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PHOTOGRAPHIC ELEMENTS CONTAINING HARDENING AGENTS HAVING ETHYLENEIMINO GROUPS

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9 Claims. (Cl. 96—111)

This invention pertains to the hardening of photographic layers which use a protein, particularly gelatin, as the colloidal carrier material.

During processing, photographic materials pass through several aqueous solutions, all of which have different pH values. When passing through these processing baths, the gelatin layers must not dissolve, swell excessively, or separate from the support. It is, therefore, important to render these gelatin layers resistant to water and to provide them with a higher melting point. This procedure is usually referred to as hardening. A great variety of substances is capable of reacting with the protein chains by cross linking but many of these substances have considerable disadvantages from the photographic point of view. An acceptable photographic gelatin hardening agent must meet the following requirements:

(1) No uncontrolled hardening must take place;

(2) Hardening must begin only after the layer has been coated and dried;

(3) Maximum hardening must be reached in a minimum time after coating;

(4) The swelling of the photographic gelatin layer in its wet state must be reduced without sacrificing the water permeability even after a prolonged storage period;

(5) The hardener must be photographically inactive as far as the photographic properties of the emulsion is concerned.

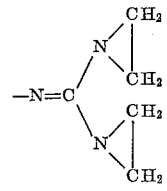
Previously suggested hardening agents fall into the following categories: Metal salts, such as zirconium, aluminum and chromium salts; aldehydes; halogen containing aldehydes, dialdehydes; 1,2 and 1,4 di-ketones such as cyclohexanedione-1,2; quinone; the chlorides of dibasic organic acids, the dianhydrides of tetracarboxlic acids; compounds with at least two reactive groups such as vinylsulfone and bisacrylamide, polyfunctional esters of methane sulfonic acid; and compounds with two or more ethyleneoxy radicals.

Some of these compounds harden gelatin reasonably well but are photographically active and can, therefore, not be used for photographic silver halide emulsions. Metal salts increase the brittleness, dialdehydes impart an undesirable color to the layers, while anhydrides and acid chlorides lower the pH value during hardening. Other compounds such as formaldehyde and mucochloric acid harden the gelatin layers uncontrollably, which means that even after one year, maximum hardening has not yet been reached. As a consequence, the sensitivity and the gradation of the photographic emulsion do not remain constant because the permeability for the developer solution undergoes a continuous change. Some compounds, for instance the esters of methanesulfonic acid, have a poor initial hardening action and must for this reason be combined with rapidly acting hardeners.

More recently, it has been proposed to use hardening

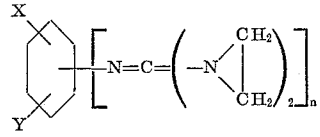
agents with at least two ethyleneimino groups which include ethyleneureas and the ethyleneimides of sulfonic acid, carbonic acid, phosphoric acid and triazine.

It has now been found that aromatic compounds of the benzene series which are substituted one or more times by the radical:



are especially suitable as hardening agents for photographic layers which contain a protein, particularly gelatin, as the colloidal carrier material for the photographic layer.

More particularly, these compounds are characterized by the following general formula:



wherein X is halogen, hydrogen, e.g., chlorine or bromine, a lower alkyl group, e.g., methyl, ethyl or propyl, lower carbalkoxy such as carbmethoxy, carbethoxy and carbpropoxy, carboxyethyleneimide; Y is hydrogen, halogen or a lower alkyl group; and n is 1 or 2.

These compounds differ from conventional organic hardeners to the important extent that they do not only harden in neutral or weakly alkaline solution but, also in a weakly acidic environment.

Although the compounds of this invention are equally effective in their hardening intensity to formaldehyde, they are superior to the latter because they can be used without limitations in photographic color emulsions in which a dye image is formed by color development with an aromatic primary amino developing agent in the presence of a color former. Color formers which are soluble in water or in aqueous alkali are used in the developer solution, while color formers which are fast to diffusion are used in their dispersed form in the silver halide emulsion. In either case, the oxidation products of the aromatic primary amino developing agent, which are formed by the development of metallic silver in the exposed image areas, react with the color former to form quinoneimine, azomethine or phenazonium dye images.

Several of the hardeners are readily soluble in water and can be easily added to the emulsion in the form of an aqueous solution. Those hardeners which are more difficultly soluble in water, can be dissolved with the aid of an organic, water-miscible solvent as exemplified by methanol, ethanol, propanol, isopropanol, acetone or dimethylformamide.

Hardening begins only after the drying of the coated layer, which means that the viscosity of the coating solution does not change during the holding and coating operations. The hardening agents are also compatible with gelatin in the dry state and do not precipitate from the coated and dried layers. Even after extended storage periods, the sensitivity and the gradation of materials treated with the hardening agents of this invention remain essentially unchanged.

The compounds of this invention can also be used as hardening agents for backing layers, filter layers, protective layers and other auxiliary layers which contain gelatin as the colloidal carrier material. The use of our hardeners reduces swelling and water solubility in a highly desirable manner. During processing, the wetted layers are touch resistant, even in their swelled state, and are not as easily damaged by mechanical handling as other gelatin layers. No after-hardening takes place and the ability of the developer solution to permeate the hardened layers is not noticeably reduced. The combined total of these highly desirable properties is undoubtedly derived from the chemical structure of the compounds of this invention. Cross linking results in substituted guanidines which are photographically inactive. No groups are split off and the permeability of the layer for the developer solution remains unchanged because the reaction produces a hydrophilic reaction product. Cross linking is accomplished by the reaction of the ethyleneimino derivatives with the reactive groups of the proteins, preferably with the amino, carboxy and mercapto groups.

The hardeners of this invention can be added to the photographic layers prior to coating by using solutions in water, inorganic solvents or in mixtures thereof. Inasmuch as the viscosity of the gelatin compositions remains unchanged, the conventional coating conditions can be adapted without change. The amount of hardening agent added is quite small and generally on the order of 0.3 to 1.5 percent based on the dry weight of the gelatin. These amounts are sufficient to produce layers with very high melting points.

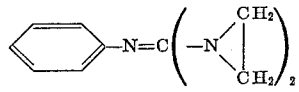
The emulsion layers, intermediate layers, and backing layers which are hardened with these compounds possess excellent adhesion to all commonly used supports including glass, paper, cellulose esters, polyesters, polycarbonates and polystyrenes. The composition of the subbing or baryta layers need not be changed and the adhesion between the individual layers is materially improved. Optical sensitization is not influenced. Even the techniques of preparing the silver halide emulsions can remain unchanged. Obviously, the compounds of this invention can be combined with other previously known hardening agents.

The hardening agents of this invention can be prepared according to the procedure described in German application F 37,323 IVD/12p, corresponding to French Patent 1,363,063, by reacting a mono or polyisocyanide dihalide with an α,β-alkyleneimine.

In preparing and using the hardening agents of this invention, care must only be taken to omit such substituents which are known to be photographically active and would therefore be capable of adversely influencing the properties of the photographic materials.

The following hardeners are mentioned for purposes of illustration:

(I)



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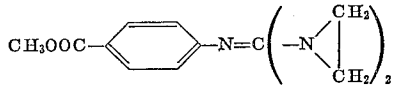

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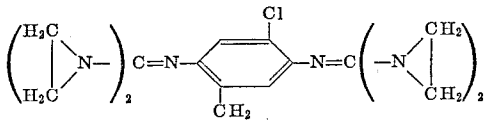

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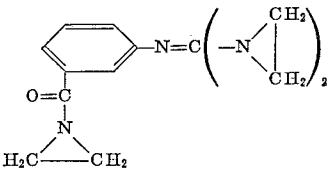

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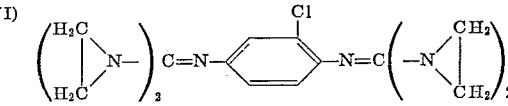


The invention is further illustrated by the following examples:

Example I

Four kilograms of a silver chlorobromide emulsion which was ready for coating and contained 65 grams of gelatin per kilogram of emulsion and had a pH value of 7 was divided into four 1 kilogram portions and 0.2, 0.3, 0.4 and 0.5 percent of the compound of Illustration III were added to the four batches. The percentage was based on the weight of the gelatin present in the emulsion.

The emulsions were coated on a baryta paper support, dried and stored for 24 hours at a temperature of 50° C. The melting points of the layers were then determined according to the conventional procedure. The following results were obtained:

	Amount of hardening agent expressed in percent based on the weight of dry gelatin			
	0.2	0.3	0.4	0.5
Melting point, ° C	50	78	100	100

It will be noted from this table that the addition of 0.4 percent of hardener results in layers which do not melt even when treated with boiling water. Swelling of the layers in the developer solution is noticeably reduced and the layers are fully touch-resistant in the wet state. The photographic properties remain unchanged.

Example II

The extent to which the layers are hardened is largely independent of their pH, as will be demonstrated by the following experiments. As in Example I, four 1 kilogram batches of a silver bromoiodide emulsion which contained 65 grams of gelatin per kilogram of emulsion were provided with 0.2, 0.3, 0.4 and 0.5 percent of the hardening agent used in Example I. Each of the emulsions was divided into three equal parts and their pH adjusted to values of 5, 7, and 9, respectively. After coating, drying and storage for 24 hours at 50° C., the following melting points were obtained:

	Amount of hardening agents expressed in percent based on the weight of gelatin			
	0.2	0.3	0.4	0.5
pH of the coating solution:				
5	52°	100°	100°	100°
7	50°	78°	100°	100°
9	50°	70°	94°	100°

The viscosity of the coating solutions did not change even when these solutions were digested for several hours at 40° C. prior to coating. The viscosity was determined only for the coating solutions which had a pH of 5 and 7 because digestion at a pH of 9 would have led to unreliable results since the gelatin becomes partly degraded at that elevated pH. The viscosity of the coating solution is expressed in terms of minutes and seconds required for the emptying of a pipette-type viscosimeter. The results

reported below are based on a 0.5 and 1.0 percent concentration of the hardening agent of Example I.

Amount and pH	Digestion time in hrs.						
	0	1	2	3	4	5	15
0.5%:							
pH 5	1'15"	1'16"	1'20"	1'22"	1'22"	1'23"	1'23"
pH 7	1'7"	1'16"	1,20"	1'20"	1'20"	1'20"	1'20"
1.0%:							
pH 5	1'7"	1'15"	1'23"	1'30"	1'30"	1'30"	1'34"
pH 7	1'9"	1'14"	1'14"	1'16"	1'18"	1'18"	1'20"
Type without hardener	1'9"	1'14"	1'14"	1'14"	1'14"	1'14"	1'14"

Example III

One gram of the compound of Illustration I was added to 1 kilogram of an aqueous gelatin solution which contained 60 grams of gelatin and a small amount of an antihalation dye. After adjusting the pH to 7.0, the mixture was coated on a subbed cellulose triacetate support, dried and stored for 24 hours at 50° C. A colored backing layer was obtained which had a melting point above 100° C. and displayed excellent touch-resistance when handled in the wet state.

Example IV

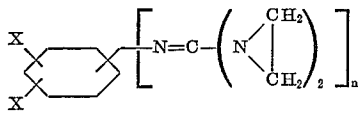
Four 1 kilogram batches of a silver chlorobromide emulsion which contained approximately 70 grams of dry gelatin was treated with 0.2, 0.3, 0.4 and 0.5 percent of the compound used in Example III. The percentage was based on the weight of dry gelatin. Each of the emulsions was divided into three equal parts and their pH adjusted to values of 5, 7, and 9, respectively. The mixtures were coated onto a subbed cellulose triacetate support, dried and stored for 24 hours at 50° C. The following results were obtained:

	Percentage of hardening agent added			
	0.2	0.3	0.4	0.5
pH of coating solution:	°C.	°C.	°C.	°C.
5	43	45	50	100
7	44	61	70	100
9	50	55	70	100

It will be noted from this table that an addition of 0.5 percent of the hardening agents rendered the hardened layer resistant to boiling water.

We claim:

1. A photographic element carrying on a suitable support a layer containing gelatin as the colloidal carrier material and containing in a hardening amount a gelatin hardening agent of the formula:

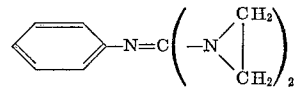


wherein X is a member of the group consisting of hydrogen, halogen, lower alkyl, lower carbalkoxy and carboxyethyleneimido; Y is a member of the group consisting of hydrogen, halogen and lower alkyl; and *n* is a positive integer ranging from 1 to 2.

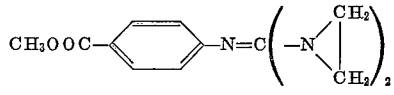
2. A photographic element according to claim 1 wherein said gelatin layer is a silver halide emulsion layer.

3. A photographic element according to claim 1 wherein said hardening amount ranges from 0.3 to 1.5 percent based on the weight of the gelatin in the layer.

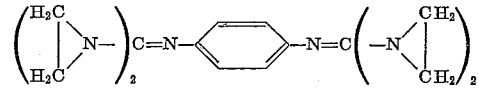
4. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



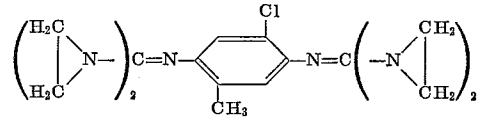
5. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



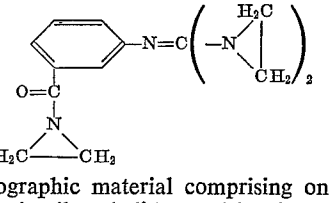
6. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



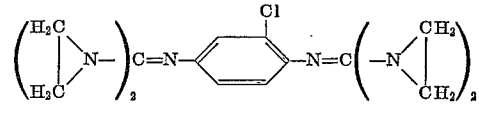
7. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



8. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



9. A photographic material comprising on a suitable support a gelatin silver halide emulsion layer containing in an amount ranging from 0.3 to 1.5 percent based on the weight of dry gelatin a hardening agent of the following formula:



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NORMAN G. TORCHIN, *Primary Examiner.*