

1

3,091,537

**HARDENING OF PHOTOGRAPHIC LAYERS**  
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This invention relates to the hardening of photographic emulsion layers or of gelatin or other polymeric materials used for colloidal layers in photographic products which comprises incorporating quaternary ammonium compounds which contain at least two epoxide groups, in compositions thereof.

Various agents have been employed for hardening gelatin or other polymers such as are employed for photographic layers or as carriers for silver halide-photographic emulsions. Some of these which might be mentioned are formaldehyde, chrome salts, dialdehydes, hydroxy aldehydes and the like. Often one or the other of the compounds which have been previously suggested for hardening purposes for photographic products exhibit disadvantages such as effect on the sensitivity of the photographic emulsion or other unwanted characteristics. Many of the hardeners suggested have been volatile, fat-soluble, or unstable in aqueous solution or have not been photographically inert.

One object of our invention is to provide for the hardening of gelatin or other polymeric materials used in photographic layers by incorporating quaternary ammonium compounds, containing at least two epoxide groups therein, in compositions of the polymeric materials. Another object of our invention is to provide gelatin or other polymeric products having carboxyl and/or amino groups therein with hardening agents which are non-volatile, stable in aqueous solution and non-fat soluble. Other objects of my invention will appear herein.

I have found that quaternary ammonium compounds containing at least two epoxide groups therein exhibit satisfactory hardening properties when used in gelatin compositions which are employed either as carriers for silver halide-photographic emulsions or for applying layers in the manufacture of photographic products. I have found in addition that these compounds exert a hardening effect upon carboxyl-bearing polymers useful for the purposes specified.

The quaternary ammonium salts containing at least two epoxide groups therein are used as hardeners in an amount at least 1/2% based on the weight of the gelatin or other polymeric material. In practice, not more than 10 percent is needed, based on gelatin weight. The proportions, however, of the hardeners in accordance with my invention are not critical, in that proportions less than 1/2% have been found to exhibit a hardening effect on gelatin or carboxyl-bearing polymers and on the other hand proportions thereof greater than 10 percent will result in a hardening effect when incorporated in compositions of gelatin or other carboxyl containing polymers.

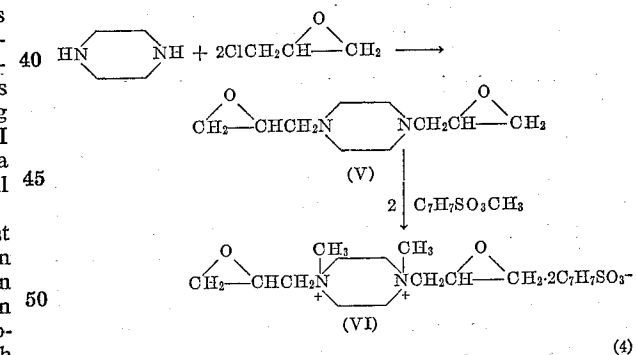
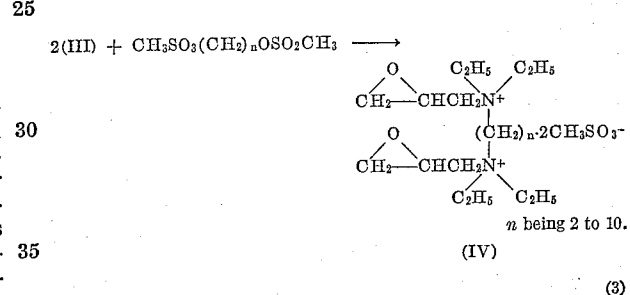
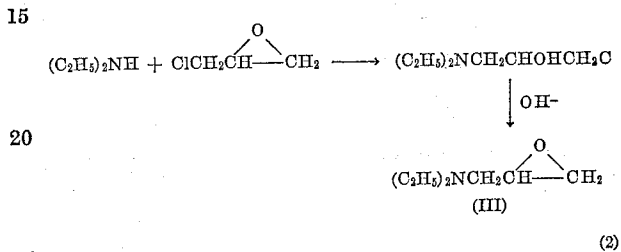
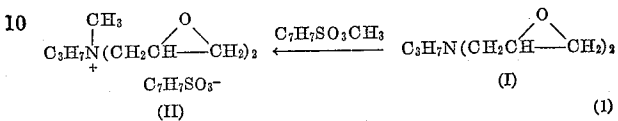
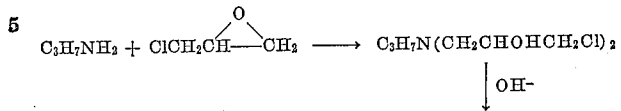
The anion of the quaternary ammonium salt may be that of any convenient acid, although because of ease in their preparation, the perchlorate and sulfonate salts have been preferred. However, the chloride, sulfate, phosphate or the like may be employed for hardening purposes to good effect.

The quaternary ammonium salts useful for hardening may be entirely aliphatic or they may contain cycloaliphatic groups or aromatic groups therein. In some cases, cyclic compounds containing nitrogen in the ring may be used to supply the nitrogen for the quaternary ammonium structure of the hardener.

Compounds useful as hardeners in accordance with my invention are relatively easily prepared in good yield

2

and may be a variety of types. The following equations exemplify procedures by which compounds useful for hardening purposes are prepared.



It is apparent from Equation 1 that the amine may consist of any of the lower aliphatic or aromatic primary amines and the alkylating agent may be selected from the alkyl sulfonates, sulfates, halides, or the like. In Equation 2 instead of a lower aliphatic secondary amine certain heterocyclic amines, such as piperidine or morpholine may be used. In Equation 3 the bisulfonate might contain unsaturation, hetero atoms or rings or the corresponding dihalide might be used. Other di-secondary amines can be employed in place of the piperazine in Equation 4. Sometimes in the preparation of the quaternary ammonium compounds, difficulty is experienced in obtaining crystalline salts. It has been found, however, that an entirely satisfactory hardener may result when the reaction product is isolated as a concentrated aqueous solution and used in that form.

The polymeric compounds which may be hardened by quaternary ammonium compounds containing bisepoxide groups in accordance with the invention are

3

those containing amino and/or carboxyl groups. Many of these polymers have been used for supplying coatings in the manufacture of photographic products or as carriers for silver halides in photographic emulsions, such as gelatin, cellulose ether phthalate and synthetic resins. Gelatin and carboxyl containing polymers are readily hardenable by incorporating quaternary ammonium compounds therein in accordance with our invention. The cellulose ethyl ethers containing carboxyl groups as have been described in U.S. Patent No. 2,725,293 as being useful as carriers for silver halide are hardenable by means of quaternary ammonium compounds in accordance with my invention. Examples of polymers containing carboxyl groups hardenable by quaternary ammonium compounds as described herein are ammonium salts of poly-(butylacrylate co-acrylic acid), sodium salts of phthalated polyvinyl alcohol, ammonium salts of phthalated gelatin, ammonium salts of copolymers of acrylic acid (30-40 mol percent) and one or more of the following esters: butyl methacrylate, butyl acrylate, ethyl acrylate, ammonium salts of poly(butylacrylate-acrylo nitrile-acrylic acid), etc.

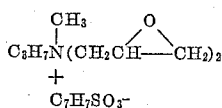
We have found that when hardeners as described herein are incorporated in compositions of these polymers and the compositions are coated out onto a surface and the coating is dried, such as by warm dry air, hardening of the polymeric material takes place in a short time as evidenced by improved resistance to the effect of hot water and by an appreciable increase in the melting point of the coating as compared with the same polymeric material in which no hardener has been incorporated. The polymeric layer is hardened by the quaternary ammonium compound upon standing or aging such as for two or three days at normal temperature. With curing at an elevated temperature hardening results in a shorter time.

The following examples exemplify methods of preparing quaternary ammonium compounds and illustrate the use of those compounds as gelatin hardeners in accordance with my invention.

#### EXAMPLE I

295 parts of epichlorohydrin was added dropwise to a mixture of 295 parts of n-propylamine and 4.5 parts of water. The temperature was maintained at 25-28° during this addition and for 6 hours thereafter. A solution of 142 parts of sodium hydroxide in 230 parts of water was then added dropwise to the mass while cooling below 25° C. After 1½ hours the top layer was separated, combined with ether extracts of the aqueous layer and the whole was dried over potassium hydroxide pellets for several days. The product obtained was filtered and distilled yielding 134 parts of product, boiling at 102.5° C. This product was N,N-bis(2,3-epoxypropyl)-propylamine.

17.3 parts of the amine so prepared was mixed with 18.6 parts of methyl paratoluene sulfonate in 20 parts of benzene and the mass was allowed to stand at 25° C. for 16 hours. The lower oily layer was separated, washed with benzene and was dissolved in 45 parts of water. This solution was washed with three separate portions of benzene and was subjected briefly to reduced pressure to remove traces of the benzene. The resulting solution contained about 42 percent by weight of bis(2,3-epoxypropyl)methylpropyl ammonium p-toluene sulfonate:



#### EXAMPLE II

A solution of 27.8 parts of 3-diethylamino-1,2-epoxy-

4

propane (prepared according to Gilman and Fullhard, JACS 71, 1420), in 25 parts of benzene was mixed with a neutral solution of 26 parts of 1,5-dimethane sulfonyl pentane in 25 parts of benzene. The mixture was allowed to stand 16 hours whereupon the mixture was heated on a steam bath for 6 hours. It was then cooled and the lower layer was separated and dissolved in 75 parts of water. After separating from the undissolved fraction the aqueous solution was treated with charcoal, washed with benzene and was treated briefly at reduced pressure to remove traces of benzene. The solution obtained contained approximately 30 percent of 1,5-pentane bis(2,3-epoxypropyl diethyl ammonium methane sulfonate).

#### EXAMPLE III

A suspension of 12 parts of 1,4-dimethanesulfonyl-2-butyne in 50 parts of benzene was mixed with 11 parts of 3-dimethylamino-1,2-epoxypropane. The mass was stirred for one hour on a steam bath, following which it was cooled and the lower layer was dissolved in 25 parts of water and washed with benzene. This solution was treated with charcoal and then with a concentrated aqueous solution of sodium perchlorate. The oil which separated gradually crystallized at 0° C. These crystals, brown in color, were extracted with acetone and ethanol. After several recrystallizations from acetonitrile-ethyl acetate, cream-colored granular crystals of 2-butyne-1,4-bis(2,3-epoxypropyl)dimethyl ammonium perchlorate were obtained.

The quaternary ammonium salts prepared in accordance with the above examples were incorporated in aqueous gelatin compositions which were coated out onto support in the form of a layer thereon. The melting properties of these layers were compared with those of gelatin to which no hardener had been added as follows:

Hardener	Percent based on gelatin	Start of melt, ° F.
No additive		86
Bis-(2,3-epoxypropyl) methyl propyl ammonium p-toluene sulfonate	1.35	212-1'
1,5-pentane-bis(2,3-epoxypropyl diethyl ammonium methane sulfonate)	0.8	149
2-butyne-1,4-bis(2,3-epoxypropyl dimethyl ammonium perchlorate)	1.6	212-2'
	1.7	212-2'

The designations 212-1' and 212-2' indicate that it was necessary to hold the temperature at boiling for one or two minutes, respectively, before any melting of the gelatin layer was observed.

#### EXAMPLE IV

222 parts of epichlorohydrin at 25° C. was added dropwise to 121 parts of a 40 percent solution of methylamine in water. Cooling was necessary to hold the temperature at 20-30° during the addition and for three hours thereafter. 208 parts of a solution of 50 percent sodium hydroxide was then added at a temperature of less than 25° C. and the mass was stirred for 1½ hours. The top layer which formed was separated and was combined with ether extracts of the bottom aqueous layer and the mass was dried over potassium hydroxide pellets for several days. The mass was filtered and distilled at reduced pressure (20 mm.) at 104-107° C.

7.1 parts of the N,N-bis(2,3-epoxypropyl)methylamine formed thereby was mixed with 9.3 parts of methyl paratoluene sulfonate and 15 parts of benzene and the materials were allowed to react for 5 hours whereupon the benzene was decanted off. The syrupy residue which resulted was dissolved in 80 parts of acetone and a solution

5

of 13½ parts of sodium perchlorate in 13.5 parts of acetone was added. The mixture was filtered, the acetone was evaporated off and the residue was dissolved in water. The solution was washed with benzene and treated with activated carbon. There was obtained 37 parts of a pale yellow solution containing 32 percent of bis(2,3-epoxypropyl)dimethyl ammonium perchlorate.

## EXAMPLE V

A solution of 102 parts of piperazine in 100 parts of methanol was added dropwise to 223 parts of epichlorohydrin and 3 parts of water. After solid began to separate an additional 200 parts of methanol was added to facilitate stirring which was carried on for three hours. The mixture was cooled, filtered, and the mixture was washed with ligroin. The product was recrystallized from 1200 parts of ethyl acetate giving 106 parts of colorless bischlorohydrin (M.P. 101.5–103°). The filtrate was cooled to –60° C. producing 16 parts of isomeric bischlorohydrin, having a melting point of 82–84° C.

45 g. of the higher melting bischlorohydrin obtained as described was mixed with a solution of 120 parts of sodium hydroxide in 200 parts of water at 50° C. The mass was stirred for ½ hour at that temperature and was extracted with benzene. This extraction was repeated ½ hour later and the two combined filtered extracts were evaporated to dryness. The crude product obtained, 1,4-bis(2,3-epoxypropyl)piperazine dihydrate, was recrystallized from ether. A mixture of 7 parts of this product and 15 parts of methyl p-toluene sulfonate in 15 parts of methanol were refluxed for one hour. The solvent was slowly evaporated from the mass at room temperature and 1.8 parts of crystals were obtained which after recrystallization from ethanol melted at 240–241.5° C. The bulk of the crystalline product melted at 205–215° C. after crystallization from ethanol. The product obtained was a quaternary ammonium salt designated as 1,4-bis-(2,3-epoxypropyl)-1,4-dimethyl piperazinium di-p-toluene sulfonate.

## EXAMPLE VI

N,N-bis(2,3-epoxypropyl)ethylamine was obtained by the procedure described in the first part of Example I except that ethylamine was employed instead of propylamine. This material was reacted with methyl paratoluene sulfonate in the manner similar to that described in Example I. There was obtained a 48 percent solution of quaternary salt designated bis(2,3-epoxypropyl)ethylmethyl ammonium paratoluene sulfonate.

The following table illustrates the hardening effects of these quaternary ammonium bisepoxides on photographic emulsions.

Table I

HARDENING OF PHOTOGRAPHIC GELATIN EMULSION BY THE QUATERNARY AMMONIUM BISEPOXIDES

Hardener (on wt. of gelatin in emulsion)	Age at 50% R.H., 77° F., days	M.P., ° C.
0.0-----	1 8	33-34 34-36
2.0% bis(2,3-epoxypropyl) methyl propyl ammonium p-toluene-sulfonate-----	2 4 7	48-55 85-90 96-104
2.0% bis(2,3-epoxypropyl) dimethyl ammonium perchlorate-----	2 4 7	97 129-130 132
2.0% bis(2,3-epoxypropyl) ethyl methyl ammonium p-toluene-sulfonate-----	2 4 7	60-76 84-97 113-115
2% 2-butyne 1,4-bis(2,3-epoxypropyl) diethyl ammonium perchlorate-----	2 4 7	92 109-115 112-119

6

The following table illustrates the hardening effect of various bisepoxides in gelatin solutions employed for photographic purposes.

Table II

HARDENING OF GELATIN BY THE ABOVE BISEPOXIDES

Hardener (on wt. of gelatin)	Age at 50% R.H., 77° F., days	M.P., ° C.	Percent swelling (15 min. in H <sub>2</sub> O at 20° C.)
0.0-----	1 8 48	33-34 33-34 33-34	800 ----- -----
2.0% bis(2,3-epoxypropyl)methyl propyl ammonium p-toluene-sulfonate-----	1 2 5 7 14 30 60	32-35 46 68 ----- ----- ----- -----	425 ----- ----- 359 338 306 294
2.0% bis(2,3-epoxypropyl)dimethyl ammonium perchlorate-----	1 2 5 14 33	33-35 75-80 112-115 ----- -----	365 ----- 289 253 252
2.0% bis(2,3-epoxypropyl)ethyl methyl ammonium p-toluene-sulfonate-----	1 2 4 5 14 34	32-36 60-65 ----- 109 ----- -----	380 ----- 309 ----- 277 273
2.0% 2-butyne 1,4-bis(2,3-epoxypropyl)-dimethyl ammonium perchlorate-----	1 2 4 34 60	36-39 79-83 115-119 ----- -----	452 ----- 332 294 291

## EXAMPLE VII

5 parts of a 48 percent solution of the quaternary ammonium salt prepared in Example VI was mixed with a solution of 2 parts of sodium tetraphenyl boride in 15 parts of water. The precipitate which formed gradually crystallized when the mass was cooled by an ice bath. The product was purified by recrystallizing from acetone. It was found to melt at 209–211° C. This material was effective as a hardener in aqueous gelatin coating compositions.

## EXAMPLE VIII

40 parts of N,N-bis(3-chloro-2-hydroxypropyl)-p-anisidine was suspended in 500 parts of dry ethyl ether and there was added thereto with stirring under reflux 40 parts of powdered potassium hydroxide. The mixture was filtered, the filtrate was shaken with activated alumina and it was then filtered and distilled giving 26 parts of N,N-bis(2,3-epoxypropyl)-p-anisidine. 5 parts of this product was heated with 4 parts of methyl p-toluene sulfonate on a steam bath for 2 hours. Treatment with benzene gave crystals which were re-crystallized from 2-butanone. This product was N,N-bis(2,3-epoxypropyl)-p-anisidine metho-p-toluene sulfonate.

Portions of a high speed bromiodide photographic emulsion optically sensitized with a cyanine dye without addition and with additions of 1.2% and 6.1% of N,N-bis(2,3-epoxypropyl)-p-anisidine metho-p-toluene sulfonate respectively were coated out upon a suitable cellulose acetate film base. The films so obtained were exposed in an Eastman 1B sensitometer and developed in Kodak Developer DK-50 for 5 minutes. The film was then fixed, washed and dried. The results obtained were set out in the following table. The relative speed values used in the table are inversely proportional to the exposure required to produce a density of 0.3 above fog. The melting points are of the coatings before processing. The value 212° F., 2 minutes, indicates that no melting was observed when the strips were subjected to this temperature for two minutes.

Hardener	Percent on weight of gel	Fresh tests			1 week 120° incubation			Reticulation	Melting point, ° F.
		Speed	$\gamma$	Fog	Speed	$\gamma$	Fog		
Control		100	1.37	0.14	83	1.05	0.17	80° F	86
N,N-Bis(2,3-epoxypropyl)-p-anisidine metho p-toluene sulfonate.	1.2	102	1.20	.11	60	.77	.16	None	1134
(1)	6.1	102	1.17	.11				None>	2212

<sup>1</sup> Stripped.      <sup>2</sup> 2 min.

The ammonium salts are most conveniently added to gelatin solutions in the form of aqueous solutions. However, if desired, some other solvent may be employed in admixture with water. If the solution of quaternary is to be stored for a long period of time it is ordinarily preferable to dissolve in some other solvent than water. For coating compositions having a pH within the range of 5-9 the effective aging time is substantially uniform. With a pH outside of this range longer aging times are ordinarily required to obtain the desired degree of resistance to the reaction of hot water. The advantage of hardening in accordance with our invention is that water insoluble coatings are obtained under conditions which are very mild; hence, the coatings can be hardened or insolubilized without any adverse effect on sensitive substances which might be present in the composition to be hardened.

I claim:

1. A photographic element comprising a layer which contains gelatin and bis-(2,3-epoxypropyl)-methyl propyl ammonium paratoluene sulfonate as a hardener for the gelatin.

2. A photographic element comprising a layer which contains gelatin and 1,5-pentane-bis-(2,3-epoxypropyl dimethyl ammonium methane sulfonate) as a hardener for the gelatin.

3. A photographic element comprising a layer which contains gelatin and 2-butyne-1,4-bis-(2,3-epoxypropyl-dimethyl ammonium perchlorate) as a hardener for the gelatin.

4. A photographic element comprising a layer which contains gelatin and bis(2,3-epoxy propyl)dimethyl ammonium perchlorate as a hardener for the gelatin.

5. A composition of matter comprising gelatin containing therein a hardening amount of N,N-bis(2,3-epoxypropyl)-p-anisidine metho-p-toluene sulfonate.

6. A composition of matter comprising an extralinear carboxyl-containing synthetic resin containing therein a hardening amount of N,N-bis(2,3-epoxypropyl)-p-anisidine metho-p-toluene sulfonate.

No references cited.