METHOD OF HARDENING GELATIN BY REACTING WITH CONJUGATED HETEROCYCLIC COMPOUNDS CONTAINING HALOGEN ATOMS AND WATER-SOLUBILIZING ACID GROUPS

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6 Claims. (Cl. 260—117)

In the manufacture of photographic layers gelatin is preferably used as the hydrophilic colloid which contains silver halides and, if desired, color couplers or dyestuffs, the gelatin being cast on to a suitable support, for example, a film, paper or glass plate. After being dried and exposed, these layers are introduced into numerous treatment baths, such as developing baths, fixing baths and, if necessary, image reversal baths or color bleaching baths. During these treatments the gelatin layers swell considerably, and gelatin may be partially dissolved away or even completely washed off.

In order to make the gelatin layers more resistant to the attack of the treatment baths they are hardened, that is to say, their swelling capacity in water and in the baths is decreased and the melting point of the aqueous layers is raised from the original 28 to 30° C. up to 60 to 95° C., or even so high that the gelatin can withstand treatment at the boiling temperature of an aqueous bath.

The conventional hardening agents include aldehydes, preferably formaldehyde, and chromium salts and alums.

The use of the conventional hardening agents has certain disadvantages. The action of the chromium salts is often very dependent on the pH-value of the cast mixtures. Alums have the same disadvantage in processing baths. When known hardening agents are added to the finished emulsions prior to casting, a viscosity variation dependent on time often occurs, so that the viscosity increases slowly during the casting operation and thus causes variation in the thickness of the layer. The aldehydes can also lead to fogging, especially in the case of highly sensitized silver halide layers. Color fog can also be caused by the hardening agent.

There is therefore a need for hardening agents that can be added to finished emulsion prior to casting without causing a change in viscosity during the casting operation, and which, within a short time after manufacture of the material, for example, 1 or 2 days or, if necessary, after 15 to 40 days, give a degree of hardness that permits the material to be used and tested in the normal manner and do not cause the layers to become horny during long periods of storage. Furthermore, such hardening agents should not cause fogging, and should exhibit a neutral behaviour towards color couplers and any other additions.

The present invention is based on the observation that gelatin can be hardened in an advantageous manner by reacting it with a colorless compound which contains at least one acid group imparting solubility in water, at least one heterocyclic six-membered ring consisting of 3 to 4 carbon atoms and 3 to 2 nitrogen atoms, and at least one halogen atom bound to a carbon atom of the six-membered ring.

By "reaction" is meant a chemical reaction between the gelatin and the halogenated six-membered ring, for example, a halogen-triazine ring, to form a homopolar bond.

The compounds to be reacted with the gelatin must contain at least one acid group imparting solubility in water, for example, a carboxylic acid or HO₂S-group, which may be present as a sulfonic acid group (bound to carbon) or in a sulfato group (bound to carbon). They must also contain at least one six-membered heterocyclic ring composed of three carbon atoms and three nitrogen atoms or four carbon atoms and two nitrogen atoms, for example, the pyridazine or pyrimidine ring. There may be mentioned compounds of the general formulae

![Chemical Structures](image-url)
in which \( R \) represents an organic substituent.

There are preferably used compounds that contain at least one monohalogen- or dihalogen-1:3:5-triazine radical. There are generally used compounds that contain bromine or especially chlorine atoms bound to the six-membered heterocyclic ring.

Among the halogen-1:3:5-triazines there are advantageously used those of the formula

\[
\begin{align*}
\text{(11)} & \quad R_1 \quad R_2 \quad \text{Halogen} \\
& \text{in which } R_1 \text{ represents an organic radical containing at least one acid group imparting solubility in water, and } R_2 \text{ represents a halogen atom or an organic radical containing at least one acid group imparting solubility in water, a hydrocarbon radical or a substituent bound to the triazine ring through an oxygen, sulfur or nitrogen atom.}\n\end{align*}
\]

At least one of the radicals \( R_1 \) and \( R_2 \) is advantageously composed of an oxygen or nitrogen atom bound to the 1:3:5-triazine ring, a hydrocarbon radical, advantageously an aliphatic hydrocarbon radical, or a radical of the benzene or naphthalene series, and at least one carboxylic acid, sulfonic acid or sulfate group. Both radicals may have this constitution and they may be identical or different from each other.

Alternatively, only one of the radicals \( R_1 \) and \( R_2 \) may have the aforesaid constitution and the other may be a halogen atom or a hydroxyl or methoxy group, or a phenoxy or amino group which may be substituted. Examples of such radicals are:

\[
\begin{align*}
& \text{(a) } \quad \text{Cl} \\
& \text{(b) } \quad \text{Cl} \\
& \text{(c) } \quad \text{Cl} \\
& \text{(d) } \quad \text{Cl} \\
& \text{(e) } \quad \text{Cl}
\end{align*}
\]

The compounds may also contain two 1:3:5-triazine rings linked together by a bridge, for example the divalent radical of a diamine, such as 1:4-diamino-benzene or an alkylene diamine.

The following are examples of radicals \( R_1 \) and \( R_2 \) which contain an acid group imparting solubility in water:

\[
\begin{align*}
& \text{(f) } \quad \text{Cl} \\
& \text{(g) } \quad \text{Cl} \\
& \text{(h) } \quad \text{Cl} \\
& \text{(i) } \quad \text{Cl}
\end{align*}
\]

Thus, for example, the following halogen compounds may be reacted with gelatin:
The heterocyclic compounds used in the method of the invention, especially the halogen-1:3:5-triazines, can be made by methods in themselves known. For example, an amino-benzene sulfonic acid may be condensed in a weakly acid medium with freshly precipitated cyanuric chloride. In order to exchange a second halogen atom for the radical of an amine or of an amino-sulfonic acid, the primary condensation product so obtained may be reacted at 30 to 40° C. in a neutral to weakly alkaline medium with the amine or with the amino-sulfonic acid.

The reaction of the gelatin with the heterocyclic halogen compound generally proceeds easily without recourse to special measures. For example, an aqueous solution of the heterocyclic compound may be brought into contact with the gelatin at a slightly raised temperature, for example, about 40° C. In most cases nothing happens for a long time. It is not until the gelatin has been dried and after a further interval of time that the halogen compound reacts with the gelatin, and the quantity of hydrobolic acid liberated thereby with respect to the proportions of the two reactants that actually react is so small that it is smoothly buffered by the excess of gelatin.

The degree of hardness of the gelatin brought about by the reaction varies depending on the constitution and proportion of the halogen compound used. The proportion of the halogen compound used is advantageously about 1 to 5%, calculated on the gelatin present. A measure of the degree of hardness produced can be obtained by determining the temperature at which the gela-
tin layer melts off the support when the layer is in contact with water of which the temperature is gradually increased. It is noteworthy, and by no means predictable, that the reaction of the heterocyclic halogen compound with the gelatin produces a hardening effect when the heterocyclic compound contains only one reactive halogen atom. If a plurality of reactive halogen atoms is present in the molecule of the heterocyclic halogen compound, as in the case, for example, with the compounds of the Formulae (a) to (e), the gelatin is hardened to a high degree, apparently owing to extensive cross-linking. In this case the groups imparting solubility in water in the heterocyclic halogen compound in no way impair the hardening effect. They have the effect of maintaining a good swelling capacity, in spite of the hardening, which is desirable. The hardening of gelatin by the method of the invention does not impair the sensitivity of the silver halide, nor does it impair the reactivity of color couplers or dyestuffs.

The following examples illustrate the invention, the parts and percentages being by weight.

**Example 1**

An aqueous solution A was prepared which contained 5% of the hardener of Formula (b) (2:4-dichloro-6-phenylamino-1:3:5-triazine-3'-sulfonic acid). Of this solution A different quantities, viz. 2 parts, 4 parts and 6 parts, were admixed each with 120 parts of an aqueous silver bromide-silver chloride emulsion containing 10 parts of gelatin in the 120 parts of emulsion. The so-obtained mixtures contained 1% or 2% or 3% of the compound of Formula (b), calculated on dry gelatin. The mixtures were cast on glass plates. After being dried and subsequently stored for 24 to 48 hours, the emulsion layers had the following melting points:

<table>
<thead>
<tr>
<th>Percentage of hardening agent calculated on the gelatine</th>
<th>0%</th>
<th>1%</th>
<th>2%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting points of the layers, °C</td>
<td>28-32</td>
<td>27</td>
<td>70-80</td>
<td>85-90</td>
</tr>
</tbody>
</table>

Similar results were obtained by using in the same manner compounds of the Formulae (a), (c), (e) and (g) as hardening agents for the gelatin, instead of the compound of the Formula (b). These compounds can be prepared by known methods. By exchanging one chlorine atom of the dichlorotriazine compounds for another substituent, for example, by using the compound of the Formula (f), and the full degree of hardening is not reached until after a longer period of storage.

The compound of the Formula (a) may be prepared as follows: 80 parts of cyanuric chloride are dissolved in 160 parts of acetone, and the solution is poured on to a mixture of 400 parts of water and 400 parts of ice. To the mixture is added a neutral solution of the sodium salt of 70 parts of 1-amino-benzene-4-sulfonic acid in 800 parts of water. The temperature is kept at 2 to 3 °C with ice. The mixture is stirred for 35 to 60 minutes until aminobenzene sulfonic acid can no longer be detected. The acid liberated during the condensation is neutralized by the dropwise addition of about 240 parts of a sodium carbonate solution of 10% strength, so that the pH-value is maintained at 7±0.5. When the condensation has finished, the compound of the Formula (a) may be completely dissolved, and it is salted out by the addition of 150 parts of a saturated sodium chloride solution. It is filtered off and dried in vacuo.

**Example 2**

To 100 parts of a silver bromide gelatin of 10% strength there was added at 40° C. 0.2 part of the disazodyestuff of the formula

![Disazodyestuff Diagram]

After casting the emulsion on safety film, and drying the layer and storing it for 24 to 48 hours, there was obtained a silver halide layer dyed blue, which, after exposure, could be converted by the silver dyestuff bleaching process into a blue component color image, and having a melting point of about 80° C., withstands well the treatment baths which attack gelatin.

**Example 3**

To separate portions of a red-sensitized silver halide emulsion which, for every thousand parts by volume, contained 30 parts of silver chloride, 70 parts of gelatin and 15 parts of one of the color couplers suitable for color development and corresponding to the formula

![Color Coupler A Diagram]

or

![Color Coupler B Diagram]

in which X represents a diffusion-inhibiting radical, for example, of the formula

![Diffusion-Inhibiting Radical]

were added 1.4 parts of one of the chloro-triazine compounds of the Formulae (a), (b), (c) and (k).

After casting the emulsions, drying the layers and keeping them for 1 to 2 days, there were obtained hardened layers capable of forming one of the layers of a multi-color material, and of withstanding the attack of the numerous baths used for processing color reversal material without impairing the activity of the color coupler.

**Example 4**

Baths were prepared which contained 2 to 10 parts of one of the chloro-triazine compounds of the Formulae (a), (b), (c), (e) and (g) dissolved in 100 parts of water.

These baths were used in the same way as conventional hardening baths, that is to say, the material to be hardened was treated in the bath for 5 to 20 minutes, after which it was rinsed for 2 to 5 minutes, and then dried. After standing for 24 hours, the materials so treated were well hardened.

The compound of the Formulae (i), (l), (m) and (n) were slower in their action. When used in proportions ranging from 2 to 6%, based on the weight of the gelatin, these compounds gave melting points from 40° C. to
65° C., depending on the proportion used, and they resulted in a greater tendency to swell which is desirable, for example, in imbibition processes.

**Example 5**

4 parts of the compound of the Formula (o) were dissolved in the cold in 100 parts of water. 10 parts of the solution so prepared were added to 100 parts of an aqueous solution of gelatine of 8 to 10% strength or to a corresponding silver halide emulsion at a temperature of 35 to 38° C.

10 cc. of the mixture so prepared were cast on a glass plate measuring 13 cm. x 18 cm., and the layer was allowed to solidify and dry. The melting point of a control layer not containing the hardening agent was 32° C. The layer containing the hardening agent had a melting point of 42° C., after 24 hours, which rose to 58 to 62° C. in the course of a few days.

The compound of the Formula (o) can be prepared by condensing in water 80 parts of cyanuric chloride with 121 parts of 2-amino-naphthalene-4,8-disulfonic acid in the form of its sodium salt, in the manner described at the end of Example 1.

**Example 6**

Gelatin emulsions were treated with 2 to 5%, based on the dry gelatin content, of the compound of Formula (p), in the manner described in Example 1. This compound can be prepared in the following manner: 110 parts of the compound of Formula (s) are treated at 40° C. in 6000 parts of water with 24 parts of monoethanolamine and 20 parts of sodium carbonate. After 30 to 60 minutes, the condensation product is precipitated with sodium chloride and dried.

By the above treatment melting point of the layer was raised to about 40° C. This degree of hardening was obtained only after a certain period of storage. The reaction with the compound (p) has an especially favorable effect on hot drying carried out on a machine.

Slow hardening also occurs when the gelatin is heated in the manner described with the condensation product of the Formula (q). This compound is obtained in a manner analogous to that described for obtaining the compound of the Formula (p), with the use of 12 parts of ethylene diamine, instead of the ethanolamine.

**Example 7**

Gelatin emulsions were treated with the compound of the Formula (r) in the manner described in Example 1. 24 hours after casting, the melting points of the emulsion layers were 68° C. to 62° C. and shortly rose to 90° C. and above. The compound of the Formula (r) is obtained by reacting the sodium salt of 94 parts of 1-hydroxy-4-aminoazobenzene-2-carboxylic acid-6-sulfonic acid with 80 parts of cyanuric chloride.

**Example 8**

A gelatin emulsion was treated with the dichloropyrimidine compound of the Formula (s) in the manner described in Example 1. Some considerable time elapsed before the gelatin reached its maximum degree of hardness. The compound of the Formula (s) is obtained in a manner analogous to that described in Example 1 by condensing the sodium salt of 70 parts of 1-aminobenzene-4-sulfonic acid with 73 parts of 2:4:6-trichloropyrimidine which has been dissolved in ethanol.

A similar effect on the gelatin obtained with the trichloropyrimidine compound of the Formula (t). This compound is prepared from 2:4:5:6-tetrachloropyrimidine and the sodium salt of 1-aminobenzene-4-sulfonic acid.

The pyrimidine compounds of the Formulae (s) and (t), which are considerably slower in their action than the triazine compounds, do not increase the viscosity of the casting mixture during the time required for casting large batches of the mixture. The freshly cast and dried layers have melting points of about 40° C. The melting points rise after a long period of storage.

Even slower in its action is the pyridazine compound of the Formula (u), which may be prepared from tetrachloropyridazine and 1-aminobenzene-3-sulfonic acid.

What is claimed is:

1. A process for hardening gelatin which comprises reacting the gelatin with a colorless compound which contains at least one acid group imparting solubility in water, which group is bound to a carbon atom, at least one heterocyclic six-membered ring consisting of 3 to 4 carbon atoms and 2 to 3 nitrogen atoms and having three conjugated double bonds, and at least one halogen atom bound to one of the ring carbon atoms of the heterocyclic ring, the carbon atoms in said heterocyclic ring having substituents selected from the group consisting of the aforesaid acid group, a halogen atom, a sulfophenylamino radical, a sulfonaphthalamino radical, a sulfatoalkylamino radical, a sulfophenoxo radical, a hydroxyalkylamino radical, a primary amino group, a β-(6-chloro-4-sulfophenylamino-1,3,5-triazine-2-ylamino)-ethylamino radical, a β-(6-chloro-4-sulfophenylamino-1,3,5-triazine-2-ylamino)-phenylenamino radical, and a β-(6-chloro-4-sulfophenoxo-1,3,5-triazine-2-ylamino)-ethylamino radical.

2. Gelatin which has been hardened by reaction with a colorless compound which contains at least one acid group imparting solubility in water, which group is bound to a carbon atom, at least one heterocyclic six-membered ring consisting of 3 to 4 carbon atoms and 2 to 3 nitrogen atoms and having three conjugated double bonds, and at least one halogen atom bound to one of the ring carbon atoms of the heterocyclic ring, the carbon atoms in said heterocyclic ring having substituents selected from the group consisting of the aforesaid acid group, a halogen atom, a sulfophenylamino radical, a sulfonaphthalamino radical, a sulfatoalkylamino radical, a sulfophenoxo radical, a hydroxyalkylamino radical, a primary amino group, a β-(6-chloro-4-sulfophenylamino-1,3,5-triazine-2-ylamino)-ethylamino radical, a β-(6-chloro-4-sulfophenylamino-1,3,5-triazine-2-ylamino)-phenylenamino radical, and a β-(6-chloro-4-sulfophenoxo-1,3,5-triazine-2-ylamino)-ethylamino radical.

3. A process for hardening gelatin which comprises reacting the gelatin with a colorless compound of the formula

\[
\text{Halogem}
\]

\[\text{C} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{N} \]

\[\text{R}_{1} \quad \text{H} \]

in which \(\text{R}_{1}\) is composed of a hydrocarbon radical, at least one −SO₂H group attached to said hydrocarbon radical and a member selected from the group consisting of an oxygen atom bound to the triazine ring and a nitrogen atom bound to the triazine ring.

4. A process for hardening gelatin which comprises reacting the gelatin with a colorless compound of the formula

\[
\text{Cl} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{Cl}
\]

\[\text{HN-R'} \]

in which \(\text{R'}\) represents a benzene radical containing at least one sulfonic acid group.
5. A process for hardening gelatin which comprises reacting the gelatin with a colorless compound of the formula

\[
\begin{align*}
N & \quad C \quad N \\
\quad & \quad \quad \quad \quad \quad \quad \quad \quad \quad Cl \\
\end{align*}
\]

in which \( R_1'' \) represents an aromatic radical of the composition \( C_{2m+4c}H_{2+8m}SO_3H \), where \( m \) and \( n \) each represents a whole number of at the most 2.

6. A process for hardening gelatin which comprises reacting the gelatin with the compound of the formula

\[
\begin{align*}
C \quad N \\
\quad & \quad \quad \quad \quad \quad \quad \quad \quad \quad Cl \\
\end{align*}
\]

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WILLIAM H. SHORT, Primary Examiner.

LEON ZITVER, Examiner.

D. P. CLARKE, H. SCHAIN, Assistant Examiners.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,288,775

November 29, 1966

Walter Anderau 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.

In the heading to the printed specification, after line 9, insert -- Claims priority, application Switzerland, April 7, 1961, 4074/61 --; column 10, lines 49 to 56, the right-hand portion of the formula, for "Halogon" read -- Halogen --.

Signed and sealed this 7th day of November 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents