁴-ethyl-N⁴-tetrahydrofurfuryl-2-methyl-p-aminophenol,
- 75 3-acetyl-amino-4-aminodimethylaniline,

N-ethyl-N- β -methanesulfonamidoethyl-4-aminoaniline,
N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-4-
aminoaniline,
the sodium salt of N-methyl-N- β -sulfoethyl-p-phenylene-
diamine, etc.

As can be seen by reference to the large number of sensitizers included within our invention, as well as the large number of color-forming compounds which can be employed in combination therewith, a number of combinations of sensitizing compounds and color-forming compounds is possible. In order to determine quickly the effectiveness of a particular combination, it has been found that the screening technique described by Pontius and Thompson in "Photo. Sci. Eng.," vol. 1, pages 4-51, can be used to get an idea of the potential effectiveness of a given combination for use in a photographic color element containing a coupler. This technique does not necessitate the preparation of any coupler dispersions, but the sensitizers can be added to ordinary photographic silver halide emulsions of the type used in black-and-white photography, such as gelatino-silver-bromide emulsions, and the emulsions exposed in an intensity scale sensitometer to daylight quality radiation for a fraction of a second (usually $\frac{1}{25}$) and processed for about 15 minutes in a phenylenediamine color developer, to which has been added 10 g. per liter of H-acid. The pH of this developer is usually adjusted to 10.8 by adding sodium hydroxide. A suitable developer composition for this screening technique is as follows:

Benzyl alcohol	cc--	10
Sodium hexametaphosphate	g--	2.0
Sodium sulfite	g--	2.0
Sodium hydroxide	g--	3.4
H-acid (1-amino-8-naphthol-3,6-disulfonic acid	g--	10.0
4-amino-3-methyl-N-ethyl-N-(β -methyl sulfonamidoethyl)aniline sulfate	g--	8.0
Sodium carbonate monohydrate	g--	40.0
Sodium bromide	g--	1.5
Sodium thiocyanate	g--	0.2
Benzotriazole	g--	.03
Water total to 1 liter, pH 10.8 $\pm$.1.		

The following technique was used to determine the effectiveness of our compounds as sensitizers in photographic silver halide emulsions designed for black-and-white photography.

An ordinary photographic silver bromide emulsion containing a sensitizing dye, a sulfur sensitizer of the type mentioned in Sheppard U.S. Patent 1,623,499, mentioned above, and gold sensitized in the manner indicated in U.S. Patent 2,448,060, mentioned above, was divided into several portions. Sensitizing compounds obtained as described above and identified by the numbers given above, were then added in solutions in an organic solvent, such as ethanol or N,N-dimethylformamide in the amounts indicated in Table I below. The various portions of emulsions were then coated on transparent supports, such as cellulose acetate, and then dried. The dried coatings were exposed for about $\frac{1}{25}$ sec. to daylight quality radiation in Eastman Type 1b Sensitometer. The coatings were then developed for about 5 minutes in a photographic developer having the following composition:

	Gram
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite (dry)	30.0
Sodium borate	10.0
Potassium bromide	0.5
Water to make one liter.	

The relative speed, as compared with a portion of the same batch of emulsion containing no sulfone bis-quaternary salt, and fog for each of the coatings, was measured. The results are given in the following table.

TABLE

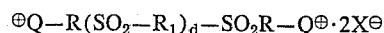
Coating No.	Compound of Example	Concentration, g./mol. Agr	Sensitizing Data	
			Speed	Fog
(a)-----	Control	-----	100	.14
(b)-----	6	3.0	129	.15
(c)-----	5	0.75	148	.38
(d)-----	5	3.0	178	.39
(e)-----	Control	-----	100	.15
(f)-----	3	0.75	142	.16
(g)-----	3	3.0	162	.17
(h)-----	Control	-----	100	.16
(i)-----	7	0.75	159	.17
(j)-----	7	3.0	174	.22
(k)-----	8	0.75	155	.20
(l)-----	8	3.0	170	.20
(m)-----	Control	-----	100	.11
(n)-----	4	0.75	142	.16
(o)-----	4	3.0	162	.17
(p)-----	Control	-----	100	.16
(q)-----	12	0.75	178	.21
(r)-----	12	3.0	240	.25
(s)-----	13	0.75	174	.22
(t)-----	13	3.0	263	.24
(u)-----	14	0.75	166	.18
(v)-----	14	3.0	224	.22
(w)-----	Control	-----	100	.13
(x)-----	16	0.75	214	.21
(y)-----	16	3.0	234	.23
(z)-----	Control	-----	100	.12
(a')-----	13	3.0	155	.14
(b')-----	Control	-----	100	.11
(c')-----	19	0.75	123	.11
(d')-----	19	3.0	141	.11

The effect of our new sulfone bis-quaternary salt sensitizers has been illustrated above with particular reference to ordinary photographic silver bromide emulsions, although it is to be understood that other silver halide emulsions can be employed to like advantage. While the prior art has previously suggested adding various sulfur sensitizers, including various thioether compounds, to photographic silver halide emulsions for the purpose of increasing sensitivity, it has been found that the sulfone compounds of our invention have marked advantages over the corresponding compounds containing thioether atoms in place of the sulfone groups. For example, while the compound of Example 5 above increased the speed of an ordinary photographic silver halide emulsion from 100 to 178 at a concentration of 3.0 g./mol. silver halide, the corresponding thioether compound decreased the speed of the same emulsion, at the same concentration, to 55 and gave a fog level of 0.48. Similarly, while the compound of Example 7 above increased the speed of an ordinary photographic silver bromide emulsion from 100 to 174 at a concentration of 3.0 g./mol. silver halide, the corresponding thioether compound decreased the speed of the same emulsion to 79 at the same concentration and gave a fog level of 0.32. While the compound of Example 8 increased the speed of an ordinary photographic silver bromide emulsion from 100 to 170, at a concentration of 3.0 g./mol. silver halide, the corresponding thioether compound decreased the speed of the same emulsion to 76 at the same concentration and gave a fog level of 0.34.

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:

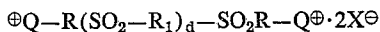
1. A photographic silver halide emulsion sensitized with a non-polymeric sensitizer selected from those represented by the following general formula:



wherein R and R₁ each represents an alkylene group, d represents a positive integer of from 1 to 3, Q[⊕] represents an organic quaternary ammonium group and X[⊖] represents an acid anion.

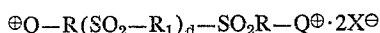
17

2. A photographic silver halide emulsion containing a sensitizing amount of a compound selected from the class represented by the following general formula:



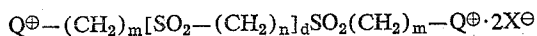
wherein R and R₁ each represents an alkylene group containing from 2 to 10 carbon atoms, d represents a positive integer of from 1 to 3, Q[⊕] represents an organic quaternary ammonium group, and X represents an acid anion.

3. A photographic silver halide developing-out emulsion sensitized with a gold salt and a labile sulfur compound and containing a sensitizing amount of a compound selected from the class represented by the following formula:



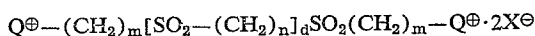
wherein R and R₁ each represents an alkylene group containing from 2 to 10 carbon atoms, d represents a positive integer of from 1 to 3, Q[⊕] represents an organic quaternary ammonium group, and X represents an acid anion.

4. A photographic silver halide emulsion sensitized with a sensitizing amount of a compound represented by the following general formula:



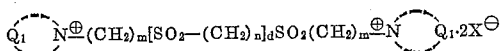
wherein d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10, X represents an acid anion, and Q[⊕] represents an organic quaternary ammonium group.

5. A photographic silver halide developing-out emulsion sensitized with a gold salt and a labile sulfur compound and containing a sensitizing amount of a compound selected from the class represented by the following general formula:



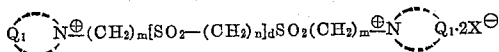
wherein d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10, X represents an acid anion, and Q[⊕] represents an organic quaternary ammonium group.

6. A photographic silver halide developing-out emulsion sensitized with a compound selected from the class represented by the following general formula:



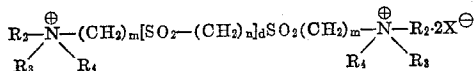
wherein d represents a positive whole number of from 1 to 3, m and n each represents a positive integer of from 2 to 10, Q₁ represents the non-metallic atoms necessary to complete a heterocyclic ring containing only one nitrogen atom in the heterocyclic ring, and X represents an acid anion.

7. A photographic silver halide developing-out emulsion sensitized with a gold salt and a labile sulfur compound and containing a sensitizing amount of a compound selected from the class represented by the following general formula:



wherein d represents a positive whole number of from 1 to 3, m and n each represents a positive integer of from 2 to 10, Q₁ represents the non-metallic atoms necessary to complete a heterocyclic ring containing only one nitrogen atom in the heterocyclic ring, and X represents an acid anion.

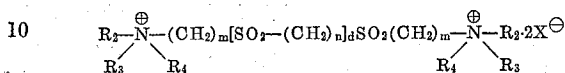
8. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of a compound selected from the class represented by the following general formula:



13

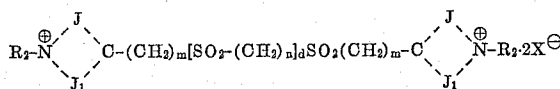
wherein R₂, R₃ and R₄ each represents a lower alkyl group, d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10, and X represents an acid anion.

9. A photographic silver halide emulsion sensitized with a gold salt and a labile sulfur compound and containing a sensitizing amount of a compound selected from the class represented by the following general formula:



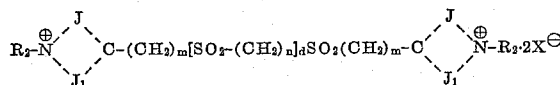
wherein R₂, R₃ and R₄ each represents a lower alkyl group, d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10, and X represents an acid anion.

10. A photographic silver halide developing-out emulsion sensitized with a sensitizing compound selected from the class represented by the following general formula:



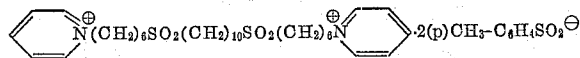
wherein R₂ represents a lower alkyl group, J and J₁ together represent the non-metallic atoms necessary to complete a pyridine nucleus, d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10 and X represents an acid anion.

11. A photographic silver halide developing-out emulsion sensitized with a gold salt and a labile sulfur compound and containing a sensitizing amount of a compound selected from the class represented by the following general formula:

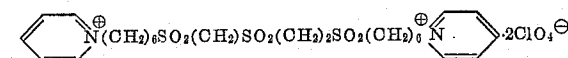


wherein R₂ represents a lower alkyl group, J and J₁ together represent the non-metallic atoms necessary to complete a pyridine nucleus, d represents a positive integer of from 1 to 3, m and n each represents a positive integer of from 2 to 10 and X represents an acid anion.

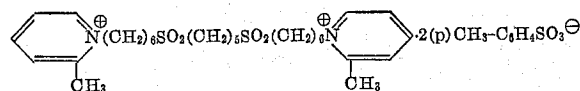
12. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of the compound represented by the following formula:



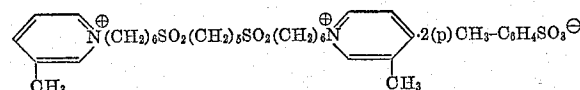
13. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of the compound represented by the following formula:



14. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of the compound represented by the following formula:

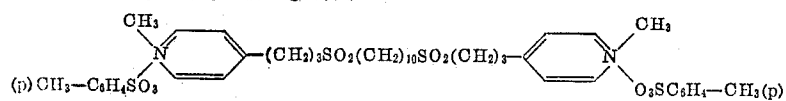


15. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of the compound represented by the following formula:



16. A photographic silver halide developing-out emulsion sensitized with a sensitizing amount of the compound

represented by the following formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,399,083	Waller et al. Apr. 23, 1946
2,694,716	Allen et al. Nov. 16, 1954
2,944,902	Carroll et al. July 12, 1960