United States Patent Office

3,642,908

Patented Feb. 15, 1972

3,642,908

VINYL AND ETHER CONTAINING SULFONES

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No Drawing. Application Nov. 13, 1967, Ser. No. 682,641, now Patent No. 3,490,911, dated Jan. 20, 1970, which is a continuation-in-part of application Ser. No. 488,797, Sept. 20, 1965. Divided and this application Aug. 22, 1969, Ser. No. 862,144

Int. Cl. C07c *147/02*

U.S. Cl. 260—607 A 2 Claims

ABSTRACT OF THE DISCLOSURE

Certain compounds containing two or more vinylsulfonylalkyl groups attached to a plurality of tertiary or quaternary nitrogen atoms and/or to a plurality of ether oxygen atoms are effective gelatin hardeners.

This is a division of Ser. No. 682,641, filed Nov. 13, 1967 now U.S. Pat. 3,490,911, which in turn is a continuation-in-part of Ser. No. 488,797, filed Sept 20, 1965, now abandoned.

This invention relates to gelatin compositions in which a hardener has been incorporated, which hardener contains two or more vinylsulfonylalkyl groups. These groups can be attached to a plurality of tertiary or quaternary nitrogen atoms or to a plurality of ether oxygen atoms or a combination thereof.

Compounds having olefinic linkages have previously been referred to as useful for gelatin hardeners but nowhere in the prior art is there any indication that vinylsulfonylalkyl compounds are useful for this purpose.

One object of our invention is to provide effective hardeners for photographic gelatin and for gelatin-containing photographic emulsions. Another object of our invention is to provide gelatin hardeners which are free from undesirable photographic properties and have good water solubility, low volatility and low physiological activity. Other objects of our invention will appear herein.

We have found that compounds containing two or more vinylsulfonylalkyl groups (that is lower alkyl from 1 to 4 carbon atoms) attached to a plurality of tertiary or quaternary nitrogen atoms and/or a plurality of ether oxygen atoms are effective hardeners for gelatin and more particularly for photographic gelatin. The term photographic gelatin is interpreted as including gelatin derivatives and physical mixtures of gelatin and other colloids, such as mixtures of gelatin with compatible synthetic polymers exemplified by copolymers of methyl acrylate and acrylic acid or butyl acrylate and acrylic acid and the like. These compounds are effective not only in compositions in which gelatin is the sole vehicle but also where the vehicle is composed of a carboxylated polymer such as ethyl acrylate-acrylic acid copolymer and butyl acrylate-acrylic acid copolymer, for example, or a mixture thereof with gelatin. Some compounds which are useful as hardeners in accordance with this invention are as follows where V is used to represent

$$CH_2{=}CHSO_3(CH_3)_m{-}$$

where m is 1 or 2. These compounds are exemplified in the following:

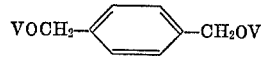
$VO(CH_2)_nOV$ n=2-10

$VOCH_2CH_2SO_2CH_2CH_2OV$

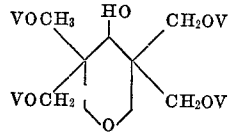
$VOCH_2CH_2NHCONHCH_2CH_2OV$

$VO(CH_2CH_2O)_nV$ n=1-4

$VOCH_2CH_2OV$

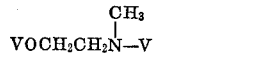


$VOCH_2C{-}CH_2OV$
$(VOCH_2)_1CCH_3$
$(VOCH_2)_4C$

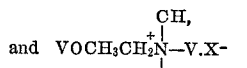


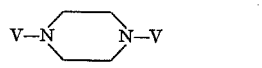
$(VOCH_2CH_2)_3N$

and $(VOCHgCH_2)_2\overset{+}{N}R.X^-$

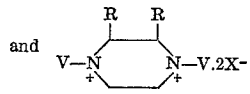


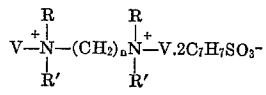
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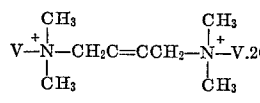


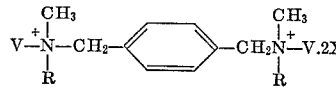


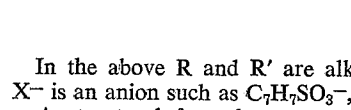
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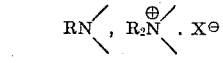


In the above R and R' are alkyl of 1–4 carbons and X^- is an anion such as $C_7H_7SO_3^-$, ClO_4^-, $CH_3OSO_3^-$.

A structural formula representing compounds useful as hardeners in accordance with our invention is as follows:

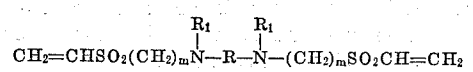
$$[CH_2{=}CHSO_2(CH_2)_mA]_nZ$$

in which n is an integer from 2 to 6; A is

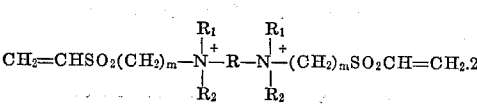


or —O—; each R is an alkyl group of 1 to 4 carbon atoms, $X^\ominus$ is an anion, such as for example $C_7H_7SO_3$—, ClO_4—, CH_3OSO_3— and the like; m is 1 or 2; Z is a polyvalent radical of n valences such as for example alkylene radicals of from 1 to 10 carbon atoms which can contain unsaturation or which can be interrupted by an arylene radical, cycloalkylene radical or by simple functional groups such as other, sulfur or amide linkages. In addition, Z can combine with other substituents together with nitrogen atoms when present, thus forming a heterocyclic ring such as piperazine, alkyl substituted piperazines and the like.

More specifically, other structural formulae are represented as follows:



and



in which R_1 and R_2 are lower alkyl groups of 1–4 carbon atoms, each *m* is 1 or 2 and R represents an alkylene chain of from 1–10 carbon atoms which can contain unsaturation or which can be interrupted by an arylene radical, a cycloalkylene radical or by simple functional groups such as ether, sulfur or amide linkages. In addition, R and both R_1's together with the two nitrogen atoms can constitute a heterocyclic ring such as piperazine, alkyl substituted piperazines and the like, and $X^{\ominus}$ is any suitable anion, such as $C_7H_7SO_3$—, ClO_4—, CH_3OSO_3—, and the like.

The hardeners in accordance with our invention, when present in the gelatin composition, exert hardening action, however, for practical purposes ordinarily the amount of hardener used would be in the range of 0.5–15%, based on the weight of the gelatin in the compositions.

The compounds described in this application can be used effectively in combination with hardenable materials in general but they are most advantageously used with natural or synthetic polymers used as vehicles or binders in preparing photographic elements. Specific materials which can be hardened according to the practice of this invention include hardenable materials such as polymers, for example, 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 or methacrylates, maleic acid, and the like.

The hardening agents described herein can be used in various kinds of photographic emulsions. In addition to being useful in orthochromatic, panchromatic and infrared emulsions, they are also useful in X-ray and other nonoptically sensitized emulsions. They can be added to the emulsions before or after the addition of any optically sensitizing dyes which may be used. They are effective in sulfur and gold sensitized silver halide emulsions.

The materials hardened in the practice of this invention can be coated on a wide variety of supports. Typical supports include those generally employed for photographic elements as exemplified by cellulose nitrate film, cellulose acetate film, polystyrene film, polyethylene terephthalate film, and related films or resinous materials as well as glass, paper, metal, wood, and the like. Supports such as paper that are coated with α-olefin polymers, particularly polymers of α-olefins containing 2–10 carbon atoms, as for example, polyethylene, polypropylene, ethylene butene copolymers, and the like, can also be employed.

In addition to the hardening agents disclosed herein, photographic emulsions and elements can also contain additional additives, particularly those known to be beneficial in photographic emulsions, as exemplified by optical sensitizers, speed increasing materials, other hardeners, plasticizers, and the like, such as those described in Henn and Goffe U.S. Pat. 3,128,180 issued Apr. 7, 1964.

The emulsions hardened by new compounds can be used in photographic elements intended for color photography and thus may contain color-forming couplers or used as emulsions to be developed by solutions containing couplers or other color-generating materials or emulsions of the mixed-packet type.

The silver halides employed in the photographic emulsions include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver chloroiodide, and the like. The silver halides used can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide emulsion.

Hardened emulsions obtained in accordance with this invention and with gelatin or other hardenable hydrophilic colloids may be used in various diffusion transfer materials.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

The following Examples 1–10 illustrate methods of preparing these hardening compounds and the tables following Examples 5 and 12 supply data indicating desirable photographic effects unexpectedly obtained using the various hardeners described herein.

EXAMPLE 1

N,N'-bis(2-vinylsulfonylethyl)piperazine

A solution of 52 parts of divinyl sulfone in 100 parts of dry chloroform is cooled to 10° C. and added dropwise thereto with stirring at 10–15° C. is a solution of 17.2 parts of anhydrous piperazine in 100 parts of chloroform. A cloudy solution forms which is stirred for 7 hours and then left overnight. The mass is then treated with charcoal and the filtrate obtained is evaporated at reduced pressure on a water bath. The crude product is recrystallied first from ethyl acetate and then three times from acetone giving a colorless product having a melting point of 125–126° C.

EXAMPLE 2

N,N'-bis(2-vinylsulfonylethyl)piperazine-bis(methoperchlorate)

A solution of 9.7 parts of N,N'-bis(2-vinylsulfonylethyl)piperazine and 16.7 parts of methyl p-toluenesulfonate in 50 parts of acetonitrile is stirred at room temperature for two hours and then refluxed overnight. The solution is treated with charcoal and the filtrate is evaporated at reduced pressure on a water bath to ½ volume and poured into ether. An oily precipitate is obtained. This precipitate is washed with ether, dissolved in a minimum amount of water and then treated with a concentrated solution of about 20 parts of sodium perchlorate in 10 parts of water. The product is induced to crystallize, is filtered, and then recrystallized from a minimum amount of water. The colorless product obtained melts at 191–192° C.

EXAMPLE 3

N,N'-bis(2 - vinylsulfonylethyl)-N,N'-dimethyl-2-butene-1,4 - diamine bis(metho-p-toluenesulfonate) (A) and the corresponding bis(methofluoborate) (B)

The metho-toluene sulfonate is prepared in essentially the same manner as in the preceding example but using instead of N,N'-bis(2-vinylsulfonylethyl)piperazine, N,N'-bis(2 - vinylsulfonylethyl)-N,N'-dimethyl - 2-butene-1,4-diamine. The colorless product designated (A) melts at 235–236° C. Some of the product is converted to the fluoborate by using aqueous fluoboric acid producing a colorless product designated (B) having a melting point of approximately 288° C. at which temperature decomposition occurs.

EXAMPLE 4

N,N'-bis(2-vinylsulfonylethyl)-N,N'-dimethylethylene-diamine bis(metho-p-toluenesulfonate)

This compound having a melting point of approximately 197° C. is prepared in the same manner as in the preceding examples but using N,N'-dimethylethylenediamine as the starting material.

EXAMPLE 5

1,2-(bisvinylsulfonylmethoxy)ethane

5,8-dioxa-3,10-dithiadodecane-1,12-diol is prepared by the reaction of two molar proportions of sodium 2-hy-

droxyethylmercaptide with 1,2-bis(chloromethoxy)ethane in methanol, followed by evaporation of the solvent.

The bis-sulfide is oxidized to the disulfone in hydrogen peroxide according to the method of H. S. Schultz et al., J. Org. Chem., 28, 1140 (1963).

1,2 - bis(2 - chloroethylsulfonylmethoxy)ethane is prepared by adding the disulfone diol to a large excess of thionyl chloride containing a catalytic amount of N,N-dimethylformamide, at room temperature. Evaporation of the excess thionyl chloride furnishes the crude chloride which is dissolved in tetrahydrofuran and treated with two molar proportions of triethylamine at 0 to 5° C. After 24 hours, the triethylamine hydrochloride and solvent are removed to give an oily product of n_D^{28} 1.4975. The identity of this product is confirmed by nmr spectroscopy and elemental analysis.

Samples of the compounds prepared in the preceding examples are added to separate portions of a high-speed silver bromoiodide emulsion which is panchromatically sensitized with a cyanine dye. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 milligrams of gelatin per square foot. A sample of each film coating is exposed on an Eastman 18 sensitometer, processed for five minutes in Kodak DK–50 developer, fixed, washed, and dried with the following results.

Example	Hardener conc., g./mole Ag	Fresh tests			Percent swell		
		Rel. speed	Gamma	Fog	Developer	Fix	Wash
1	2.4	110	1.22	.13	920	450	780
1	7.2	132	1.12	.22	820	390	630
1	14.4	120	.98	.28	420	240	330
Control		100	1.20	.11	1,100	540	940
2	2.4	120	1.22	.07	1,000	510	700
2	7.2	115	1.28	.05	690	370	510
2	14.4	107	1.27	.05	460	270	360
Control		100	1.22	.10	1,200	560	810
3	4.8	123	1.28	.18			660
3	14.4	112	1.23	.18			510
3	4.8	123	1.30	.18			720
3	14.4	129	1.30	.17			750
4	4.8	102	1.30	.13			520
4	14.4	76	.93	.08			360
Control		100	1.32	.15			800
5	2.4	49	1.30	.10			400
Control		100	1.55	.16			800

EXAMPLE 6

1,2-bis(2-vinylsulfonylethoxy)ethane

A few drops of a solution made by reacting sodium with excess ethylene glycol are added to a stirred solution of 6.2 parts of ethylene glycol in 23.6 parts of freshly distilled divinyl sulfone stabilized with less than 0.1% of hydroquinone. A rapid temperature rise indicates reaction is occurring. The reaction temperature is kept below 35° C. and a few crystals of hydroquinone are added. After 48 hours, the reaction mixture is neutralized with glacial acetic acid and any volatile compounds are removed under vacuum (0.5 mm., 30° C., five hours) and the mass is filtered. A product is obtained having an average molecular weight of approximately 293.

EXAMPLE 7

1,4-bis(2-vinylsulfonylethoxy)butane

A procedure is effected in the same manner as the preceding example but using 24 parts of divinyl sulfone and 9 parts 1,4-butanediol in 20 parts of dry dichloromethane as the reaction medium. A liquid product is obtained having an average molecular weight of approximately 227.

EXAMPLE 8

Bis[2-(2-vinylsulfonylethoxy)ethyl]sulfone

The procedure described is repeated using 25 parts of divinyl sulfone and 15.4 parts of bis(2-hydroxyethyl) sulfone in 20 parts of dry dimethyl sulfoxide using sodium ethoxide catalyst. A liquid product is obtained having an average molecular weight of approximately 325.

EXAMPLE 9

N,N'-bis[2-(2-vinylsulfonylethoxy)ethyl]urea

25 parts of divinyl sulfone and 14.8 parts of N,N'-bis(2-hydroxyethyl)urea are reacted in 25 parts of dry acetonitrile and 15 parts of dimethyl sulfoxide using sodium ethoxide catalyst. A product is obtained having an average molecular weight of approximately 384.

EXAMPLE 10

1,14-bis(vinylsulfonyl)-3,6,9,12-tetraoxatetradecane

25 parts of divinyl sulfone and 15 parts of triethylene glycol are reacted to give the product designated herewith. The product obtained has an average molecular weight of 309.

EXAMPLE 11

N,N-bis[2-(2-vinylsulfonylethoxy)ethyl]dimethylammonium p-tosylate

The reaction of 23.8 grams of N-methyldiethanolamine and 47.3 grams of divinylsulfone in 300 milliliters of acetonitrile containing sodium methoxide as catalyst and 0.1 gram of hydroquinone yields an amine adduct which is quaternized in solution with 37.2 grams of methyl p-tosylate. Isolation by precipitating into ether produces a light-colored oil of n_D^{25} 1.5310.

EXAMPLE 12

N,N-bis[2-(2-vinylsulfonylethoxy)ethyl]dimethylammonium perchlorate

By treating 21.7 grams of the tosylate of the preceding example with 6 grams of sodium perchlorate in acetonitrile produces, after filtering and removing of the solvent, a viscous oil in n_D^{25} 1.4883.

Samples of the compounds prepared in Examples 6–12 are added to separate portions of a high-speed silver bromoiodide emulsion which are panchromatically sensitized with a cyanine dye. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 mg. of gelatin per square foot. Samples of the various films are exposed on an Eastman 1B sensitometer, processed for five minutes in Kodak Developer DK–50, fixed, washed, and dried. The proportions of hardener used, the example from which the hardener was derived, the photographic tests on the fresh coatings and the perecntage of swell as compared with the control are as follows:

Example No.	Hardener conc. (g./mole Ag)	Fresh tests			Percent swell
		Rel. speed	Gamma	Fog	
6	Control	100	1.23	.13	750
	2.4	95	1.18	.12	420
	7.2	89	1.13	.12	270
	14.4	85	1.12	.10	220
7	Control	100	1.32	.20	750
	14.4	87	1.20	.14	300
8	Control	100	1.34	.21	750
	7.2	80	1.13	.16	290
9	14.4	82	1.18	.16	230
10	Control	100	1.25	.19	760
	7.2	105	1.20	.16	340
11	Control	100	1.34	.28	620
	2.4	170	1.17	.35	480
	7.2	219	1.00	.37	320
	14.4	204	0.97	.35	230
12	2.4	178	1.05	.39	410
	7.2	155	0.87	.43	280
	14.4	191	0.93	.46	260

The hardeners in accordance with our invention have shown themselves to be useful in color photography such as in photographic emulsions in which color couplers have been incorporated. The use of these hardeners results in reduced stain with no adverse sensitometric effects when used in levels producing satisfactory hardness in contrast with some of the aldehyde types of gelatin hardeners. No adverse effect upon dye hue or stability of the emulsion has been observed. For instance,

in a photographic product in which coatings of the following structure were applied to a support these hardeners have been used with good effect:

Layer 6—gelatin layer
Layer 5—red-sensitive silver chlorobromide gelatin consisting of 90 mole percent bromide and a phenolic cyan coupler of the type described in U.S. Pat. 2,423,730.
Layer 4—gelatin layer and an ultraviolet absorber
Layer 3—green-sensitive silver chlorobromide gelatin emulsion consisting of 80 mole percent chloride and a pyrazolone magenta coupler of the types described in U.S. Pat. 2,600,788.
Layer 2—gelatin layer
Layer 1—blue-sensitive silver chlorobromide gelatin emulsion consisting of 98 mole percent bromide and an acyl acetanilide yellow coupler of the type described in U.S. Pat. 2,875,057.

The hardeners in accordance with our invention can be used in all six of the layers of the product or they can be used in the emulsion compositions with other hardeners being used in the gelatin layers if desired. In such use improvement in stain is obtained as compared with the use of a hardener such as formaldehyde or mucochloric acid.

Silver halide emulsions containing the hardeners of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Pats. 2,352,014 of Rott issued June 20, 1944; 2,543,181 of Land issued Feb. 27, 1951; and 3,020,155 of Yackel, Yutzy, Foster and Rasch issued Feb. 6, 1962. The emulsions can also be used in diffusion transfer color processes which utilize a diffusion transfer of an imagewise 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. Such processes are described in Rogers U.S. Pat. 2,983,606 issued May 9, 1961; Weyerts et al. U.S. Pat. 3,253,915 issued May 31, 1966; and Whitmore U.S. Pat. 3,227,552 issued Jan. 4, 1966. Silver halide emulsions containing the hardeners of the invention can be processed in stabilization processes such as the ones described in U.S. Pat. 2,614,927 of Broughton and Woodward issued Oct. 21, 1952, and as described in the article "Stabilization Processing of Films and Papers," by H. D. Russell, E. C. Yackel and J. S. Bruce in P.S.A. Journal, Photographic Science and Technique, volume 16B, October 1950.

The hardeners of this invention can be used to harden silver halide emulsion and other photographic layers containing silver halide developing agents such as polyhydroxy benzene, amino phenol phenol and 3-pyrazolidone developing agents.

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.

We claim:

1. Bis[2-(2-vinylsulfonylethoxy)ethyl]sulfone.
2. 1,2-bis-(vinylsulfonylmethoxy)ethane.

No references cited.

LEWIS GOTTS, Primary Examiner

D. R. PHILLIPS, Assistant Examiner

U.S. Cl. X.R.

96—111; 106—12 S; 260—117, 268 R, 345.9, 501.1 S, 553 D, 567.6 B, 584 R

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,642,908 Dated February 15, 1972

Inventor(s) Donald M. Burness, Stanley W. Cowan and Charles J. Wrigh

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

Column 2, line 4, "$VOCH_2C-CCH_2OV$" should read ---$VOCH_2C{\equiv}CCH_2OV$---.

Column 2, lines 10-15, "$(VOCHgCH_2),\overset{+}{N}R.X^-$" should read ---$(VOCH_2CH_2)_3\overset{+}{N}R.X^-$---.

Column 2, line 15, "and $VOCH_3CH_2\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{R}{|}\text{-}V.X^-$" should read

---and $VOCH_3CH_2\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{R}{|}\text{-}V.X^-$ ---.

Column 2, line 28, "$V\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{CH_3}{|}\text{-}CH_2C{=}CCH_2\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{CH_3}{|}\text{-}V.2C_7H_7SO_3^-$"

should read ---$V\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{CH_3}{|}\text{-}CH_2C{\equiv}CCH_2\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\overset{CH_3}{|}\text{-}V.2C_7H_7SO_3^-$ --- .

Column 2, line 56, "other" should read ---ether---.

Column 6, line 61, under the Heading "Percent Swell", "480" should read ---430---.

Signed and sealed this 5th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents