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3,392,023

GELATIN-SILVER HALIDE EMULSION CONTAINING A SALT OF TRIS(BETA-SULFATOETHYL)-SULFONIUM INNER SALT

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ABSTRACT OF THE DISCLOSURE

Certain sulfonium salts containing two or more sulfate ester linkages in positions beta to the sulfonium salt groups are particularly advantageous as hardeners for use in gelatin-silver halide photographic emulsions, including photographic emulsions in which gelatin is only a part of the vehicle for the silver halide. Other polymeric materials such as polyvinyl alcohol and ethyl acrylate-acrylic acid copolymer, for example, can be present in addition to gelatin. The disodium salt of tris(beta-sulfatoethyl) sulfonium inner salt is illustrative of the hardening agents employed.

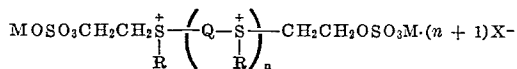
This invention relates to gelatin compositions containing therein as a hardener a sulfonium salt containing two or more sulfate ester linkages in positions beta to the sulfonium salt groups.

Various compounds have been suggested as hardeners for gelatin particularly in photographic applications. Often the suggested compounds adversely affect the photographic materials either when freshly added or after the products have been stored for a time. Often other disadvantages appear.

One object of my invention is to provide addenda for photographic emulsions which serve not only as hardeners but also may act as antifoggants to improve the properties thereof. Another object of my invention is to provide compositions of matter composed of beta-sulfatoethylsulfonium salts. A further object of my invention is to provide hardeners for photographic emulsions which do not significantly decrease the sensitometric properties thereof either when freshly added or after storage. Other objects of my invention will appear herein.

I have found that certain sulfonium salts containing two or more sulfate ester linkages in positions beta to the sulfonium salt groups are useful for the hardening of gelatin particularly when employed for photographic purposes. These hardeners are particularly advantageous for use in gelatin-silver halide photographic emulsions which include photographic emulsions in which gelatin may be only a part of the vehicle for the silver halide. The vehicle for the silver halide emulsion may be made up entirely of gelatin or may contain in addition to the gelatin some other polymeric material such as polyvinyl alcohol, ethyl acrylate-acrylic acid copolymer, butyl acrylate-acrylic acid copolymer, or some other suitable vinyl or acrylic polymeric material. The hardener is effective in hardening polymers generally having hydrophilic groups, e.g. OH, carboxyl, etc. Thus it is useful in compositions in which the binder or colloid is entirely a synthetic polymer having a hydrophilic radical therein.

I have found that the compounds represented by the following structural formula are useful as gelatin hardeners in accordance with my invention:



in which n is 0 or 1; R is an alkyl radical of 1 to 6 carbon atoms or $-\text{CH}_2\text{CH}_2\text{OSO}_2\text{M}$; Q is an alkylene chain of

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1 to 10 carbon atoms which may contain unsaturation or phenylene, cycloalkylene or a hetero atom as part of the chain; M is a suitable cation such as ammonium, alkali metal or alkaline earth metal and X^- represents any suitable anion as for example Cl^- , RSO_3^- , or the like.

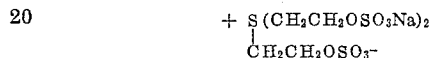
Also included are zwitterion compounds derived from the above by removal of one or more equivalents of MX such as the disodium salt of tris(beta-sulfatoethyl) sulfonium inner salt.

The hardeners in accordance with my invention are effective when present in a gelatin composition in any concentration, however, usually amounts of 0.5–5% based on the weight of the gelatin will be found to be conveniently useful.

The following examples illustrate my invention:

Example I

The disodium salt of tris(beta-sulfatoethyl)sulfonium inner salt having the structural formula



was added at two concentrations to separate portions of a high-speed silver bromiodide photographic emulsion which had been 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. A sample using the emulsion without the hardener addition was also made. A sample of each film coating was exposed on an Eastman 1B sensitometer, processed for five minutes in Kodak DK-50 developer, fixed, washed, and dried with the following results.

| Hardener, g./100 g. of Gelatin | Fresh | | | 120°, 1 Wk. Inc. | | | Percent Swell in H ₂ O |
|--------------------------------------|---------------|----------|-----|------------------|----------|-----|---|
| | Rel. Speed | γ | Fog | Rel. Speed | γ | Fog | |
| 100 | 1.25 | .13 | | 60 | .97 | .38 | 750 |
| 100 | 1.32 | .13 | | 48 | .75 | .26 | 490 |
| 95 | 1.32 | .11 | | 52 | .75 | .15 | 320 |

The percent swell in water of the emulsion layers was determined by immersing strips of coatings thereof on film base in distilled water at 68° F. for a time and from measurements taken before and after this immersion determining the percentage increase in thickness of the emulsion layer.

Example II

Two portions of a high speed silver halide photographic emulsion in which the vehicle for the silver halide was a mixture of gelatin 25% and the sodium salt of ethyl acrylate-acrylic acid copolymer (75%) were taken. To one portion was added 5 parts of disodium salt of tris(beta-sulfatoethyl)sulfonium inner salt per 100 parts of vehicle. Each emulsion was coated out on clear cellulose acetate film support at the rate of 750 mg. of emulsion per square foot of support. The vertical swell of these samples with and without hardener in accordance with the invention in DK-50 developer and in water was determined, with the following results:

| Hardener, g./100 g. of vehicle | Percent Vertical Swell at 25° C. | |
|-----------------------------------|----------------------------------|------------------|
| | DK-50 | H ₂ O |
| None | ca. 1,200 | Washed off |
| 5 | 450 | 120 |

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 as described hereinabove, and as defined in the appended claims.

I claim:

1. A gelatin-silver halide photographic emulsion containing as a hardener therein the disodium salt of tris(beta-sulfatoethyl)sulfonium inner salt.

2. A gelatin-silver halide photographic emulsion containing as a hardener therein a di-salt of tris(beta-sulfatoethyl)sulfonium inner salt, and wherein said di-salt is selected from the group consisting of ammonium, alkali metal and alkaline earth metal.

3. A silver halide photographic emulsion in which the vehicle for the silver halide is a mixture of gelatin and ethyl acrylate-acrylic acid copolymer containing as a hardener therein a di-salt of tris(beta-sulfatoethyl)sulfonium inner salt, and wherein said di-salt is selected from the group consisting of ammonium, alkali metal and alkaline earth metal.

4. A silver halide photographic emulsion in which the vehicle for the silver halide is a mixture of gelatin and ethyl acrylate-acrylic acid copolymer containing as a hardener therein the disodium salt of tris(beta-sulfatoethyl)sulfonium inner salt.

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