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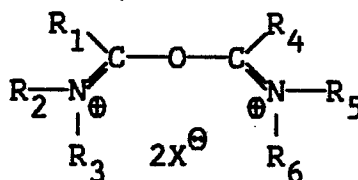
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(54) Method and composition for hardening gelatin.

(57) A method for hardening gelatin comprising combining the gelatin to be hardened with a compound of the formula:



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ , and  $X^-$  are as herein defined. The compounds of this formula effectively harden gelatin with little or no after-hardening. These compounds are useful in hardening gelatin in photographic elements.

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## METHOD AND COMPOSITION FOR HARDENING GELATIN

This invention relates to a method and hardener composition for hardening gelatin, particularly in photographic elements.

Gelatin is commonly used as a vehicle in photographic materials. Quite often, numerous layers in photographic elements, such as light-sensitive silver halide layers, filter layers, backing layers, antihalation layers, and overcoat layers, use gelatin as the primary binder.

Photographic elements are generally processed in aqueous processing solutions. Such processing results in excessive swelling and loss of strength of the gelatin binder unless the gelatin has been hardened. If the processing solution is maintained at a warm temperature, e.g., 40°C, the gelatin binder can dissolve, causing the layers of the element to disintegrate, unless the gelatin has been hardened.

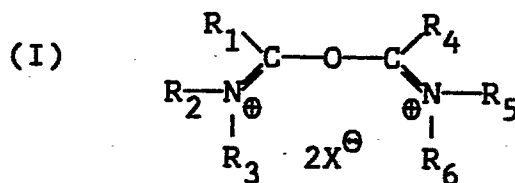
A number of compounds have been used to harden gelatin. These include formaldehyde and free aldehydes as described in U.S. Patent 3,232,764, active esters as described in U.S. Patent 3,542,558, epoxy compounds as described in U.S. Patent 3,047,394, aziridines as described in U.S. Patent 2,950,197, and others well-known in the art. These compounds harden, or crosslink, gelatin, thus increasing its mechanical strength and reducing the swellability and solubility of the gelatin in aqueous processing solutions.

The above-described hardening compounds are, however, subject to a number of disadvantages. Some take an exceedingly long time after being cast and dried to give the desired degree of gelatin hardening, requiring elements containing gelatin hardened with those compounds to be aged for an extended time while the hardening process is completed. In other words, these hardeners exhibit after-hardening. Additionally, a number of compounds exhibit adverse effects on the photographic properties of elements in which they are used. Such adverse effects can include an increase in fog or a reduction in light sensitivity or photographic speed.

In order to avoid the time and expense of keeping large quantities of gelatin-containing photographic elements for long periods while the hardening process is completed, a number of so-called fast-acting hardeners have been described in the art. For example, U.S. Patent 4,063,952 describes a carbamoyl pyridinium hardening compound in which the pyridine ring carries a sulfoalkyl substituent. European Patent Application 162,308 describes a chloroformamidinium hardener, and U.S. Patent 4,612,280 describes an N-succinimidylxyformamidinium hardener. These hardeners, however, suffer from a number of problems. Some of these hardeners exhibit after-hardening. Others have severe handling difficulties due to their hygroscopic nature, or poor hydrolytic stability, or both. Also, some of these hardeners adversely affect either the physical properties of photographic elements in which they are used (e.g., tackiness), or their sensitometric properties (e.g., speed loss). These problems are often aggravated by the fact that relatively large amounts of hardener are often required to achieve the desired hardening effect, leading to relatively large amounts of sometimes deleterious by-products.

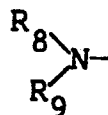
It is therefore desirable to provide a hardener that provides rapid and efficient hardening of gelatin, while avoiding adverse side-effects, such as after-hardening.

The present invention provides for hardening of gelatin by combining it with a compound of the formula:



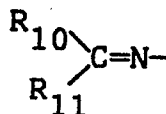
In this formula, R, represents hydrogen, alkyl, aralkyl, aryl, alkenyl, -YR<sub>n</sub>,

the group



5

the group



10 with Y representing sulfur or oxygen, and  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ , and  $R_{11}$ , each independently representing alkyl, aralkyl, aryl, or alkenyl. Alternatively,  $R_8$  and  $R_9$ , or  $R_{10}$  and  $R_{11}$ , may together form a ring structure.  $R_{10}$  and  $R_{11}$  may each also represent hydrogen. Also,  $R_1$  together with  $R_2$  may form a heterocyclic ring.

$R_2$  and  $R_3$  each independently represents alkyl, aralkyl, aryl, or alkenyl, or, combined with  $R_1$ , or each other, forms a heterocyclic ring.

15  $R_4$ ,  $R_5$ , and  $R_6$  are defined as are  $R_{11}$ ,  $R_2$ , and  $R_3$ , respectively, and are the same as or different from  $R_{11}$ ,  $R_2$ , and  $R_3$ .

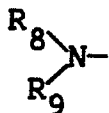
$X^\ominus$  represents an anion or an anionic portion of the compound to form an intramolecular salt.

Compounds of the invention according to formula (I) are described in further detail below.

20  $R_1$  represents hydrogen, alkyl, aralkyl, aryl, alkenyl,  $-YR_7$ ,

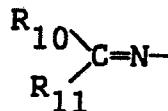
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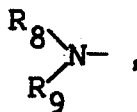
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with Y representing sulfur or oxygen, and  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ , and  $R_{11}$ , each independently representing alkyl, aralkyl, aryl, or alkenyl. Alternatively,  $R_8$  and  $R_9$ , or  $R_{10}$  and  $R_{11}$ , may together form a ring structure.  $R_{10}$  and  $R_{11}$  may each also represent hydrogen. Also,  $R_1$  together with  $R_2$  may form a heterocyclic ring, which may be further condensed with another ring.

35 Preferably,  $R_1$  is hydrogen, alkyl of 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, or dodecyl), aralkyl of from 7 to 20 carbon atoms (e.g., benzyl, phenethyl), aryl of from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), alkenyl of from 2 to 20 carbon atoms (e.g., vinyl, propenyl),

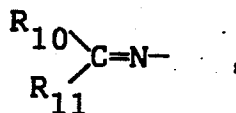
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50  $R_1$  can combine with  $R_2$  or  $R_3$  to form a heterocyclic ring of 5 to 8 atoms. This ring contains the nitrogen atom to which  $R_2$  and  $R_3$  are attached in formula (I) and may contain an additional nitrogen atom, or an oxygen or sulfur atom. Examples of such rings include pyridine, quinoline, isoquinoline, thiazole, benzothiazole, thiazoline, oxazole, benzoxazole, imidazole, benzimidazole, and oxazoline.

$R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ , and  $R_{11}$  are preferably alkyl of 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, or dodecyl), aralkyl of from 7 to 20 carbon atoms (e.g., benzyl, phenethyl), aryl of from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), or alkenyl of from 2 to 20 carbon atoms (e.g., vinyl, propenyl).

55  $R_8$  and  $R_9$ , or  $R_{10}$  and  $R_{11}$ , can also combine to form a ring structure of 5 to 8 atoms. The  $R_8$ - $R_9$  ring contains the nitrogen atom to which  $R_8$  and  $R_9$  are attached, and may also contain an additional nitrogen atom, or an oxygen or sulfur atom. The  $R_{10}$ - $R_{11}$  ring may also contain one or more nitrogen atoms, an oxygen atom, a sulfur atom, or any combination thereof. Examples of such rings include pyrrolidine,

piperadine, and morpholine.

$R_2$  and  $R_3$  each independently represents alkyl, aryl, aralkyl, alkenyl, or may combine with  $R_1$  or each other to form a heterocyclic ring. Preferably,  $R_2$  or  $R_3$  may each be hydrogen, alkyl of 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, or dodecyl), aralkyl of from 7 to 20 carbon atoms (e.g., benzyl, phenethyl), aryl of from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), or alkenyl of from 2 to 20 carbon atoms (e.g., vinyl, propenyl).  $R_2$  and  $R_3$  also preferably combine with each other to form a heterocyclic ring of 5 to 8 atoms. This ring contains the nitrogen atom to which  $R_2$  and  $R_3$  are attached, and may also contain an additional nitrogen atom, or an oxygen or sulfur atom. Examples of such rings include pyrrolidine, piperadine, and morpholine. Either of  $R_2$  or  $R_3$  can combine with  $R_1$  to form a heterocyclic ring, as described above in reference to  $R_1$ .

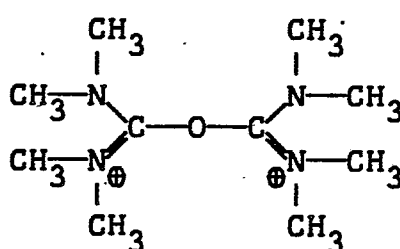
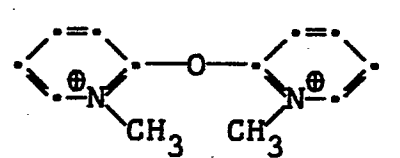
$R_4$ ,  $R_5$ , and  $R_6$  are defined the same as described above from  $R_1$ ,  $R_2$ , and  $R_3$ , respectively.  $R_4$ ,  $R_5$ , and  $R_6$  may each be the same as or different from  $R_1$ ,  $R_2$ , and  $R_3$ .

$X^\ominus$  represents an anion or an anionic portion of the compound, which forms an intramolecular salt. Any anion that forms a salt compound according to formula (I) that is useful to harden gelatin according to the invention can be used. Preferred anions include a sulfonate ion such as methylsulfonate or p-toluene sulfonate  $CF_3SO_3^\ominus$ ,  $BF_4^\ominus$ ,  $PF_6^\ominus$ , and  $ClO_4^\ominus$ .

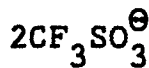
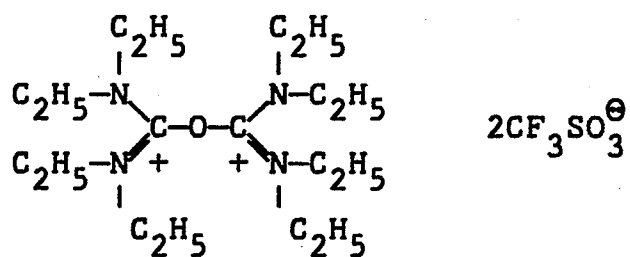
In addition to the above-described alkyl, aralkyl, aryl, alkenyl, and heterocyclic groups, groups, also useful as  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ , and  $R_8$  include substituted alkyl, aralkyl, aryl, alkenyl, and heterocyclic groups. Useful substituents include halogen, alkoxy of from 1 to 20 carbon atoms, aryloxy of from 6 to 20 carbon atoms, a sulfo group, N,N-disubstituted carbamoyl, N,N-disubstituted sulfamoyl, and other groups known to those skilled in the art that do not prevent the compounds from functioning as hardeners according to the invention.

Examples of compounds of formula (I) are shown below in Table I.

Table I

|    |                                                                                     |                     | <u>Compound</u> |
|----|-------------------------------------------------------------------------------------|---------------------|-----------------|
| 25 |                                                                                     |                     |                 |
| 30 |   | $2CF_3SO_3^\ominus$ | 1               |
| 35 |  | $2CF_3SO_3^\ominus$ | 2               |

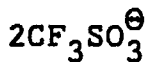
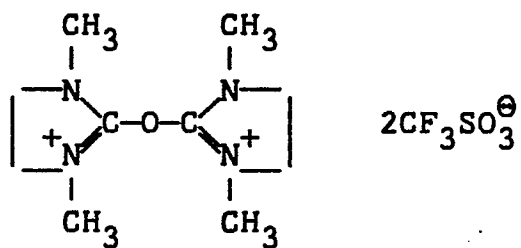
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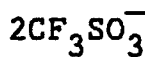
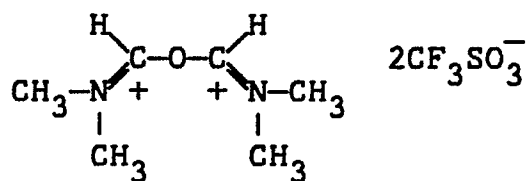
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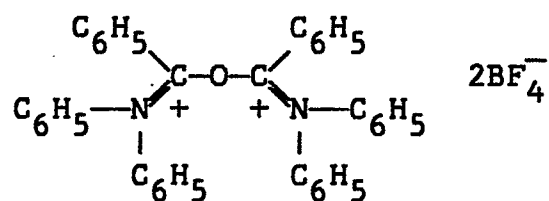
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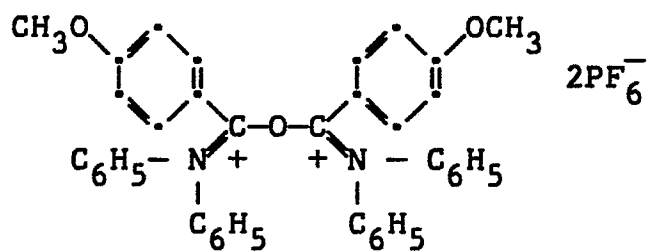
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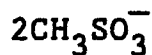
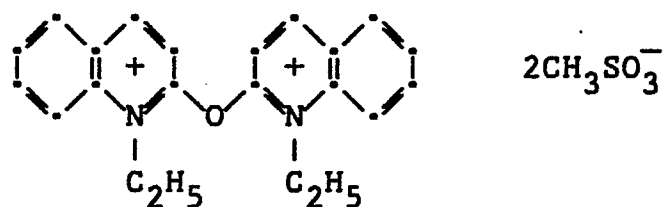
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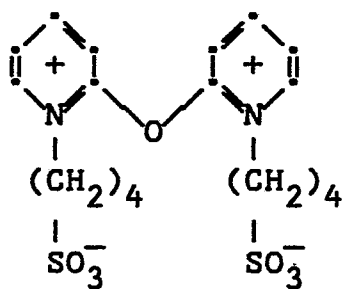
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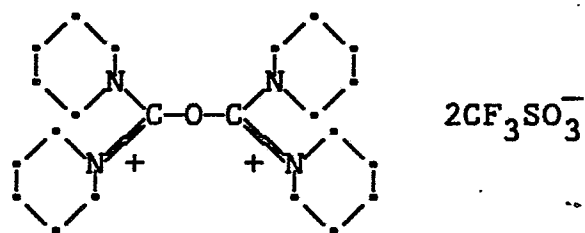
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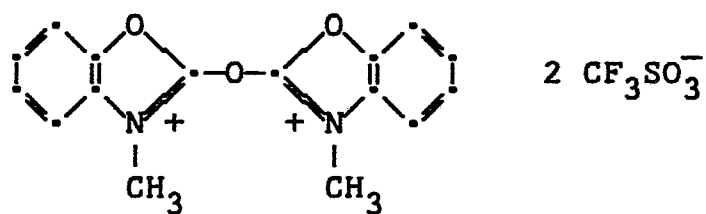
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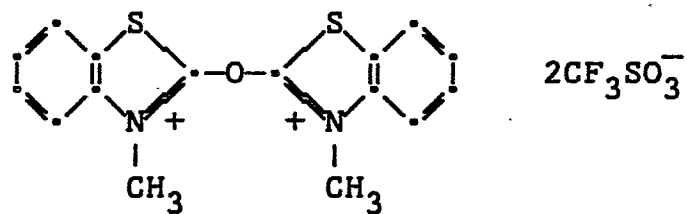
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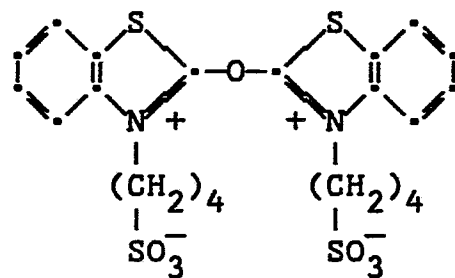
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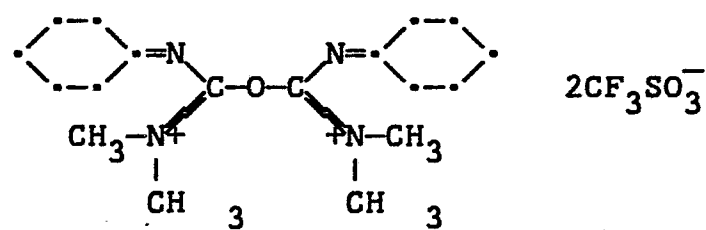
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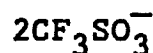
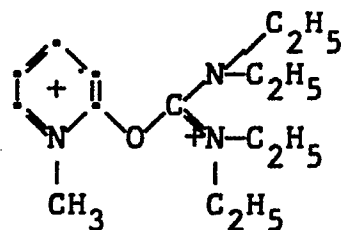
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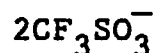
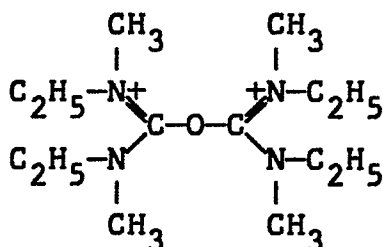
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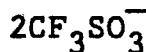
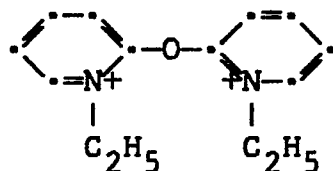
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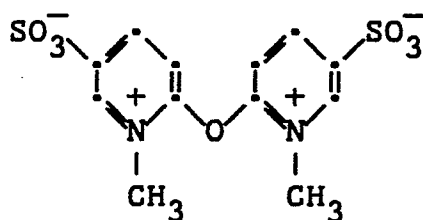
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The compounds of formula (I) can be made by techniques known to those skilled in the chemical synthesis art. Useful synthesis techniques are described in Journal of the American Chemical Society, 103, 9839 (1981). The preparation of compounds of formula (I) is further described below in the synthesis examples.

The compounds of formula (I) can be used to harden any type of gelatin. Types of gelatin useful in the practice of the present invention include alkali-treated gelatin, acid-treated gelatin, partially phthalated gelatin, double-dipped gelatin (i.e., gelatin treated with both alkali and acid), and the like.

According to the present invention, gelatin is hardened by combining it with a compound of formula (I). The method of hardening gelatin according to the invention can be advantageously be utilized to harden gelatin in photographic layers. The present invention provides rapid hardening of gelatin with little or no after-hardening while avoiding many of the adverse photographic effects found with prior art hardeners, such as speed loss and fog. The hardening compounds of formula (I) also are not highly hygroscopic as are many prior art hardening compounds, making them easy to handle. Additionally, the gelatin hardened according to the invention exhibits desirable physical properties, such as low tackiness.

According to the present invention, gelatin is hardened by combining it with a hardening compound according to formula (I). This is accomplished by techniques known to those skilled in the art. For example, the an aqueous solution of the hardening compound can be applied directly to an unhardened gelatin layer that has been coated on a support. Alternatively, the hardening compound can be mixed with a gelatin-containing coating dispersion shortly before coating it onto a support. Another way of using the compounds of formula (I) is to coat the compound in one layer of a photographic element in a manner such that it will diffuse into other layers of the element to harden those other layers.

The compounds of formula (I) according to the invention can also be used to partially harden gelatin. This is done, for example, by increasing the chain length of the gelatin, as described in U.S. Patent 4,421,847.

The amount of hardener used to harden gelatin according to the present invention will vary according to

the purpose for which the gelatin is being used, the degree of hardening desired, and the particular compound of formula (I) that is used. If only a slight amount of hardening is desired, relatively small amounts of hardening compound can be used. If a greater degree of hardening is desired, relatively large amounts of hardener would be used. The amount of hardener used according to the present invention is preferably between 0.01 and 20 weight percent, based on the weight of dry gelatin, and more preferably between 0.05 and 10 weight percent, based on the weight of dry gelatin.

The hardening compound of formula (I) that is used in the present invention can be used alone, in combination with another hardening compound according to formula (I), or in combination with any of a number of hardening compounds or hardening accelerators known in the art. Examples of known hardening compounds include formaldehyde and free dialdehydes, sulfonate esters, epoxides, blocked active olefins, and others, as described in Research Disclosure, item 17643, section X (1978). Examples of known hardening accelerators include nonprotonic solvents, as described in German OLS 2,417,586, tert-amines and their salts, as described in British Patent 1,269,983, and polyhydric alcohols.

The present invention is especially useful for hardening gelatin used in gelatin-containing layers in photographic elements. Such elements are well-known in the art. Examples of elements useful in the practice of the present invention include color negative film, color reversal film, color positive film, color print paper, color reversal print paper, black and white film, black and white paper, X-ray film, microfilm, and others well-known in the art. Color films and papers generally contain a red-sensitive silver halide layer, a blue-sensitive silver halide layer, and a green-sensitive silver halide layer. The red-sensitive layer usually has a cyan dye-forming coupler associated therewith, the blue-sensitive layer usually has a yellow dye-forming coupler associated therewith, and the green-sensitive layer usually has a magenta dye-forming coupler associated therewith.

Photographic elements with which the present invention is useful generally include, in addition to the above-described light-sensitive layers, various additional layers, such as filter layers, subbing layers, interlayers, antihalation layers, and the like, as described in Research Disclosure, item 17643 (1978). This Research Disclosure item also describes various addenda, such as surfactants and other coating aids, dye stabilizers, antifoggants, development inhibitor releasing compounds, filter dyes, optical brighteners, antistatic compounds, and the like, that can be included in photographic elements useful in the present invention, either in separate layers or in any of the above-described layers.

The gelatin-containing layers in photographic elements that are advantageously hardened by treatment with the compounds of formula (I) may utilize gelatin as the only binder in the layers, or the gelatin may be combined with other materials. Such materials include, for example, dispersions of water insoluble or slightly soluble polymers, or hydrophilic colloidal polymer materials. Such materials include acrylate polymers, vinyl alcohol polymers, halogenated styrene polymers, poly(sulfonic acid), poly(sulfinic acid), and others described in detail in Research Disclosure, item 17643, section IX (1978).

The invention is further described in the following examples.

#### Synthesis Example 1 -Bis(tetramethylformamidinium) ether ditriflate (compound 1)

To a solution of 11.6 g tetramethylurea in 100 ml  $\text{CH}_2\text{Cl}_2$ , 16.8 ml of triflic anhydride in 50 ml  $\text{CH}_2\text{Cl}_2$  was added dropwise. The mixture was evaporated on a rotatory evaporator at room temperature to yield a yellowish oily residue. The residue was dissolved in 100 ml  $\text{CH}_2\text{Cl}_2$  and 11.6 g tetramethylurea in 50 ml  $\text{CH}_2\text{Cl}_2$  was added, at which point a precipitate was formed. The mixture was stirred under nitrogen overnight, after which the precipitate was filtered, washed with  $\text{CH}_2\text{Cl}_2$ , and dried to obtain a colorless crystalline material with a melting point of 258-260°C. IR and NMR analysis indicated that the crystalline material was bis(tetramethylformamidinium) ether ditriflate.

#### Synthesis Example 2 -Bis(1-methyl-2-pyridinium) ether ditriflate (compound 2)

To a solution of 0.2 moles of N-methyl-2-pyridone in 150 ml  $\text{CH}_2\text{Cl}_2$ , 16.8 ml of triflic anhydride was added dropwise. A precipitate formed and the mixture was stirred under nitrogen at room temperature for 72 hours. The precipitate was filtered, washed with  $\text{CH}_2\text{Cl}_2$ , and dried to yield a colorless crystalline material with a melting point of 193-195°C. IR and NMR analysis indicated that the material was bis(1-methyl-2-pyridinium) ether ditriflate.



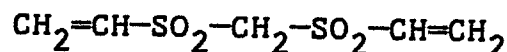
Comparative Example

A test material was prepared by coating a layer containing a mixture of gelatin at a level of 900 mg/ft<sup>2</sup> and colloidal silver at a level of 45 mg/ft<sup>2</sup> onto an Estar™ film base. The coated film base was cut into a series of test strips, which were treated with hardening compounds shown in Tables I and II by immersing each strip in an aqueous solution of the compound for 5 minutes, removing the excess solution from the surface of the element, and air-drying at 50°C. The degree of after-hardening was determined by measuring the hardness of the freshly hardened gelatin layer compared to the hardness of a hardened gelatin layer after aging. Hardness of the gelatin layer was measured by gradually immersing the test strip in a 0.8 weight percent aqueous solution of Takamine™, a proteolytic enzyme, at a rate of 0.2 in/min. The solution was adjusted to a pH of 7.2 and held at 25°C. The wedge length (the length of the strip from where the gelatin was completely removed to the last part of the strip to contact the enzyme solution) was measured and the hardness of the gelatin layer was calculated using the formula:

$$\text{hardness} = \frac{(\text{mm wedge length})(5 \text{ min/in})}{(25.4 \text{ mm/in})(0.9 \text{ g/ft}^2)}$$

Table IICompound

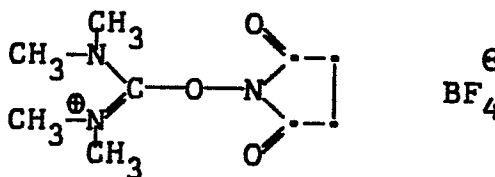
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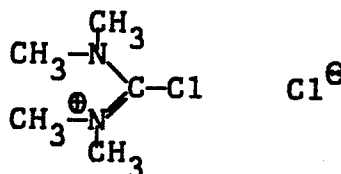
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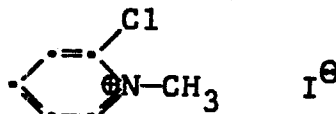
21



22



23



Compound 21 is compound 8 of U.S. Patent 4,612,280. Compound 22 is compound 1 of EP 162,308. The results of this test are shown in Table III.

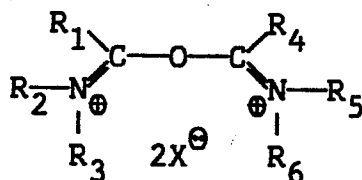
Table III

| hardener | mmoles hardener<br>per 100g gelatin | enzymolysis hardness<br>(mins. to erode 1 g/ft <sup>2</sup> gelatin) | "fresh" (age)        | aged (age)    |
|----------|-------------------------------------|----------------------------------------------------------------------|----------------------|---------------|
| 1        | 10                                  | 24.3 (0-6 day avg.)                                                  | 24.3 (0-6 day avg.)  | 24.9 (6 days) |
| "        | 15                                  | 33.3 ("")                                                            | 33.3 ("")            | 30.6 ("")     |
| "        | 20                                  | 43.2 (0-4 day avg.)                                                  | 43.2 (0-4 day avg.)  | 42.9 (4 days) |
| 2        | 10                                  | 33.3 (1 hr)                                                          | 33.3 (1 hr)          | 32.6 (5 days) |
| 19       | 10                                  | 4.3 (5 hrs)                                                          | 4.3 (5 hrs)          | 18.0 (7 days) |
| 20       | 10                                  | 6.8 (0-14 day avg.)                                                  | 6.8 (0-14 day avg.)  | 6.3 (14 days) |
| "        | 15                                  | 8.6 (0-10 day avg.)                                                  | 8.6 (0-10 day avg.)  | 8.5 (10 days) |
| "        | 20                                  | 10.4 (1-10 day avg.)                                                 | 10.4 (1-10 day avg.) | 10.5 ("")     |
| 21       | 10                                  | 5.9 (3 hrs)                                                          | 5.9 (3 hrs)          | 10.7 (8 days) |
| "        | 15                                  | 12.0 (4 hrs)                                                         | 12.0 (4 hrs)         | 14.7 (6 days) |
| "        | 20                                  | 11.2 (4 hrs)                                                         | 11.2 (4 hrs)         | 19.7 ("")     |
| 22       | 10                                  | 17.5 (0-7 day avg.)                                                  | 17.5 (0-7 day avg.)  | 16.0 (7 days) |
| 23       | 10                                  | 15.7 (2 hrs)                                                         | 15.7 (2 hrs)         | 26.5 (3 days) |

Table III shows that compounds 1 and 2 of the invention resulted in no evidence of after-hardening, while compounds 19, 20, and 23 resulted in significant after-hardening. Table III also shows that compounds 1 and 2 of the invention yielded a higher degree of hardening than was achieved by an equivalent molar amount of the hardener compounds 19, 20, 21, 22, or 23.

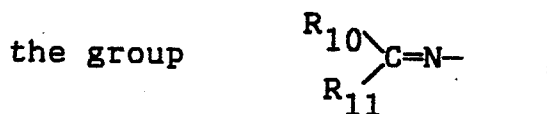
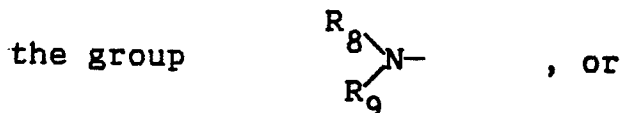
### Claims

1. A method for hardening gelatin, comprising combining gelatin and a hardening compound, characterized in that the compound has the formula:



wherein

R<sub>1</sub> represents hydrogen, alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms, -YR<sub>7</sub>,



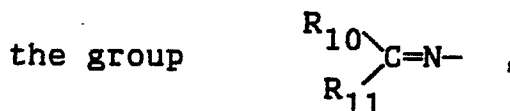
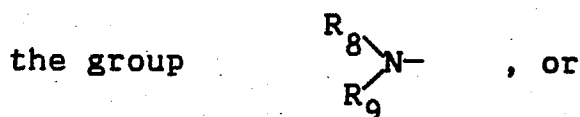
wherein Y represents sulfur or oxygen, and R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, and R<sub>11</sub>, each independently represents alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms, or R<sub>8</sub> and R<sub>9</sub> together form a heterocyclic ring, or R<sub>10</sub> and R<sub>11</sub> are each independently hydrogen or together form a ring structure, or R<sub>1</sub> together with R<sub>2</sub> or R<sub>3</sub> forms a heterocyclic ring,

R<sub>2</sub> and R<sub>3</sub> each independently represents alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms, or, taken together with R<sub>1</sub>, or each other, forms a heterocyclic ring,

R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> are defined as are R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>, respectively, and are the same as or different from R<sub>1</sub>, R<sub>2</sub>, or R<sub>3</sub>, and

X<sup>-</sup> represents an anion or an anionic portion of the compound to form an intramolecular salt.

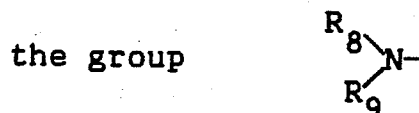
2. A method according to Claim 1 wherein R<sub>1</sub> and R<sub>4</sub> each independently represents hydrogen, alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms, -YR<sub>7</sub>,



wherein Y represents sulfur or oxygen, and R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, and R<sub>11</sub>, each independently represents alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms, or R<sub>10</sub> and R<sub>11</sub> are each independently hydrogen, and

R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, and R<sub>6</sub> each independently represents alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms,

3. A method according to Claims 1 or 2 wherein R<sub>1</sub> and R<sub>4</sub> each independently represents hydrogen, alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms, -YR<sub>7</sub>, or



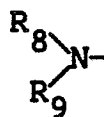
wherein Y represents sulfur or oxygen, and R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> each independently represents alkyl of 1 to 20

carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms, and

R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, and R<sub>6</sub> each independently represents alkyl of 1 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or alkenyl of 2 to 20 carbon atoms,

5 4. A method according to Claims 1-3 wherein R<sub>1</sub> and R<sub>4</sub> each independently represents

the group



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5. A method according to Claims 1-4 wherein at least one combination of two members of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>9</sub>, R<sub>10</sub>, and R<sub>11</sub> forms a ring structure.

6. A method according to Claims 1-5 wherein at least one combination of two members of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> forms a heterocyclic ring.

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7. A method according to Claims 1-6 wherein at least one combination of either R<sub>1</sub> and R<sub>2</sub>, or R<sub>4</sub> and R<sub>5</sub> forms a heterocyclic ring.

8. A method according to Claims 6 or 7 wherein the heterocyclic ring is a pyridylum ring.

9. A method according to Claims 1-8 wherein R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>8</sub>, and R<sub>9</sub> each independently represents alkyl of 1 to 20 carbon atoms.

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10. A method according to Claims 1-9 wherein R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>8</sub>, and R<sub>9</sub> are each methyl or ethyl.

11. A composition comprising gelatin characterized in that it is hardened by the method of Claims 1-10.

12. A photographic element comprising a support having thereon at least one layer comprising gelatin characterized in that the gelatin is hardened by the method of Claims 1-10.

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| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                             |                                                |                                               |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|-----------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Citation of document with indication, where appropriate, of relevant passages                                                                                                                                                                               | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | TETRAHEDRON LETTERS, vol. 24, no. 36, 1983, pages 3919-3920, Pergamon Press Ltd., London, GB; T. GRAMSTAD et al.:<br>"The reaction of trifluoromethanesulphonic anhydride with carbonyl compounds"<br>* Whole document *                                    | 1-12                                           | G 03 C 1/30                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 102, 1980, pages 6361-6362, American Chemical Society, Columbus, Ohio, US; P.J. STANG et al.:<br>"Preparation and characterization of novel dication ether salts:<br>Ar+OAr+.2CF3SO3-"<br>* Whole document * | 1-12                                           |                                               |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                             |                                                | TECHNICAL FIELDS SEARCHED (Int. Cl.4)         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                             |                                                | G 03 C 1/00                                   |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                             |                                                |                                               |
| Place of search<br>THE HAGUE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                             | Date of completion of the search<br>29-04-1988 | Examiner<br>MAGRIZOS S.                       |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |                                                                                                                                                                                                                                                             |                                                |                                               |