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2,976,152

PHOTOGRAPHIC GELATIN LAYERS CONTAINING TRIAZINE HARDENERS

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20 Claims. (Cl. 96—111)

This invention relates to the hardening of gelatin, and more particularly to the hardening of photographic gelatin layers and silver halide emulsion layers containing gelatin as the colloidal carrier material.

In the preparation of photographic gelatin layers and gelatin silver halide emulsion layers, it has been the practice to treat the aqueous gelatin dispersions and gelatin silver halide emulsions prior to coating with a hardening agent in order to reduce the tendency of the gelatin layers to soften, melt or reticulate during processing, particularly at temperatures which are higher than the temperature of 68° F. (20° C.) normally specified for the processing of photographic materials. Compounds which have been used for the hardening of gelatin and gelatin emulsion layers include formaldehyde, hydroxylaldehydes, acrolein, glyoxal and its derivatives, as well as mixtures of such aliphatic aldehydes with an aromatic hydroxy compound such as phenol, resorcinol or resorcylic aldehyde.

Although these compounds accomplish their desired function of increasing the melting point of gelatin, they cause unwanted side effects particularly when used in the concentrations needed to accomplish that degree of hardening which is needed for high temperature processing. Among these defects are excessive fog, desensitization, and loss of contrast and gradation in the processed film. The hardeners described in the literature also cause the very undesirable defect which is known as "after-hardening," meaning that the melting point increases during storage along with a corresponding increase in fog and desensitization.

Most hardeners have very poor compatibility with color emulsions. Inasmuch, as the reaction of the hardener with gelatin is slow and never goes to completion, there is always unreacted hardener left in the dry photographic emulsion layer which reacts with the color former, the color developers or both. As a result of this reaction, a hardened color film is subject during processing to the formation of color fog and color stain.

It has, therefore, been proposed to add agents to the emulsion or to the processing solutions which will react with the residual hardeners. It has also been suggested to use hardeners which are obtained by the reaction of formaldehyde and nitrogenous compounds such as methylol-urea or dimethylol-diketopiperazine in which case the hardening action results from the gradual liberation of the formaldehyde in the emulsion. However, the use of these hardening techniques, while partly effective with black and white emulsions, will not prevent the formation of color stain in color emulsions.

It has also been suggested to use as hardeners heterocyclic compounds which carry in a vicinal position to a carbonyl group one or more vinyl groups in which case the hardening action has been described as being a function of the vinyl groups. It is easy to realize that such unsaturated substituents must be suspected of having a strong reducing action on the silver halide which may

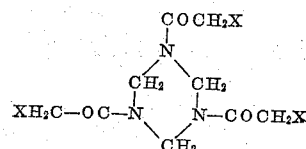
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lead to the formation of colored development fog in color positive materials.

It is among the objects of the present invention to provide a novel hardening agent for photographic gelatin and gelatin silver halide emulsions leading to products having improved physical and photographic properties. Other objects will be apparent from the following description.

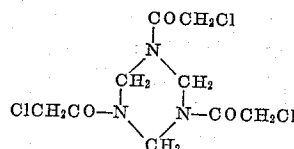
I have found that the addition of 1,3,5-tris(halogenoacetyl)perhydro-1,3,5-triazine to a gelatin solution or gelatin silver halide emulsion increases the melting point of the layers obtained therefrom without causing any adverse effects such as fog, desensitization or loss of contrast. The materials obtained are stable and do not deteriorate during storage due to after-hardening. Color emulsions, particularly those which contain color formers fast to diffusion, are free from color stain and development fog.

The 1,3,5-tris(halogenoacetyl)perhydro-1,3,5-triazines used in accordance with my invention are characterized by the following general formula:

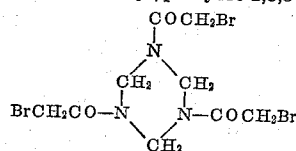


wherein X is a halogen atom, e.g., a chlorine, bromine or iodine atom.

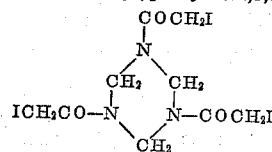
The following 1,3,5-tris(halogenoacetyl)perhydro-1,3,5-triazines are illustrative:



1,3,5-tris(chloroacetyl)perhydro-1,3,5-triazine



1,3,5-tris(bromoacetyl)perhydro-1,3,5-triazine



1,3,5-tris(iodoacetyl)perhydro-1,3,5-triazine

The foregoing compounds are prepared by analogy to the method described in the Journal of the American Chemical Society, vol. 70, page 3079, by reacting one molar equivalent of s-trioxane with at least three molar equivalent of a halogenoacetonitrile in the presence of an acid such as sulfuric acid, phosphoric acid or hydrochloric acid.

In the preparation of non-curling layers, filter layers, antihalation layers, anti-abrasion layers or silver halide emulsion layers, a sufficient quantity of the 1,3,5-tris(halogenoacetyl)perhydro-1,3,5-triazine is added to give the selected degree of hardening. While the exact amount of the triazine derivative may be varied depending on the particular type of gelatin dispersion or emulsion employed, amounts ranging from 3.0 to 45.0 grams of hardener per kilogram of dry gelatin present in the dispersion are preferred. In these amounts, effective hardening is obtained

to the extent that the treated gelatin layers will not melt even in boiling water, while the keeping qualities of the emulsion will not be affected by any adverse effect such as "after-hardening" loss of speed and gradation or color fog when used in color materials.

The advantages of my novel hardeners are especially pronounced when they are used in color materials including color films and papers which contain color formers fast to diffusion. Such materials are prepared according to the methods described in U.S. Patents 2,179,228, 2,179,239, 2,186,849 and 2,220,187 and consist of several integral emulsion layers coated on a clear cellulose ester film base, opaque base or paper. Each of the emulsions is sensitized to one of the primary colors of light, namely blue, green, and red. Usually, the top layer is blue sensitive, the middle layer is green sensitive, and the bottom layer is red sensitive. Each of the three silver halide emulsion layers contains dye-forming compounds fast to diffusion.

During the development of the silver image by an aromatic amino developing agent, these dye-forming compounds unite with the oxidation products of the developing agent to form an azomethine or indoaniline dye. Alternatively, the emulsion layer may be free from color formers in which case the film is processed with the color formers in the color developers by the selective second exposure and color development method as described in U.S. Patents 1,897,866, 1,900,870, 1,928,709, and 1,980,941.

Multicolor film in which each element bears a color yielding layer comprising a hydrophilic film-forming synthetic polymer containing a plurality of hydroxyl groups and having a plurality of color components and, in addition, containing light-sensitive silver salts is described in U.S. Patents 2,397,864, 2,397,865, 2,397,866, and 2,397,867.

Materials in which the developed picture is a phenazonium dye image formed by development with a 1,2,4-triaminobenzene developer are described in U.S. Patents 2,486,440, and 2,570,116.

While the following examples describe in detail the methods for accomplishing the aforesaid objects, it is to be understood that they are given merely for the purpose of illustration and are not to be construed as limiting the scope of the invention.

Example I

An ammonia type silver halide emulsion having a pH of 7.8 and containing 10 percent aqueous gelatin was maintained at a temperature of 40° C. and mixed with varying amounts of a solution of 1,3,5-tris(chloroacetyl)-perhydro-1,3,5-triazine. The emulsion was coated on a film base and dried at room temperature. The following results were obtained:

Milligrams of hardener per gram of gelatin	Melting point, ° C.		
	Fresh	3 Day	10 Day
0.....	33.0	33.0	33.0
3.....	56	80	90+
5.....	85.2	90+	90+
10.....	90+	90+	90+

Photographic tests showed that the hardened material was free from fog and had not lost any speed or contrast when compared with the unhardened type. The hardened material had excellent storage stability and did not suffer from any deterioration of photographic properties during storage.

The hardener used in this example was prepared as follows:

A mixture of 45 grams of chloroacetonitrile and 2 milliliters of concentrated sulfuric acid was heated to reflux (123° C.) and a solution of 18 grams of s-trioxane and 30 grams of chloroacetonitrile were added dropwise

to the stirred mixture. The reaction was exothermic. The rate of addition was regulated such that the heat liberated was sufficient to maintain moderate refluxing.

After the addition was complete, the reaction mixture was cooled in an ice bath, 100 milliliters of ethanol were added and the mixture stirred until the product crystallized out. The solid was removed by filtration and the filter cake washed three times with ethanol.

The solid was recrystallized from ethanol with the use of charcoal. The yield was 22 grams of white crystals. Melting point 177.5° C.

	Calculated	Pound
15 Analysis:		
C.....	34.20	34.18
H.....	3.79	3.63
N.....	13.30	13.43
Cl.....	33.52	33.40

Example II

Example I was repeated with the exception that the pH of the emulsion was adjusted to a value of 5.5 and that the 1,3,5-tris(chloroacetyl)perhydro-1,3,5-triazine was replaced by 1,3,5-tris(bromoacetyl)perhydro-1,3,5-triazine. The following results were obtained:

Milligrams of hardener per gram of gelatin	Melting Point, ° C.		
	Fresh	3 Day	10 Day
0.....	33.0	33.0	33
5.....	37.1	40.3	70.0
10.....	90+	90+	90+

The photographic results obtained were essentially identical with those of Example I.

Example III

A cellulose acetate butyrate film base was coated with a red sensitive silver halide emulsion containing 1-octadecyl-2-[2'-(1'-hydroxynaphthyl)-benzimidazole-5-sulfonic acid as a cyan color former. The red sensitive was overcoated with a green sensitive gelatin silver halide emulsion containing 1-(4'-phenoxy-3'-sulfophenyl)-3-stearyl-5-pyrazole as a magenta color former. The green sensitive emulsion was overcoated with a blue sensitive gelatin emulsion containing 2-(4'-benzoylacetylaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid as a yellow color former. Each of the gelatin layers contained 50 cc. of a solution of 1 part of 1,3,5-tris(chloroacetyl)-perhydro-1,3,5-triazine dissolved in 20 parts of dimethylformamide and 80 parts of methanol. Based on the gelatin concentration present in the emulsion, the amount of hardener corresponded to about 6 grams per kilogram of dry gelatin.

The finished multilayer color film was dried, exposed through a multicolor transparency and processed by reversal development to a duplicate color transparency as follows:

The film was first developed for 14 minutes in a black and white developer of the following composition:

	Grams
Metol	3
Sodium sulfite	50
Hydroquinone	6
Sodium carbonate	40
Sodium thiocyanate	2
Potassium bromide	2
Water to make 1 liter.	

The developed film was short stopped for 2 minutes in a bath of the following composition:

	Grams
Acetic acid	10
Sodium acetate	20
Water to make 1 liter.	

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The material was then hardened for 5 minutes in a 3 percent aqueous solution of potassium chrom alum and washed in water for 3 minutes.

The washed film was given a second exposure for 3 minutes to the light of a No. 1 photoflood lamp 30 inches away from the film and color developed for 15 minutes in a developer of the following composition:

	Grams
Sodium sulfite -----	2
p-Aminodiethylaniline hydrochloride -----	4
Sodium carbonate (monohydrate) -----	67.5
Potassium bromide -----	1
Water to make 1 liter.	

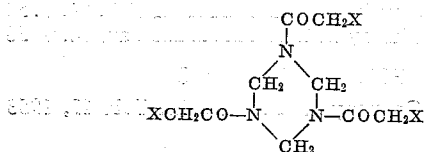
The film was then short stopped for 1 minutes, hardened for 3 minutes and washed in water for 5 minutes; bleached for 10 minutes in an aqueous solution containing 6 percent potassium ferricyanide, 1.5 percent of potassium bromide and 2 percent of a sodium phosphate-sodium bisulfate buffer; washed in water for 5 minutes, fixed for 5 minutes in a 20 percent aqueous hypo solution, washed in running water for an additional 5 minutes and then dried. The finished transparency had a gradient of 1.5.

All processing solutions were maintained at a temperature of 90° F. (33° C.) which was considerably higher than the normally recommended processing temperature of 68° F. (20° C.). In spite of this high temperature, the finished film was free of any reticulation defects and did not show any color stain. These results were vastly superior to those obtained with two comparison films. The first, which did not contain any hardener, melted in the first developer whereas a film hardened with formaldehyde showed bad reticulation and a very pronounced pink stain.

From the foregoing examples, it is clearly apparent that my hardening procedure is not only applicable to the preparation of photographic black and white emulsions, but also to the preparation of color emulsions.

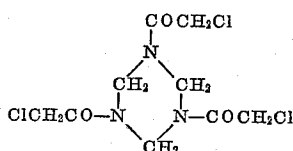
I claim:

1. The method of producing a hardened gelatin layer in a photographic silver halide element which comprises uniformly mixing with the aqueous gelatin dispersion used in the preparation of said layer, prior to coating upon a support, a hardening amount of 1,3,5-tris-(halogenoacetyl)perhydro-1,3,5-triazine hardening agent selected from the group of compounds having the following general formula:



wherein X represents a halogen atom selected from the group consisting of chlorine, bromine and iodine; and coating said aqueous gelatin dispersion onto a suitable base.

2. The method of producing a hardened gelatin layer in a photographic silver halide element which comprises uniformly mixing with the aqueous gelatin dispersion used in the preparation of said layer, prior to coating upon a support, a hardening amount of a hardening agent of the following formula:

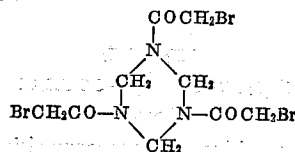


and coating said aqueous gelatin dispersion onto a suitable support.

3. The method of producing a hardened gelatin layer

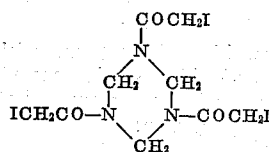
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in a photographic silver halide element which comprises uniformly mixing with the aqueous gelatin dispersion used in the preparation of said layer, prior to coating upon a support, a hardening amount of a hardening agent of the following formula:



and coating said aqueous gelatin dispersion onto a suitable support.

4. The method of producing a hardened gelatin layer in a photographic silver halide element which comprises uniformly mixing with the aqueous gelatin dispersion used in the preparation of said layer, prior to coating upon a support, a hardening amount of a hardening agent of the following formula:



and coating said aqueous gelatin dispersion onto a suitable support.

5. The method according to claim 1, wherein said gelatin layer is a silver halide emulsion layer.

6. The method according to claim 2, wherein said gelatin layer is a silver halide emulsion layer.

7. The method according to claim 3, wherein said gelatin layer is a silver halide emulsion layer.

8. The method according to claim 4, wherein said gelatin layer is a silver halide emulsion layer.

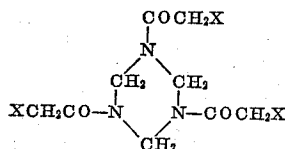
9. The method according to claim 1, wherein said gelatin layer is a silver halide emulsion layer containing a color former fast to diffusion capable of forming upon development with a primary amino developer, an image selected from the group consisting of azomethine, indoaniline and phenazonium dye images.

10. The method according to claim 2, wherein said gelatin layer is a silver halide emulsion layer containing a color former fast to diffusion capable of forming upon development with a primary amino developer, an image selected from the group consisting of azomethine, indoaniline and phenazonium dye images.

11. The method according to claim 3, wherein said gelatin layer is a silver halide emulsion layer containing a color former fast to diffusion capable of forming upon development with a primary amino developer, an image selected from the group consisting of azomethine, indoaniline and phenazonium dye images.

12. The method according to claim 4, wherein said gelatin layer is a silver halide emulsion layer containing a color former fast to diffusion capable of forming upon development with a primary amino developer, an image selected from the group consisting of azomethine, indoaniline and phenazonium dye images.

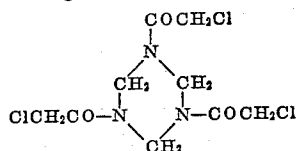
13. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing a hardening amount of a 1,3,5-tris-(halogenoacetyl)perhydro-1,3,5-triazine selected from the group of compounds having the following general formula:



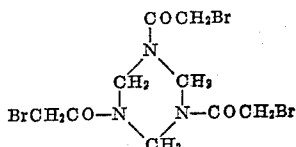
wherein X represents a halogen atom selected from the group consisting of chlorine, bromine and iodine.

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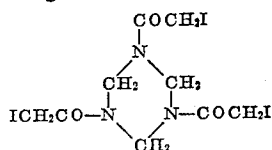
14. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing a hardening amount of a compound having the following formula:



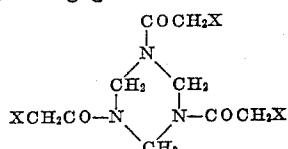
15. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing a hardening amount of a compound having the following formula:



16. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing a hardening amount of a compound having the following formula:



17. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing in addition to a color former fast to diffusion capable of forming upon development with a primary amine developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dye images and a hardening amount of a hardening agent selected from the group of compounds having the following general formula:

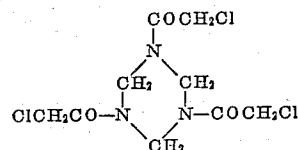


wherein X represents a halogen atom selected from the group consisting of chlorine, bromine and iodine.

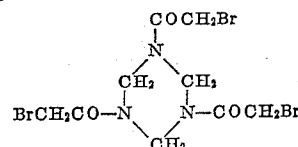
18. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing in addition to a color former fast

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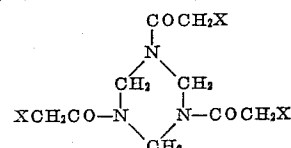
to diffusion capable of forming upon development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dye images, and a hardening amount of a hardening agent of the following formula:



19. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing in addition to a color former fast to diffusion capable of forming upon development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dye images, and a hardening amount of a hardening agent of the following formula:



20. A photo-sensitive element comprising a support and a gelatin silver halide emulsion coated thereon, said emulsion containing in addition to a color former fast to diffusion capable of forming upon development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dye images, and a hardening amount of a hardening agent of the following general formula:



wherein X represents a halogen atom selected from the class consisting of chlorine, bromine and iodine.

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