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3,325,287

PHOTOGRAPHIC GELATIN HARDENING COMPOSITION

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 No Drawing. Filed Nov. 26, 1963, Ser. No. 326,219
 10 Claims. (Cl. 96—111)

This invention relates to an aqueous gelatin composition and hardening of gelatin with the water-soluble dichlorotriazine compounds to impart enhanced resistance to water.

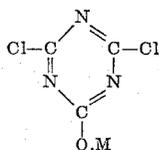
In most photographic materials, gelatin is used as their constituting elements, in silver halide emulsion layers, protective coatings, substratum layers to film base, anti-halation layers, backing layers and so on. In photographic uses, such a gelatin layer is often treated with a succession of aqueous solutions which may vary in pH and in temperature. The layers composed of untreated gelatin have poor resistance to water; in water the gelatin layers swell excessively and are scratched easily. Especially at high temperature, the gelatin layers dissolve in aqueous solutions.

A number of classes of compounds have been found useful for treating gelatin to improve the resistance to water. These compounds are called hardeners in photographic arts. These include, for example, inorganic compounds such as chromium potassium sulfate and organic compounds such as aldehyde, polyfunctional epoxide, polyfunctional ethylene-imine, and polyfunctional activated vinyl compounds. The use of these hardeners in photographic products has been well known.

Almost all hardeners of the classes known heretofore, however, have exhibited unwanted effects when used in photographic products. One serious drawback concerns the unwanted effects on photographic properties; for example, an increase in fog of the emulsion and a loss of photographic sensitivity. Other difficulties frequently encountered with such hardeners are insufficient water-solubility causing nonuniformity of the gelatin layer, chemical instability of hardeners in solid or solution state, or toxicity in handling. Some hardeners lose their hardening effect when used in the presence of other kinds of photographic additives such as stabilizers and colorforming couplers.

One object of our invention is to provide hardeners for gelatin which exhibit no detrimental photographic effects. Another object of our invention is to provide substances which when mixed make the gelatin insoluble in aqueous solutions of varying pH or temperature. A further object of our invention is to provide for hardening of gelatin by the use of water-soluble dichlorotriazine compounds. Other objects of our invention will appear herein.

We have found that gelatin is made resistant to water even at elevated temperature by incorporating therein water-soluble salts of 2,4-dichloro-6-hydroxy-s-triazine, characterized by the general formula:



wherein M represents an alkali- or alkaline-earth metal, e.g. a sodium, potassium, lithium, calcium, barium, or strontium atom, or a quaternary ammonium group, e.g. an ammonium tetramethylammonium, tetraethylam-

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monium, tetrapropylammonium, or tetrabutylammonium group.

The cationic group represented by M in the foregoing formula can be selected from a wide range of cationic groups, because it plays a role only as a counter ion to a 2,4-dichloro-6-oxy-s-triazine anion which takes a part in crosslinking gelatin molecules.

The foregoing compounds are prepared by partial hydrolysis of cyanuric chloride in an alkaline aqueous solution under carefully controlled conditions, in a manner analogous to that described in the Journal of the Society of Organic Synthetic Chemistry, Japan, vol. 18, p. 175-183 (1960).

A water-soluble salt of 2,4-dichloro-6-hydroxy-s-triazine may be added to a gelatin composition directly in the form of a partial-hydrolysis liquid product without separating a solid salt, as illustrated in the examples.

One advantage of our novel hardeners is a fast rate of hardening of gelatin in photographic products. The fast hardening is important in order to manufacture photographic products of constant quality without "after-hardening." Another advantage of our hardeners is that they have no influence on the photographic properties. A further advantage of our novel hardeners is that hardening process is not affected adversely by the presence of other kinds of photographic additives. Consequently our novel hardeners are especially suited for hardening color photographic materials with color-forming couplers incorporated in gelatin layers. A further advantage of our novel hardeners is the very low level of toxicity to human bodies.

Incorporating our novel hardeners in gelatin layers is performed in various ways, for example, by adding a hardener to a gelatin solution before coating or by dipping a dried gelatin layer into a hardener solution.

To obtain effective hardening a pH of an aqueous gelatin composition is preferably kept within a range of 5 to 12. Beyond the range, a salt of 2,4-dichloro-6-hydroxy-s-triazine is hydrolyzed gradually to a di- or tri-hydroxy derivative which gives a weaker hardening effect than a monohydroxy derivative does.

While the exact amount of our novel hardeners may be varied depending on the particular type of gelatin dispersion or emulsion employed, the amounts ranging 1.0 to 50 grams of hardeners per kilogram of dry gelatin are preferred in general, but when it is used in photographic materials 1.0 to 30 grams are most suitable. In these amounts, effective hardening is obtained to the extent that the treated gelatin layers are not damaged by the photographic process even at elevated temperature.

In some cases, our novel hardeners can be used in combination with other classes of hardeners known heretofore, to give a better hardening effect.

While the following examples describe in detail the methods for accomplishing the objects stated above, 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 our invention.

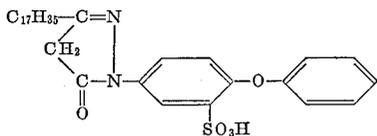
EXAMPLE 1

66 grams of cyanuric chloride were added little by little to an alkaline solution of 90 grams of sodium bicarbonate in 430 milliliters of water at 35° C. over one hour. The solution was kept at 35° C. for further one hour to produce a clear solution, and filtered. The filtrate was cooled overnight at about 5° C. to separate 50 grams of crude sodium salt of 2,4-dichloro-6-hydroxy-s-triazine as a precipitate. The pure hardener was obtained by recrystallizing the crude one from a slightly alkaline aqueous solution containing sodium bicarbonate.

Analysis.—Calculated for C₃Cl₂N₃ONa: C, 25.00%; N, 22.34%. Found: C, 24.83; N, 22.17%.

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20 milliliters of a 2% aqueous solution of the hardener obtained were added to 1 kilogram of iodobromide photographic emulsion containing 80 grams of gelatin and 15 grams of a coupler formulated below. The emulsion was adjusted to a pH of 7, cast over a film base of polyethylene terephthalate, and dried.



Melting points of the emulsion layer were measured by the method commonly used in photographic arts, in comparison with an emulsion not treated with the hardener. The results are as follows:

	Time elapsed after coating			
	4 days	15 days	28 days	2 days, 45° C., 80% R.H.
	Melting points in water, ° C.			
Not treated with hardener.....	32	32	32	32
Treated with hardener....	70	85	above 90	above 90

When developed in a color developer containing 4-amino-3-methyl-N,N-diethylaniline, the emulsion treated with the hardener showed the same photographic properties, color densities, speed, and fog, as those of the type not treated.

EXAMPLE 2

With vigorous stirring a hot solution of 660 grams of cyanuric chloride in 2.4 liters of acetone was added dropwise to a solution of 663 grams of sodium bicarbonate in 4 liters of water over one hour at 35° C. to obtain a clear solution of a pH of about 8.5. The solution was cooled to 20° C., filtered, and added with enough water to make 6.6 liter. Analysis indicated that the solution contained about 10 weight percent of sodium salt of 2,4-dichloro-6-hydroxy-s-triazine. The solution was mixed with 1 kilogram of iodobromide photographic emulsion containing 70 grams of gelatin. A cellulose triacetate film base was coated with the emulsion and dried at room temperature. The following results were obtained:

Milliliters of the 10% hardener solution per 1 kg. of emulsion:	Time elapsed after coating		
	Fresh	4 days	28 days
	Melting points in water, ° C.		
0.....	32	32	32
2.....	45	75	above 90
4.....	70	above 90	above 90
6.....	85	above 90	above 90

Photographic tests showed that the hardened film 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.

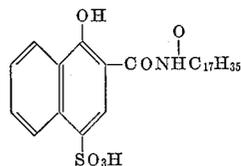
EXAMPLE 3

A 10% aqueous solution of potassium salt of 2,4-dichloro-6-hydroxy-s-triazine was prepared by using 792 grams of potassium bicarbonate instead of sodium bicarbonate described in the Example 2.

5 milliliters of the 10% hardener solution obtained were added to 1 kilogram of chlorobromide photographic emulsion containing 80 grams of gelatin and 10 grams of a coupler formulated below. The emulsion was adjusted

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to a pH of 7, cast over a cellulose triacetate film base, and dried at room temperature.



The following results were obtained:

	Time elapsed after coating		
	4 days	15 days	28 days
	Melting points in water, ° C.		
Not treated with hardener.....	32	32	32
Treated with hardener.....	85	above 90	above 90

When developed in a color developer containing 4-amino-3-methyl-N,N-diethylaniline, the hardened emulsion showed the same photographic properties, color densities, speed, and fog, as those of the unhardened type.

EXAMPLE 4

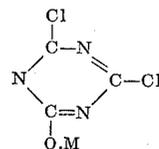
A solution of 92 grams of cyanuric chloride in 300 milliliters of dioxane was poured into 700 milliliters of cold water of 0 to 5° C. with vigorous stirring to give a cyanuric chloride suspension. At the same temperature to this suspension 1,000 milliliters of 10% aqueous solution of tetramethyl ammonium hydroxide were added dropwise for one hour. The mixture was continued to be stirred for sufficient time to give a clear solution. The resulting solution was adjusted to a pH of about 8 and added with water to make 2.4 liters. Analysis of chlorine indicated that the solution contained 5 weight percent of tetramethyl ammonium salt of 2,4-dichloro-6-hydroxy-s-triazine. 20 milliliters of the solution were added to 1 kilogram of 8% gelatin solution containing silver colloid. The dispersion was coated onto paper to produce a positive material for the diffusion transfer copying process. The hardened gelatin layer stored for 1 month at room temperature did not dissolve even in boiling water.

EXAMPLE 5

A gelatin layer coated on a cellulose triacetate film base was dipped in a 0.1% aqueous solution of sodium salt of 2,4-dichloro-6-hydroxy-s-triazine at pH 8 and 10° C. for 5 minutes. The layer was dried and stored for a month at room temperature. The hardened layer did not melt in water up to 90° C., while the unhardened one melted at 32° C.

We claim:

1. A gelatin layer having a support therewith, the gelatin of which is hardened by incorporating in an aqueous gelatin solution of pH 5 to 12, 0.1 to 5 percent based on the weight of gelatin of a compound having the formula:



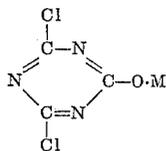
wherein M is a member selected from the group consisting of alkali metals, alkaline earth metals, and NR₄ radicals, and R is an alkyl radical containing 1 to 4 carbon atoms; casting said gelatin solution on said support and drying.

2. The gelatin layer as claimed in claim wherein said alkali metal is sodium.

3. The gelatin layer as claimed in claim 1 wherein said alkali metal is potassium.

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4. A photographic silver halide-gelatin layer having a support therewith, the gelatin of which is hardened by incorporating in an aqueous emulsion of pH 5 to 12, 0.1 to 3 percent based on the weight of gelatin of a compound having the formula:



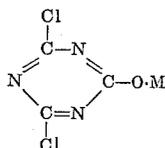
wherein M is a member selected from the group consisting of alkali metals, alkaline earth metals, and NR_4 radicals, and R is an alkyl radical containing 1 to 4 carbon atoms; casting said emulsion on said support and drying.

5. The photographic emulsion layer as claimed in claim 4 wherein said alkali metal is sodium.

6. The photographic emulsion layer as claimed in claim 4 wherein said alkali metal is potassium.

7. The photographic emulsion layer as claimed in claim 4 wherein said aqueous emulsion contains a color-forming coupler.

8. A gelatin layer having a support therewith, the gelatin of which is hardened by incorporating by dipping said layer in an aqueous solution of pH 5 to 12 containing a hardening amount of compound having the formula:



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wherein M is a member selected from the group consisting of alkali metals, alkaline earth metals, and NR_4 radicals, and R is an alkyl radical containing 1 to 4 carbon atoms; and drying.

9. The gelatin layer as claimed in claim 8, wherein said alkali metal is sodium.

10. The gelatin layer as claimed in claim 8, wherein said alkali metal is potassium.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

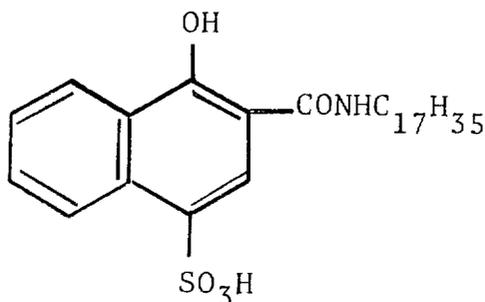
Patent No. 3,325,287

June 13, 1967

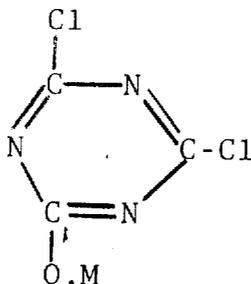
Nobuo Yamamoto et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 50, "effect" read -- effect --; column 4, lines 3 to 9, the formula should appear as shown below instead of as in the patent:



column 4, lines 60 to 65, the formula should appear as shown below instead of as in the patent:



column 4, line 72, for "claim" read -- claim 1 --.

Signed and sealed this 6th day of August 1968.

(SEAL)
Attest:

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