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3,834,902

PHOTOGRAPHIC MATERIAL CONTAINING A MESYLATE COMPOUND AS HARDENER AND ANTIFOGGANT**Charles J. Wright, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.****No Drawing. Filed Sept. 29, 1972, Ser. No. 293,696****Int. Cl. G03c 1/00, 1/30, 1/34, 1/40, 1/68; G03g 5/00**
U.S. Cl. 96—1.8**10 Claims****ABSTRACT OF THE DISCLOSURE**

Photographic elements are disclosed containing a hydrophilic colloid layer hardened with a compound having the structural formula:



wherein A contains no more than nine atoms linking the sulfonyl groups and is an alkylene or oxaalkylene group having up to three oxygen atoms and m is 0 or 1. The hardener also serves as an antifoggant in photographic applications.

This invention relates to 2-mesyloxyethylsulfonyl compounds and to hydrophilic colloid compositions and layers hardened thereby. In a specific aspect this invention relates to photographic elements incorporating a 2-mesyloxyethylsulfonyl compound having hardening and antifoggant properties.

In the photographic arts hydrophilic colloids—typically refined gelatins—have been used to suspend silver halide grains and thereby to form radiation-sensitive compositions which when coated onto suitable supports are capable of forming photographic elements. Typically a variety of addenda are employed to alter the properties of both the gelatin and the silver halide grains. It has been recognized previously in the art that without special modifiers hydrophilic colloids such as gelatins ingest large quantities of water when brought into contact with aqueous solutions, causing appreciable swelling, and are easily abraded. Also, unmodified gelatin coatings tend to melt at relatively low temperatures, thereby limiting their temperature range of utility. To alter these deficiencies of unmodified photographic gelatins it has heretofore been recognized that certain addenda generically designated as “hardener addenda” or simply “hardeners” may be incorporated into radiation-sensitive compositions and coatings to obviate at least one of the above undesirable gelatin characteristics.

In order to serve the needs of the photographic arts it is desirable not only that a hardener ameliorate the deficiencies of gelatins as noted above, but that the hardener meet certain additional practical criteria. For example, the hardener should cause hardening or setting of the emulsion sufficiently slowly to permit coating of the photographic emulsion onto a support, but it should not set up so slowly that after-hardening takes place—i.e. the emulsion continues to harden undesirably during storage of a fabricated photographic element. Also, the hardener should possess sufficiently low levels of toxicity so as not to pose a significant hazard to manufacturing personnel. Further, the hardener should not undesirably reduce or interfere with the desired photographic properties of the element into which it is incorporated. For example, the hardener should not contribute to the reduction of silver halide to produce fogging of a photographic emulsion or coating. These criteria for hardeners are all the more challenging when it is borne in mind that the composition of photographic gelatins are themselves not fully understood and that the mechanisms of hardening are not entirely appreciated.

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In addition to the above considerations, it must be recognized that the hardener is only a part of what typically is a comparatively complex photographic system. For example, in addition to the radiation-sensitive silver halide and the gelatin to be hardened photographic emulsions typically contain numerous additional addenda. With so many criteria being applied to hardeners and in view of the complexity of photographic emulsions it is not then surprising that there is presently no known way of predicting the suitability of significantly differing types of compounds as hardeners in photographic emulsions, and the art has relied upon empirical methods to discover new types of hardeners. Beyond this, the selection of hardeners having both satisfactory hardening and other desirable and advantageous photographic characteristics permitting their substitution for or supplementing of other photographic addenda has remained in the realm of chance discovery.

Tesoro U.S. Pat. 3,201,434, issued Aug. 17, 1965, teaches the utility of certain compounds containing methane sulfonic acid moieties as crosslinking agents for fibrous polymers. Tesoro, however, does not teach or suggest any utility of these crosslinking agents with hydrophilic colloids nor utility in a photographic environment. Allen et al. U.S. Pats. 2,816,125 and 2,726,162, issued Dec. 10, 1957 and Dec. 6, 1955, respectively, disclose di-(methanesulfonyl) compounds in which the methanesulfonyl (or mesyloxy) groups are joined by divalent aliphatic hydrocarbon or other radicals. These compounds are recognized to be useful hardeners for photographic gelatins.

It is one object of this invention to provide a new class of compounds useful as hardeners for hydrophilic colloids.

It is a second object of this invention to provide a new class of compounds capable of functioning simultaneously as hardener and anti-foggant addenda in radiation-sensitive hydrophilic colloids—i.e. photographic emulsions.

It is another object to provide novel hydrophilic colloid compositions utilizing a hardener that exhibits a desirable rate of hardening.

It is a more specific object to provide novel photographic compositions and elements containing in a photographic emulsion a hydrophilic colloid hardener and anti-foggant that exhibits anti-foggant characteristics.

In one aspect this invention is directed to a composition comprising a hardenable hydrophilic colloid and a hardening concentration of a compound having the structural formula:



wherein A contains no more than nine atoms linking the sulfonyl groups and is an alkylene or oxaalkylene group having up to three oxygen atoms and m is 0 or 1.

In another aspect this invention is directed to a radiation-sensitive hydrophilic colloid composition as set forth above and to a photographic element containing at least one radiation-sensitive layer comprised of a hydrophilic colloid composition as set forth above.

It has been discovered quite unexpectedly that the 2-mesyloxyethylsulfonyl compounds defined as useful in the practice of this invention produce in hydrophilic colloids improved hardening characteristics and when utilized in radiation-sensitive colloids—e.g. photographic emulsions, produce both the desired combination of hardening characteristics and anti-foggant characteristics. These 2-mesyloxyethylsulfonyl compounds harden hydrophilic colloids to reduce swelling and abrasion thereof. Additionally, these 2-mesyloxyethylsulfonyl compounds harden hydrophilic colloids at elevated temperatures. Still further, the colloids hardened with these 2-mesyloxy-

ethylsulfonyl compounds are not hardened so rapidly as to interfere with their being coated onto a support, yet they do not exhibit substantial after-hardening characteristics. At the same time colloids hardened with the 2-mesyloxyethylsulfonyl compounds utilized in the practice of this invention do not pose a hazard to manufacturing personnel. It is quite surprising that hydrophilic colloids hardened with 2-mesyloxyethylsulfonyl compounds according to this invention possess improved hardening characteristics. It is even more surprising that, when the hydrophilic colloid is a radiation-sensitive colloid, such as a photographic emulsion, the 2-mesyloxyethylsulfonyl compounds of this invention are useful both as hardeners and as anti-foggant addenda.

Compounds which can be combined with hydrophilic colloids according to this invention to provide a combination of desirable colloid hardening characteristics and, in photographic applications, anti-fogging properties are defined by the structural formula:



wherein A contains no more than nine atoms linking the sulfonyl groups and is an alkylene or oxaalkylene group having up to three oxygen atoms and m is 0 or 1. Exemplary of such compounds are

bis(2-mesyloxyethyl)sulfone;
bis(2-mesyloxyethylsulfonyl)methane;
1,1-bis(2-mesyloxyethylsulfonyl)ethane;
1,2-bis(2-mesyloxyethylsulfonyl)ethane;
1,3-bis(2-mesyloxyethylsulfonyl)propane;
1,4-bis(2-mesyloxyethylsulfonyl)butane;
1,6-bis(2-mesyloxyethylsulfonyl)hexane;
1,9-bis(2-mesyloxyethylsulfonyl)nonane;
bis(2-mesyloxyethylsulfonylmethyl)ether;
bis[2-(2-mesyloxyethylsulfonyl)ethyl] ether;
bis[4-(2-mesyloxyethylsulfonyl)butyl] ether;
1,6-bis(2-mesyloxyethylsulfonyl)-2,5-dioxahexane; and
1,8-bis(2-mesyloxyethylsulfonyl)-3,6-dioxaoctane.

The compounds useful in the practice of this invention are prepared by means well known in the art, such as, for example, by the action of methanesulfonyl chloride on the particular sulfone diol selected. The diols in turn are prepared conveniently by the catalytic oxidation process of Schultz et al. [*J. Org. Chem.* 28, 1140 (1963)] and as further described in U.S. Pats. 3,005,852 issued Oct. 24, 1961; 3,006,962 issued Oct. 31, 1961; and 3,006,963 issued Oct. 31, 1961.

The hydrophilic colloids which are hardenable by the above bis(2-mesyloxyethylsulfonyl) compounds can be formed from one or more hydrophilic, water permeable colloid forming natural or synthetic polymers. Specific polymers which can be hardened according to the practice of this invention include hardenable polymers such as gelatin, colloidal albumin, acid or water-soluble vinyl polymers, cellulose derivatives, proteins, various polyacrylamides, dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials as exemplified by amine-containing polymers of alkyl acrylates, methacrylates, acrylic acid, sulfoalkyl acrylates and methacrylates, acrylic acid-acrylate copolymers, and the like. Suitable synthetic polymers include those described, for example, in Nottorf, U.S. Pat. 3,142,568, issued July 28, 1964; White U.S. Pat. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289, issued Nov. 22, 1966; Dykstra U.S. Pat. 3,411,911, issued Nov. 19, 1968; Smith U.S. Pat. 3,488,708, issued Jan. 6, 1970; and Dykstra Canadian Patent 774,054. The use of the hardeners of this invention with polymers having active ketomethylene groups, as described in Smith U.S. Pat. 3,488,708, cited above, is the separate invention of Osterhoudt and Smith disclosed in concurrently filed patent application U.S. Ser. No. 293,695, 75

titled "Photographic Element Comprising A Vinylsulfonyl Crosslinked Polymer Having Active Ketomethylene Groups."

The hydrophilic colloid to be hardened is typically utilized as a layer or coating on a support. A wide variety of supports, such as polymeric film, wood, metal, glass and the like, may be utilized to form hydrophilic colloid coated elements according to this invention. Where a photographic element is contemplated the support can take such forms as those set forth in paragraph X of *Product Licensing Index*, Vol. 92, December 1971, publication 9232, at page 108.

Where the hydrophilic colloid is to be utilized in combination with a support to form a photographic element, it will contain in or on it a radiation-sensitive material. This material can be panchromatic or orthochromatic material, sensitive only to X-rays or sensitive to selected portions of the electromagnetic spectrum. In one form of the invention the radiation-sensitive portion of the photographic element can contain a single, unitary hydrophilic colloid layer having dispersed therein the radiation-sensitive material together with photographic addenda to form a photographic emulsion layer or coating. In alternative forms the radiation-sensitive portion of the photographic element can comprise a plurality of layers with the radiation-sensitive material or materials being contained in some or all of the layers. For example, as is characteristic of color photography, a plurality of layers can be present sensitized within separate segments of the visible spectrum.

Suitable radiation-sensitive colloid compositions which can be employed in practicing this invention are sensitive to electromagnetic radiation and include such diverse materials as silver salts, zinc oxide, photosensitive polycarbonate resins and the like. Silver halides are preferred radiation-sensitive materials and are preferably associated with a colloid dispersion vehicle to form an emulsion coating or layer. Specific preferred silver halide containing photographic emulsions and processes for their preparation and use are disclosed in paragraph I of *Product Licensing Index*, Vol. 92, December 1971, publication 9232, at page 107. The radiation-sensitive colloids can additionally include a variety of conventional photographic addenda, such as development modifiers, plasticizers and lubricants, brighteners, spectral sensitization agents and color forming materials as set forth in paragraphs IV, XI, XIV and XXII, respectively, of *Product Licensing Index*, Vol. 92, December 1971, publication 9232, at pages 107-110. While it is contemplated that the mesyloxyethylsulfonyl compounds utilized in the practice of this invention may serve as the sole hardener and/or anti-foggant addendum present, it is appreciated that other conventional hardeners and/or anti-foggants may also be incorporated into the hydrophilic colloid, such as those set forth, for example, in paragraphs V and VII of *Product Licensing Index*, Vol. 92, December 1971, publication 9232, pages 107 and 108.

While a wide range in concentrations of 2-mesyloxyethylsulfonyl compounds disclosed herein is effective for achieving the desired combination of hardening characteristics in hydrophilic colloids and, in radiation-sensitive colloids, anti-foggant characteristics, a particularly effective concentration is from about 0.5 to 6 percent by weight, based on the weight of the hardenable material present in the hydrophilic colloid—i.e. the dry weight (excluding the weight of any water present) of the gelatin or the like making up the colloid. It has been found that about 1 percent to about 3 percent by weight, based on the weight of the hardenable material present in the hydrophilic colloid, is particularly effective in achieving both superior hardening and, in radiation-sensitive colloids, anti-fogging activity.

In order to achieve uniform hardening and/or anti-fogging activity it is preferred to uniformly disperse the 2-mesyloxyethylsulfonyl compounds in the hydrophilic

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colloid to be modified. According to one technique, referred to as forehardening, the mesyloxyethylsulfonfyl compound is dissolved in a volatile solvent, such as a lower alkyl alcohol, acetone, etc., and the solution is uniformly blended with the hydrophilic colloid to be modified. Typically the hydrophilic colloid has at this stage an amount of water associated therewith which is in excess of that ultimately desired. Immediately after blending the colloid is deposited on a suitable support to form a layer or coating. The colloid is then hardened on the support and such volatile solvent and/or dispersants as are associated with the colloid and mesyloxyethylsulfonfyl compound solution are removed by evaporation either at ambient or elevated temperatures, typically below about 100° C.

It is also contemplated that the 2-mesyloxyethylsulfonfyl compounds of this invention may be associated with hydrophilic colloids after they have been positioned on supports as coatings or layers. The support bearing a hydrophilic colloid coating to be hardened may be immersed in a solution containing the mesyloxyethylsulfonfyl compound therein so that the solution either surface hardens the colloid layer or permeates and uniformly hardens the colloid layer. This hardening technique, referred to as prehardening, finds particular utility in hardening certain photographic elements after exposure but before processing to form the photographic image. In this way a level of hardening can be imparted to the photographic element that might be objectionable in storage and use prior to exposure, but which is quite advantageous in preventing damage to the colloid layer of the photographic element during processing.

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

EXAMPLE 1

Bis(2-mesyloxyethylsulfonfylmethyl) Ether

This compound has the formula



and is prepared as follows:

5 - Oxa-3,7-dithianonane-1,9-diol was prepared by the reaction of two molar proportions of sodium 2-hydroxyethylmercaptide with bis(chloromethyl) ether in methanol followed by evaporation of the solvent.

The bis-sulfide was oxidized to the disulfone with hydrogen peroxide according to the procedure of H. S. Schultz cited above.

To a solution of the sulfone diol in 2:3 ethyl acetate: acetonitrile was quickly added two molar proportions each of 2,6-lutidine and methanesulfonyl chloride and the mixture stirred for 16 hours at room temperature. After removal by filtration of the precipitated 2,6-lutidinium chloride and evaporation of the solvent, the residue was triturated with hot methanol. Two recrystallizations of the residue from acetonitrile-methanol give colorless product, m.p. 142.5–144° C.

EXAMPLE 2

Bis[2-(2-mesyloxyethylsulfonfyl)ethyl] Ether

This compound has the formula



and is prepared as follows:

The procedure of Example 1, starting with bis(2-chloroethyl) ether, was used to prepare the colorless product, which was recrystallized from ethyl acetate, m.p. 87.5–88.5° C.

EXAMPLE 3

1,2-Bis[2-(2-mesyloxyethylsulfonfyl)ethoxy]ethane

This compound has the formula



and is prepared as follows:

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The procedure of Example 1, starting with 1,8-dichloro-3,6-dioxaoctane, was used to prepare the colorless mesylate, recrystallized from methanol, m.p. 43–45° C.

EXAMPLE 4

Bis (2-mesyloxyethyl) Sulfone

This compound having the formula

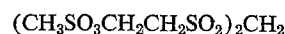


was prepared by a procedure essentially similar to that employed in the preceding examples by reacting bis(2-hydroxyethyl) sulfone in a mixture of ethyl acetate and acetonitrile with methanesulfonyl chloride and 2,6-lutidine.

EXAMPLE 5

Bis(2-mesyloxyethylsulfonfyl)methane

This compound having the formula



was prepared by the reaction of two molar proportions of 2-mercaptoethanol with formalin in refluxing benzene with a sulfuric acid catalyst. After all of the water had azeotropically removed, the reaction mixture was neutralized with potassium carbonate and distilled. The resulting 3,5-dithiaheptane-1,7-diol was then oxidized to the disulfone as in Example 1.

By a procedure essentially similar to that used in Example 1, two molar proportions of methanesulfonyl chloride were reacted with bis(2-hydroxyethylsulfonfyl)methane in tetrahydrofuran solution with pyridine employed as the hydrogen chloride acceptor. Recrystallization of the crude product from ethyl acetate-acetonitrile gave colorless bis(2-mesyloxyethylsulfonfyl)methane, m.p. 117–119° C.

EXAMPLE 6

Hardening and Antifogging Testing

Samples of the compounds listed in the tables were added to separate portions of a high-speed silver bromide emulsion which was panchromatically sensitized with a cyanine dye. Each emulsion sample was coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 mg. of gelatin per square foot and dried. The 2 week incubations were carried out at 49° C. and 50 percent Relative Humidity. A sample of each film coating was exposed on an Eastman 1B sensitometer, processed for 5 minutes in Kodak DK-50 developer, fixed, washed and dried. The sensitometric results are presented in Table I.

A sample of each film coating was further tested for hardness, after a 3 day incubation at 38° C. and 50 percent Relative Humidity, by immersing in water at 25° C. for 3 minutes and then calculating the percent swell of the emulsion after measuring the thickness of the swollen samples. The results of these hardness tests are presented in Table II.

Comparing the previously known mesylates with the mesyloxyalkylsulfonfyl compounds of the present invention, it can be seen that the mesyloxyalkylsulfonfyl compounds of this invention are generally superior to the known mesylates in limiting the percentage swell of the gelatin. While the known mesylate bis(2-mesyloxyethyl) ether in certain concentrations limits the percentage of swell more effectively than bis[2-(2-mesyloxyethylsulfonfyl)ethyl] ether, this latter compound is shown in Table I to be a more effective anti-fogging compound. Hence, each of the mesyloxyalkylsulfonfyl compounds of the present invention are demonstrably superior to known mesylates in either hardening or anti-fogging characteristics and most are superior in both respects.

TABLE I

Example	Conc., percent of gelatin	Fresh		49° C., 50% Relative humidity, 2 wk. incubation	
		Gamma	Fog	Gamma	Fog
Control.....	0	1.41	0.17	1.02	0.63
Bis(2-mesyloxyethyl) ether.....	3	1.28	0.15	0.67	0.32
Control.....	0	1.41	0.17	1.02	0.63
1,2-bis(mesyloxy)ethane.....	3	1.28	0.15	0.82	0.30
Control.....	0	1.43	0.13	1.05	0.34
Bis(2-mesyloxyethyl) sulfone.....	3	1.45	0.10	0.98	0.15
Control.....	0	1.41	0.17	1.02	0.63
Bis(2-mesyloxyethylsulfonylmethyl) ether.....	3	1.00	0.08	0.73	0.18
Control.....	0	1.41	0.17	1.02	0.63
Bis[2-(2-mesyloxyethylsulfonyl)ethyl] ether.....	3	1.18	0.12	0.80	0.22
Control.....	0	1.41	0.17	1.02	0.63
1,2-Bis[2-(2-mesyloxyethylsulfonyl)ethoxy]ethane.....	3	1.28	0.10	0.60	0.14
Control.....	0	1.37	0.15	1.15	0.84
Bis(2-mesyloxyethylsulfonyl)methane.....	3	1.00	0.08	1.05	0.11

TABLE II
Swell data for 2-mesyloxyethyl sulfones

Example	Conc., percent of gelatin	Percent swell
Control.....	0	660
Bis(2-mesyloxyethyl) ether.....	1	420
Do.....	3	320
Do.....	6	311
Control.....	0	660
1,2-bis(mesyloxy)ethane.....	1	540
Do.....	3	410
Do.....	6	380
Control.....	0	720
Bis(2-mesyloxyethyl) sulfone.....	1	560
Do.....	3	440
Do.....	6	360
Control.....	0	660
Bis(2-mesyloxyethylsulfonylmethyl) ether.....	1	400
Do.....	3	280
Do.....	6	250
Control.....	0	660
Bis[2-(2-mesyloxyethylsulfonyl)ethyl] ether.....	1	400
Do.....	3	350
Do.....	6	360
Control.....	0	660
1,2-bis[2-(2-mesyloxyethylsulfonyl)ethoxy]ethane.....	1	350
Do.....	3	340
Do.....	6	260
Control.....	0	760
Bis(2-mesyloxyethylsulfonyl)methane.....	1	580
Do.....	3	260
Do.....	6	210

EXAMPLE 7

In a similar fashion, significant hardening and anti-fogging results were obtained when the coatings comprise multilayer color reproducing photographic elements containing in each of three separate layers dye-forming coupler compounds and photosensitive silver halide. The hardeners were added initially to the non-photosensitive interlayers and/or overlayer between and over the light sensitive layers. However, the hardeners were not balanced and therefore migrated into the light sensitive layers. These coatings are described in U.S. Pat. 2,956,879 of VanCampen issued Oct. 18, 1960. The results were obtained under the same conditions above-described and affirm the same good results previously disclosed.

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

What is claimed is:

1. A photographic element comprising a support and at least one hydrophilic colloid layer containing a radiation-sensitive material selected from the group consisting of silver halide, zinc oxide, and photo-sensitive polycar-

bonate resins hardened with a compound having the structural formula:



wherein A contains no more than nine atoms linking the sulfonyl groups and is an alkylene or oxaalkylene group having up to three oxygen atoms and m is 0 or 1.

2. A photographic element comprising a support and at least one gelatin layer containing a radiation-sensitive material selected from the group consisting of silver halide, zinc oxide, and photosensitive polycarbonate resins hardened with a compound having the structural formula:



wherein A contains no more than nine atoms linking the sulfonyl groups and is an alkylene or oxaalkylene group having up to three oxygen atoms and m is 0 or 1.

3. A photographic element according to claim 1 in which said layer contains from 0.5 to 6 percent by weight of said hardener compound based on the weight of colloid present in said layer.

4. A photographic element according to claim 1 in which said layer contains a dye-forming coupler.

5. A photographic element according to claim 1 in which said layer contains a photosensitive silver halide.

6. A photographic element according to claim 1 in which said hardener has two 2-mesyloxyethylsulfonyl radicals coupled through an aliphatic hydrocarbon or ether linking radical.

7. A photographic element according to claim 1 in which said hardener compound is a bis(2-mesyloxyethylsulfonyl-alkyl) ether.

8. A photographic element according to claim 1 in which said hardener compound is bis(2-mesyloxyethyl) sulfone.

9. A photographic element according to claim 1 in which said hardener compound is a bis(2-mesyloxyethylsulfonyl)-dioxaalkane.

10. A photographic element according to claim 1 in which said hardener compound is a bis(2-mesyloxyethylsulfonyl)-alkane.

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