

- [54] **STABILIZATION OF SILVER HALIDE EMULSIONS WITH 1,1 BIS-SULFONYL ALKANES**
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- [22] Filed: **June 1, 1970**
- [21] Appl. No.: **42,580**
- [52] U.S. Cl. **96/61, 96/109**
- [51] Int. Cl. **G03c 5/38, G03c 1/34**
- [58] Field of Search **96/109, 61**

[56]

References Cited

UNITED STATES PATENTS

- 3,220,839 11/1965 Herz et al.96/109
- 3,301,678 1/1967 Humphlett et al.96/61

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[57]

ABSTRACT

Silver halide emulsions and photographic elements containing a 1,1 bis-sulfonyl alkane stabilizing agent are stabilized after exposure by an alkaline activation treatment.

20 Claims, No Drawings

STABILIZATION OF SILVER HALIDE EMULSIONS WITH 1,1 BIS-SULFONYL ALKANES

This invention relates to the art of photography. More particularly, this invention relates to stabilization of photographic silver halide emulsions and elements with novel stabilizing agents, obviating the necessity of conventional fixing.

After a photographic silver halide emulsion is developed and a silver image is produced in the areas of exposure, the silver halide in the unexposed areas is conventionally washed out as a soluble complex with a fixing solution. It would be convenient to have the fixing agent incorporated directly in the emulsion.

The suitability of a fixing agent for incorporation in an emulsion depends on many factors, but it has been difficult to find compounds which are satisfactory because of the sensitive nature of the element. Most active fixing agents such as hypo, for example, cannot be incorporated into the light-sensitive element because of the prefixing which takes place, that is, the compound reacts to fix the silver halide prematurely and light sensitivity is lost. Other less active fixing compounds may show such inactivation (pre-stabilization) on long-term keeping, so that light sensitivity is lost after a period of time. Other still less active fixing agents, while they do not react prematurely, may act with only insufficient completeness so that they do not do a satisfactory fixing job. This results in subsequent background printup and instability in the processed image. Still other known fixing agents cannot be incorporated in light-sensitive coatings because of solubility relationships or because of interaction with other components of the system. It would be highly desirable to have a fixing agent which could be satisfactorily incorporated into a light-sensitive coating and which would not interfere with sensitometric properties so that stable coatings could be made.

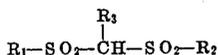
It is an object of this invention to provide novel stabilizing agents for silver halide emulsions and photographic elements.

It is also an object of this invention to provide a process for stabilizing photographic elements having novel stabilizing agents incorporated therein by a simple alkaline activation step.

These and other objects of this invention are accomplished by incorporating in a photographic silver halide emulsion or in a layer of a photosensitive element a 1,1 bis-sulfonyl alkane. It has been found that the β -disulfones used in the present invention do not desensitize the emulsion or stabilize the emulsion prior to development. By means of a simple alkaline activation step, the disulfones then act as effective stabilizers.

The β -disulfones and their chemical reactions have been described in the literature. For example, the preparation of these compounds and reactions in which they are involved is described in Suter, *Organic Chemistry of Sulfur*, on pages 735 and 739. However, it has now been discovered that particular β -disulfones, namely, 1,1 bis-sulfonyl alkanes, are excellent stabilizers when incorporated in photographic silver halide emulsions or in a layer of a photosensitive element.

Suitable 1,1 bis-sulfonyl alkanes used in the present invention can be represented by the general formula



wherein R_1 and R_2 each represent a lower alkyl group and R_3 represents H or a lower alkyl group. The term "lower alkyl" as employed herein is preferably an alkyl group containing from about one to four carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl and the like. The term "alkyl" as employed herein also includes substituted alkyl groups, and is preferably a substituted lower alkyl group containing from one to four carbon atoms. Thus, substituted lower alkyl groups such as a hydroxyalkyl group, e.g., β -hydroxyethyl, ω -hydroxybutyl, etc.; an alkoxyalkyl group, e.g., β -methoxyethyl, ω -butoxybutyl, etc.; a carboxyalkyl group, e.g., β -carboxyethyl, ω -carboxybutyl, etc.; a sulfoalkyl group, e.g., β -sulfoethyl, ω -sulfobutyl, etc.; a sulfatoalkyl group, e.g., β -sulfatoethyl, ω -sulfatobutyl,

etc.; an acryloxyalkyl group, e.g., β -acetoxyethyl, ω -butyryloxybutyl, etc.; an alkoxyalkyl group, e.g., β -methoxyalkyl-ethyl, ω -ethoxyalkylbutyl, etc., are preferred.

1,1 Bis-sulfonyl alkanes within the above formula include 1,1 bis-(methylsulfonyl)ethane; 1,1 bis-(ethylsulfonyl)ethane; 1,1 bis-(methylsulfonyl)propane; 1,1 bis-(ethylsulfonyl)propane; 1-ethylsulfonyl-1-methylsulfonyl methane; 1-ethylsulfonyl-1-methylsulfonyl ethane; etc. Especially preferred 1,1 bis-sulfonyl alkanes are bis(methylsulfonyl)methane, bis(ethylsulfonyl)methane, bis(β -hydroxyethylsulfonyl)methane, bis(carboxymethylsulfonyl)methane, and bis(β -carboxyethylsulfonyl)methane.

When the novel disulfone stabilizers described herein are incorporated in a silver halide emulsion, or contiguous to the silver halide, they serve as incorporated fixing agents. These addenda do not prevent development of exposed areas of the emulsion but protect the unexposed areas of the emulsion against printout after development of the emulsion. Thus, with emulsions containing the addenda of the invention, silver images can be formed and stabilized without the use of a conventional fixing process. The subject addenda are stable and do not act as fixing agents in acidic or neutral media such as in emulsions. However, under aqueous alkaline conditions which usually occurs during development, the subject addenda become active fixing agents. If the developing solution is not sufficiently alkaline to activate the disulfones of the invention at the rate desired, the developed element can thereafter be immersed in a stronger alkaline bath for fixing.

The concentration of the novel disulfone stabilizers described herein which may be incorporated into photosensitive elements should be sufficient to stabilize all undeveloped silver halide and is usually at least about one mole of stabilizer per mole of silver halide in the silver halide emulsion or photosensitive element, preferably about 2 to about 10 moles of stabilizer per mole of silver halide depending upon the solubility of the particular agent employed.

A photosensitive element according to the invention comprises a support having thereon a photographic silver halide emulsion layer, the element containing either in the emulsion layer or in a separate layer, preferably contiguous to the emulsion layer, at least one mole per mole of silver halide of the novel disulfone stabilizing agents described herein. When it is desired to stabilize such element, it is exposed, developed and then treated in an aqueous alkaline medium to form a complex of unexposed and undeveloped silver halide with the stabilizing agent, thus providing a stable image. If desired, the developing step, as such, can be omitted by incorporating a developing agent directly into the photographic element or silver halide emulsion. The alkaline treatment thus serves to initiate development and then complexing of the unexposed and undeveloped silver halide with the stabilizing agent to provide a stable image.

Suitable developing agents useful in the present invention include hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones, phenylenediamines, combinations thereof, etc. The amount of developer to be employed can be varied over a wide range as is well known to those skilled in the art, depending upon the particular developer employed, its location in the system, etc.

When incorporated in silver halide emulsions or photographic elements as described herein, the novel disulfones of the invention are relatively inert at pH's below about 8 or 9 and can be coated at that pH or below. However, alkaline activation at pH's at about 10 or above renders these disulfones very effective stabilizers.

While it is not necessary to have an auxiliary developing agent present in the photographic element of the invention, such auxiliary developing agent can be employed, if desired, to improve maximum density of the developed image.

The silver halide emulsions which can be employed with this invention can be silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof.

The emulsions can be coarse or fine-grain and can be prepared by any of the well-known procedures in emulsion making such as single-jet emulsions, double-jet emulsions, such as Lippman, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. No. 2,222,264 of Nietz et al. issued Nov. 19, 1940; U.S. Pat. No. 3,320,069 of Illingsworth issued May 15, 1967; and U.S. Pat. No. 3,271,157 of McBride issued Sept. 6, 1966. Surface image emulsions can be used or internal image emulsions can be used such as those described in U.S. Pat. No. 2,592,250 of Davey et al. issued Apr. 8, 1952; U.S. Pat. No. 3,206,313 of Porter et al. issued Sept. 14, 1965; and Belgian Pat. No. 704,255. The emulsions can be regular grain emulsions such as those described in Klein and Moisar, *Journal of Photographic Science*, Volume 12, No. 5, September-October (1964) pages 242-251. If desired, mixtures of surface and internal image emulsions can be used as described in U.S. Pat. No. 2,996,382 of Luckey et al. issued Aug. 15, 1961. Negative-type emulsions can be used or direct positive emulsions can be used such as those described in U.S. Pat. No. 2,184,013 of Leermakers issued Dec. 19, 1939; U.S. Pat. No. 2,541,472 of Kendall et al. issued Feb. 13, 1951; U.S. Pat. No. 3,367,778 of Berriman et al. issued Feb. 6, 1968; British Pat. 723,019; French Pat. No. 1,520,821; U.S. Pat. No. 2,563,785 of Ives issued Aug. 7, 1951; U.S. Pat. No. 2,456,953 of Knott et al. issued Dec. 21, 1968; and U.S. Pat. No. 2,861,885 of Land issued Nov. 25, 1958.

The silver halide emulsions employed in the practice of the invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed.

The silver halide emulsions employed in the practice of the invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described, for example, in U.S. Pat. No. 1,623,499 of Sheppard issued Apr. 5, 1927; U.S. Pat. No. 2,399,083 of Waller et al. issued Apr. 23, 1946; U.S. Pat. No. 3,297,447 of McVeigh issued Jan. 10, 1967 and U.S. Pat. No. 3,297,446 of Dunn issued Jan. 10, 1967.

If desired in preparing a photographic silver halide emulsion, spectral sensitizers can be added to the emulsion before a chemical sensitizer is added. This can result in a speed increase as compared to an emulsion wherein the chemical sensitizer is added before the spectral sensitizer. For example, the silver halide emulsion can be spectrally sensitized with anhydro-5,5'-dichloro-3,9-diethyl-3'-(3-sulfobutyl) thiocarbo-cyanine hydroxide; 5-[di-(1-ethyl-2(1H)-%naphthothiazolyli-dene) iso-propylidene]-1,3-di-(β -methoxyethyl) barbituric acid; anhydro-5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl) oxacarbo-cyanine hydroxide, sodium salt; or anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl) benzimidazolocarbo-cyanine hydroxide and then chemically sensitized with sulfur and gold sensitizers, or sulfur, gold and selenium sensitizers, as described. Heat treatment can be carried out after the spectral sensitizer is added.

Cationic hydroxyalkyl surfactants, such as quaternary salts, which contain an omega-hydroxyalkyl group can be employed as chemical sensitizers for silver halides, e.g., a silver halide dispersed in gelatin or synthetic polymeric vehicles. Compounds which are cationic surfactant sulfonium compound chemical sensitizers are set out in U.S. Pat. No. 2,271,623 and U.S. Pat. No. 2,275,727 as well as various quaternary ammonium compounds. Tetraalkyl quaternary ammonium salts, pyridinium quaternary salts, piperidinium salts, pyrazolium quaternary salts, and quinolinium salts which contain an omega-hydroxyalkyl group are suitable compounds which can be employed to increase the photographic speed of silver halide.

The silver halide emulsions employed in the practice of the invention can contain speed increasing compounds such as polyalkylene glycols, cationic surfactants and thioethers or

combinations of these as described, for example, in U.S. Pat. No. 2,886,437 of Piper issued May 12, 1959; U.S. Pat. No. 3,046,134 of Dann et al. issued July 24, 1962; U.S. Pat. No. 2,944,900 of Carroll et al. issued July 12, 1960; and U.S. Pat. No. 3,294,540 of Goffe issued Dec. 27, 1966.

The described silver halide emulsions employed in the practice of the invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include, for example, thiazolium salts; azaindenes; mercury salts as described, for example, in U.S. Pat. No. 2,728,663 of Allen et al. issued Dec. 27, 1955; urazoles; sulfocatechols; oximes described, for example, in British Pat. No. 623,448; nitron; nitroindazoles; mercap-totetrazoles; polyvalent metal salts described, for example, in U.S. Pat. No. 2,839,405 of Jones issued June 17, 1958; palladium, platinum and gold salts described, for example, in U.S. Pat. No. 2,566,263 of Trevelli et al. issued Aug. 28, 1951 and U.S. Pat. No. 2,597,915 of Yutzy et al. issued May 27, 1952.

The photographic and other hardenable layers of a photo-graphic element used in the practice of the invention can be hardened by various organic or inorganic hardeners alone or in combination, such as aldehyde hardeners and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, azirindenes, active olefins, isocyanates, carbodiimides, mixed-function hardeners and polymeric hardeners such as oxidized polysaccharides such as dialdehyde starch and oxyguargum and the like.

A photographic element and emulsions described in the practice of the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable hydrophilic materials include those naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of the photographic element employed in the practice of the invention can also contain, alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds, such as in latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described in U.S. Pat. No. 3,142,586 of Nottorf issued July 28, 1964; U.S. Pat. No. 3,193,386 of White issued July 6, 1965; U.S. Pat. No. 3,062,674 of Houck et al. issued Nov. 6, 1962; U.S. Pat. No. 3,220,844 of Houck et al. issued Nov. 30, 1965; U.S. Pat. No. 3,287,289 of Ream et al. issued Nov. 22, 1966; and U.S. Pat. No. 3,411,911 of Dykstra issued Nov. 19, 1968. Particularly effective are those water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and those which have cross-linking sites which facilitate hardening or curing as well as those having recurring sulfobetaine units as described in Canadian Pat. No. 774,054.

The photographic elements employed in the practice of the invention can contain antistatic or conducting layers. Such layers can comprise soluble salts such as chloride, nitrate and the like evaporated metal layers, ionic polymers such as those described in U.S. Pat. No. 2,861,056 of Minsk issued Nov. 18, 1958 and U.S. Pat. No. 3,206,312 of Sterman et al. issued Sept. 14, 1965 or insoluble organic salts such as those described in U.S. Pat. No. 3,428,451 of Trevoiy issued Feb. 18, 1969.

The photographic emulsions and other layers of a photo-graphic element employed in the practice of the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose acetate film, poly(vinylacetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials as well as glass, paper, metal

and the like. Typically a flexible support is employed, especially a paper support which can be partially acetylated or coated with baryta and/or an alpha olefin polymer, particularly a polymer of an alpha olefin containing two to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

Paper supports which can contain acidic materials to control pH can be especially useful. Such paper supports can contain acids such as boric acid and phthalic acids, as described, for example, in U.S. Pat. No. 3,250,619 and U.S. Pat. No. 3,326,744.

The photographic elements employed in the practice of the invention can contain plasticizers and lubricants such as polyalcohols, glycerin and diols as described, for example, in U.S. Pat. No. 2,960,404 of Milton et al. issued Nov. 1, 1966; fatty acids or esters such as described in U.S. Pat. No. 2,588,765 of Robijns issued Mar. 11, 1952; and U.S. Pat. No. 3,121,160 of Duane issued Feb. 11, 1964; and silicone resins such as those described in British Pat. No. 955,061.

The photographic elements employed in the practice of the invention can contain surfactants such as saponin, anionic compounds, such as alkyl aryl sulfonates described, for example, in U.S. Pat. No. 2,600,831 of Baldsiefen issued June 17, 1952 and amphoteric compounds such as those described in U.S. Pat. No. 3,133,816 of Ben-Ezra issued May 19, 1964.

The described photographic elements containing an incorporated developing agent can contain an antioxidant such as a water-soluble sulfite or bisulfite, e.g., sodium formaldehyde bisulfite, such as described in U.S. Pat. No. 3,212,895 of Barbier et al. and U.S. Pat. No. 3,418,132 of Kitz.

The photographic elements employed in the practice of the invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, and polymeric beads including beads described, for example, in U.S. Pat. No. 2,922,101 of Jelley et al. issued July 11, 1961 and U.S. Pat. No. 2,701,245 of Lynn issued Feb. 1, 1955.

The described photographic elements employed in the practice of the invention can also contain a brightening agent including stilbene, triazine, oxazole, and/or coumarin brightening agents. Water-soluble brighteners such as those described in German Pat. No. 972,067 and U.S. Pat. No. 2,933,390 of McFall et al. issued Apr. 19, 1960 or dispersions of brighteners can be used such as those described in German Pat. No. 1,150,274 and U.S. Pat. No. 3,406,070 of Oetiker et al. issued Oct. 15, 1968 and French Pat. No. 1,530,244.

The photographic silver halide emulsions employed in the practice of the invention can be X-ray or other nonspectrally sensitized emulsions or they can contain spectral sensitizing dyes. The photographic silver halide emulsions can conveniently be orthosensitized or pansensitized with spectral sensitizing dyes. For instance, these emulsions can be spectrally sensitized by treating with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion such as described in French Pat. No. 1,482,774. Spectral sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pat. No. 2,526,632 of Brooker et al. issued Oct. 24, 1950; U.S. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950; U.S. Pat. No. 2,493,748 of Brooker et al. issued Jan. 10, 1950; and U.S. Pat. No. 3,384,486 of Taber et al. issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (trinuclear or tetranuclear) cyanines, complex (trinuclear or tetranuclear) merocyanines, holopolar cyanines, styryls, hemicyanines, such as enamine hemicyanines, oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain al-

kyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei described as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolinones and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups or heterocyclic nuclei. Combinations of these dyes can be used if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, such as ascorbic acid derivatives, azaindenes, cadmium salts and organic sulfonic acids as described in U.S. Pat. No. 2,933,390 of McFall et al. issued Apr. 19, 1960 and U.S. Pat. No. 2,937,089 of Jones et al. issued May 17, 1960.

The various layers including the photographic emulsion layer of the photographic element employed in the practice of the invention can contain light absorbing materials and filter dyes such as those described in U.S. Pat. No. 3,253,921 of Sawdey issued May 31, 1966; U.S. Pat. No. 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Pat. No. 2,527,583 of Silberstein et al. issued Oct. 31, 1950; and U.S. Pat. No. 2,956,879 of VanCampen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. No. 3,282,699 of Jones et al. issued Nov. 1, 1966.

The sensitizing dyes and other addenda such as the described silver halide developing agents and silver halide stabilizer precursors used in the practice of the invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including those described in U.S. Pat. No. 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Pat. No. 3,342,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Pat. No. 2,996,287 of Audran issued Apr. 15, 1961; and U.S. Pat. No. 3,425,835 of Johnson et al. issued Feb. 4, 1969.

After exposure, the resulting latent image in a photographic element according to the invention can be developed and stabilized by contacting the element with an alkaline activator. An especially suitable activator is an aqueous alkaline solution comprising potassium hydroxide at a pH of about 10 to about 14.5, especially 12 to 14.5.

Alkaline activators which can be employed in developing a latent image in a photographic element as described include any of those which provide the desired activation of the described silver halide developing agents and silver halide stabilizer precursors. These include, for instance, aqueous alkaline activator solutions commonly employed in rapid access processing of photographic elements, such as those employed in so-called reader-printers. Alkaline activators which are suitable include inorganic alkali such as alkali metal hydroxides, especially sodium hydroxide, potassium hydroxide and/or lithium hydroxide, alkali metal carbonates, such as sodium carbonate and potassium carbonate, sodium or potassium phosphates, and organic alkaline development activators such as quaternary ammonium bases and salts and alkanolamines such as ethanol amine, and similar alkaline materials and/or alkali releasing materials. Such development activators can be applied to the photographic element employed in the practice of the invention in any suitable manner, including for example, dipping, spraying and/or surface applications such as with rollers, as described in U.S. Pat. No. 3,025,779 of Russell et al. issued Mar. 20, 1962 or by surface application processing as described in U.S. Pat. No. 3,418,132 of Kitz issued Dec. 24, 1968.

If desired an alkaline solution can be employed containing conventional silver halide developing agents such as those described. So-called web processing can be employed as described, for example, in U.S. Pat. No. 3,179,517 of Tregillus et al. issued Apr. 20, 1965 or so-called stabilization processing as described in Russell et al., *PSA Journal*, Volume 16b, Aug. 1950.

If desired the alkaline activator, especially an aqueous alkaline activator solution can contain a hardener as described.

The time for processing a photographic element in the practice of the invention, that is developing and stabilizing a desired latent image, can vary over a wide range, typically between about 1 second to several minutes depending on the desired image, processing conditions and the like.

The conditions for processing can also vary, but usually ambient pressures and temperatures of about 20° C. to about 30° C. are employed. If desired, higher temperatures can be used such as temperatures up to about 90° C.

It can be useful in some cases to wash the resulting photographic element after processing with water, such as a water rinse, for about 1 second to about 5 minutes to remove water-soluble compounds. This can improve post processing stability and reduce any stain.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

The following coating composition is prepared and coated at 0.004 inch wet thickness on a baryta-coated paper base:

Water	40 ml.
Gelatin, 15% solution	40 ml.
Bis(methylsulfonyl)methane	3 g.
1-Phenyl-2-carbohexyloxy-3-pyrazolidone	0.8 g.
Hydroquinone	2 g.
Negative-type, medium speed, gelatino-silver chloride-gelatin emulsion containing 40 mg. silver/ml.	5 ml.

This composition contains approximately 8 moles of the stabilizer compound per mole of silver. After drying, the resulting photographic element is then exposed to an image and then immersed for 10 seconds in a solution at 75° F. containing 5 percent sodium hydroxide, 5 percent sodium sulfite and 5 percent sodium sulfate. The element is then washed in water. A blue-black image of excellent density and emulsion speed is obtained with a white background that is stable to the continued effect of light.

EXAMPLES 2-4

Example 1 is repeated but with bis(ethylsulfonyl)methane, bis(β -hydroxyethylsulfonyl)methane and bis(carboxymethylsulfonyl)methane in place of the bis(methylsulfonyl)methane. Similar results are obtained.

EXAMPLE 5

A photographic element is prepared according to the procedure of Example 1. A portion of the element is incubated for 7 days at 120° F. and 35 percent Relative Humidity. Both portions of the element are then processed as in Example 1. The following sensitometric values are obtained:

Coating	Contract	D_{max}
Fresh	0.72	1.02
Incubated	0.74	1.08

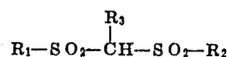
This data clearly indicate that there was no prestabilization of the light-sensitive material since the element retains its ability to be fully developed by alkaline activator after a full week at 120° F. and 35 percent Relative Humidity.

The invention has been described with particular reference to certain preferred embodiments thereof, but it is understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a 1,1 bis-sulfonyl alkane stabilizing agent.

2. The photographic emulsion of claim 1 wherein said stabilizing agent has the formula



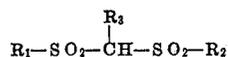
5 wherein R_1 and R_2 each represent an alkyl group containing one to four carbon atoms and R_3 represents H or an alkyl group containing one to four carbon atoms.

3. The photographic emulsion of claim 2 wherein R_1 and R_2 each represent methyl, ethyl, hydroxyethyl, carboxymethyl or carboxyethyl groups and R_3 represents H.

4. The photographic emulsion of claim 3 wherein R_1 and R_2 each represent a methyl group.

5. A photosensitive element comprising a support having thereon a photographic silver halide emulsion layer, said element containing at least one mole per mole of silver halide of a 1,1 bis-sulfonyl alkane stabilizing agent.

6. The photosensitive element of claim 5 wherein said stabilizing agent has the formula

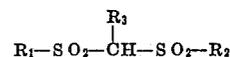


7. The photosensitive element of claim 6 wherein R_1 and R_2 each represent methyl, ethyl, hydroxyethyl, carboxymethyl or carboxyethyl groups and R_3 represents H.

8. The photosensitive element of claim 7 wherein R_1 and R_2 each represent a methyl group.

9. The photosensitive element of claim 5 which includes a photographic silver halide developing agent incorporated therein.

10. The photosensitive element of claim 9 wherein said stabilizing agent has the formula



11. The photosensitive element of claim 10 wherein R_1 and R_2 each represent methyl, ethyl, hydroxyethyl, carboxymethyl or carboxyethyl groups and R_3 represents H.

12. The photosensitive element of claim 11 wherein R_1 and R_2 each represent a methyl group.

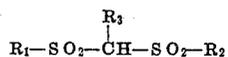
13. A process for stabilizing a photographic element comprising:

a. exposing a photosensitive element comprising a support having thereon a photographic silver halide emulsion layer, said element containing at least 1 mole per mole of silver halide of a 1,1 bis-sulfonyl alkane stabilizing agent.

b. developing exposed silver halide of said exposed element, and

c. complexing resulting unexposed and undeveloped silver halide with said stabilizing agent in an aqueous alkaline medium thus providing a stable image.

14. The process of claim 13 wherein said stabilizing agent has the formula



15. The process of claim 14 wherein R_1 and R_2 each represent methyl, ethyl, hydroxyethyl, carboxymethyl or carboxyethyl groups and R_3 represents H.

16. The process of claim 15 wherein R_1 and R_2 each represent a methyl group.

17. A process for stabilizing a photographic element comprising:

a. exposing a photosensitive element comprising a support having thereon a photographic silver halide emulsion layer, said element containing at least 1 mole per mole of silver halide of a 1,1 bis-sulfonyl alkane stabilizing agent.

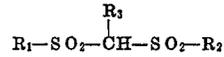
b. developing exposed silver halide of said exposed element, and

c. complexing resulting unexposed and undeveloped silver halide with said stabilizing agent in an aqueous alkaline medium thus providing a stable image.

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- a. exposing a photosensitive element comprising a support having thereon a photographic silver halide emulsion layer, said element containing at least one mole per mole of silver halide of a 1,1 bis-sulfonyl alkane stabilizing agent, said element also containing a silver halide developing agent incorporated therein, and
 - b. treating said element in an aqueous alkaline medium to initiate development of exposed silver halide and then complexing of unexposed and undeveloped silver halide with said stabilizing agent to provide a stable image.
18. The process of claim 17 wherein said stabilizing agent has the formula

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- 5 wherein R_1 and R_2 each represent an alkyl group containing one to four carbon atoms and R_3 represents H or an alkyl group containing one to four carbon atoms.
- 10 19. The photographic emulsion of claim 18 wherein R_1 and R_2 each represent methyl, ethyl, hydroxyethyl, carboxymethyl or carboxyethyl groups and R_3 represents H.
- 20 20. The photographic emulsion of claim 19 wherein R_1 and R_2 each represent a methyl group.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,647,453 Dated March 7, 1972

Inventor(s) Grant M. Haist, James R. King and David A. Pupo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 1, line 71, " ω hydroxybutyl" should read
--- ω -hydroxybutyl---

In Column 2, line 20, "printout" should read
---print-out---

In Column 3, line 51 "2(1H)-7/8" should read
---2(1H)- β ---

In Column 7, line 26, "0.8 g." should be directly across from 1-Phenyl-2-carbohexyloxy-3-pyrazolidone" and under "3 g."

In Column 7, line 56, "Contract" should read
---Contrast---

Signed and sealed this 21st day of November 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents