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[54] PROCESS FOR THE RAPID HARDENING OF GELATIN

[75] Inventors: **Ikutaro Horie; Kameji Nagao**, both of Minami-Ashigara, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Minami-Ashigara, Japan

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[51] **Int. Cl.** **G03c 1/00**; B44d 1/44
[58] **Field of Search** .... 117/93.1 DH, 34, 164; 34/1

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Primary Examiner—William D. Martin
Assistant Examiner—John H. Newsome
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] ABSTRACT

A process for the rapid hardening of gelatin comprising coating a support with an aqueous gelatin solution containing as a hardener at least one of a halogenated diazine compound, a halogenated triazine compound, a compound having an active vinyl radical, a mucohalogen acid or a derivative thereof and a substituted or an unsubstituted 2,3-dihydroxy-1, 4-dioxane, drying at a constant rate for a period of time and irradiating with a high frequency microwaves is disclosed.

9 Claims, No Drawings

PROCESS FOR THE RAPID HARDENING OF GELATIN

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for hardening gelatin.

2. Description of the Prior Art

In the manufacture of photographic light sensitive materials, gelatin is used as a material for, e.g., a binder for the silver halide emulsion, a protective colloid layer, an intermediate layer, an under coat layer for the film base, an antihalation layer, a backing layer, etc. The light sensitive material having some of these layers containing gelatin is treated with treating liquids of various compositions under various conditions after exposure. If the layers containing gelatin of the photographic material are not treated with a hardener in the treatments as described above, they have a poor water resistance and are swollen excessively by the treatments and tend to be damaged. Occasionally gelatin is dissolved off of the support with a treatment at a high temperature. These situations damage greatly the performance of the light sensitive material. Various kinds of gelatin hardeners have been used previously to eliminate these disadvantages of gelatin.

As a gelatin hardener, inorganic compounds such as chromium alum as well as organic compounds such as aldehyde compounds, active vinyl compounds and ethyleneimino compounds are known. These hardeners may be added to the emulsion or the treating liquid depending upon the purpose.

However, some of these hardeners require a very long reaction time to harden the gelatin sufficiently, so that a considerably long time has been required to obtain the desired physical properties (for example, water resistance and mechanical strength, such as abrasion resistance etc. of the photographic gelatin layer) and the desired photographic properties (for example, for density, maximum density etc.) in the light sensitive material.

It has been reported that the photographic gelatin layer coated on a support can be irradiated with a high frequency to dry it. While it is possible to dry in a short time according to this method, it has a great disadvantage in that it adversely affects the hardening of gelatin.

SUMMARY OF THE INVENTION

As a result of much research to solve these problems, this invention has been accomplished. This invention relates to a process for the rapid hardening of gelatin comprising coating a support, such as a synthetic resin film, a glass or a paper, with an aqueous gelatin solution containing at least one of a halogen substituted diazine and a halogen substituted traizine compound, a compound having an active vinyl radical, a mucohalogen acid or a derivative thereof, and a substituted and an unsubstituted 2, 3-dihydroxy-1,4-dioxane, and after drying at a constant rate for a period of time, irradiating with high frequency microwaves.

DETAILED DESCRIPTION OF THE INVENTION

Suitable examples of halogenated diazine and triazine compounds as a hardener which can be used in this invention are those described in U.S. Pat. Nos. 2,983,611, 3,325,287 and 3,549,377, and British Pat. Nos. 1,072,008 and 1,193,290, for example, 4-chloro-2,6-bis(methylsulfonyl)-1,3-diazine, 4-chloro-2-ethylsulfonyl-6-methyl-1,3-diazine,2,4-dibromo-6-methylsulfonyl-1,3-diazine,2,4,5-tribromo-6-methylsulfonyl-1,3-diazine,4,5-dichloro-6-methyl-2-phenylsulfonyl-1,3-diazine, 2,3-dichloroquinoxaline-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-6-chloro-7-sulfonic acid chloride, N,N-bis(hydroxyethyl)aminodichlorotriazine, the sodium salt of 2,4-dichloro-6-oxy-s-triazine, or 2,4-bis(1-aziridinyl)-6-chloro-1, 3,5-triazine and the like.

As compounds having an active vinyl radical, suitable examples are those described in U.S. Pat. Nos. 3490911 and 3539644 and British Pat. No. 994,869, for example, methylene bisacrylamide, 1,2-bis(2-vinylsulfonylmethoxy)ethane, or bis(2-vinylsulfonylethyl)ether and the like.

Suitable mucohalogen acids and their derivatives are those described in U.S. Pat. Nos. 2,080,019 and 3,579,374 and Belgian Pat. No. 725,964, for example, mucochloric acid, mucobromic acid, 3-bromo-2-phenoxymalealdehydic acid, 3-chloro-2-phenoxymalealdehydic acid, 2-(p-carboxyphenoxy)-3-chloromalealdehydic acid, 2-(p-methoxyphenoxy)-3-chloromalealdehydic acid, 2-(p-tert-pentylphenoxy-3-chloromalealdehydic acid, 2-(p-octylphenoxy)-3-chloromalealdehydic acid, 2-(m-pentadecyl)-3-chloromalealdehydic acid, or 3-chloro-2-phenylthiomalealdehydic acid and the like.

As the substituted and unsubstituted 2,3-dihydroxy-1,4-dioxanes, suitable examples are those described in U.S. Pat. No. 2,870,013, British Pat. No. 1,270,578 (corresponding to U.S. patent application Ser. No. 201,999 filed Nov. 24, 1971 which is a continuation application of U.S. patent application Ser. No. 850,673 filed Aug. 15, 1969), German Offenlegungsschrift No. 2,104,816 (corresponding to U.S. patent application Ser. No. 112,014 filed Feb. 2, 1971), for example, 2,3-dihydroxy-1,4-dioxane, 5-chloromethyl-2,3-dihydroxy-1,4-dioxane, 5-phenoxymethyl-2,3-dihydroxy-1,4-dioxane,2-methyl-2,3-dihydroxy-1, 4-dioxane, 2,5,6-trimethyl-2,3-dihydroxy-1,4-dioxane, and the like.

The amount of these hardeners which is added will depend on the hardening effects obtained therewith but generally the amount ranges from 1 to 300 mg per g of dried gelatin, perferably from 1 to 100 mg per g of dried gelatin.

The aqueous gelatin solutions, to which this invention may be applied, include gelatin solutions, acetylated gelatin solutions and succinated gelatin solutions and also includes use as, for example, coating solutions for silver halide emulsion layers, protective colloid layers, intermediate layers, under coat layers for film bases, antihalation layers and backing layers. These layers of the photographic sensitive material contain gelatin, and it is also applicable to gelatin solutions for encapsulating microcapsules and the like. These and other gelatin derivatives are described in U.S. Pat. Nos. 2,518,666, 2,525,753 and 2,614,928.

In the application of this invention to a photographic light sensitive material having gelatin-containing layers, the photographic gelatin layers can contain various additives such as coating aids, anti-foggants, chemical sensitizers, spectral sensitizers, plasticizers, such as glycerine, dicarboxylic acid esters described in U.S. Pat. No. 2,940,854, lower alkyl esters of ethylene bisglycolic acid described in U.S. Pat. No. 2,904,434, couplers, swelling controlling agents such as those described in U.S. Defensive Publication No. T873,003 (April 7, 1970) and antistatic agents.

The term "drying at a constant rate for a period of time" as used in this invention will be illustrated as follows: If a support is coated with an aqueous solution of gelatin and dried at a constant temperature and humidity, the water content during the drying process is reduced initially in proportion to the time and the rate of reduction in the water content is then gradually lowered (that is, the water content is reduced initially at a constant rate and then at a falling rate); the former drying stage is described as drying at a constant rate for a period of time.

The irradiation with a high frequency electric field can be carried out after the drying at the constant rate and therefore, the application of a high frequency electric field after the completion of the drying provides good results without losing the effects of this invention. A suitable frequency which can be from are those bands designated IMS bands having frequencies of 13.56MHz 27.12MHz, 40.68MHz, 915MHz, 24.50MHz, 58.50MHz, 10600MHz, and 18000MHz. Use of frequencies of 2450MHz and 915MHz as approved by various governmental agencies for industrial use are suitably used to obtain the effects of this invention.

The irradiation time with the high frequency microwaves, which may vary depending on the intensity of the high frequency electric field generally is preferably from 1 sec. to 20 min.

By using this invention, the hardening reaction of gelatin is promoted to reduce the reaction time so that the physical and photographic properties of the photographic light sensitive material having gelatin-containing layers are constant resulting in an improved performance of the material with great advantages.

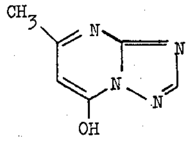
This invention will be illustrated in greater detail by reference to the following examples. Unless otherwise indicated, all parts and percents are by weight.

EXAMPLE 1

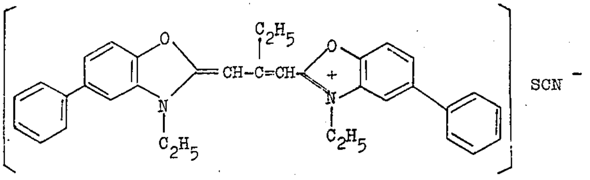
A gelatin-silver iodide emulsion (containing 0.3 mol of silver halide per kg of emulsion), in which the gelatin content was adjusted to 5% and which contained silver bromide particles which had been previously gold- and sulfur-sensitized (containing 5 mol% of silver iodide), was prepared. Subsequently, the following Compounds (1) to (4) in the amounts indicated per g of the emulsion were added.

Compound (1)	(anti-foggant)	0.5 mg
Compound (2)	(optical sensitizer)	1.5 mg
Compound (3)	(coupler)	1.5 mg
Compound (4)	(coating aid)	0.2 mg

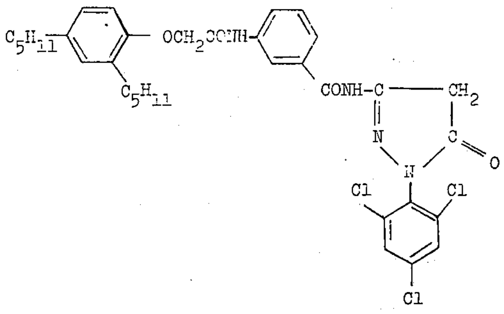
Compound (1)



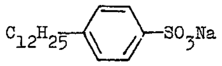
Compound (2)



Compound (3)



Compound (4)



Further, 3mg of the sodium salt of 2-oxy-4,6-dichloro-s-triazine as a hardener per g of dried gelatin were added, a film of acetyl cellulose was coated therewith so that the dried thickness would be 5μ, dried at a dry bulb temperature of 35°C and a wet bulb temperature of 24°C, dried and stored according to the following steps (a) to (f) immediately after the completion of the constant rate drying (the water content of the coated layer was 30% in this test) or immediately after coating and cooling in the case of (g) to yield Sample (a) to (g):

a. Stored at 25°C and 45% relative humidity (abbreviated hereinafter as RH).
b. Irradiated with a high frequency (to minimize problems due to the electric wave, the test was performed using 2450MHz, 5 KW, the same conditions were also used hereinafter) for 30 sec and stored then at 25°C 45% RH.
c. Stored at 25°C and 45% RH after irradiating with a high frequency for 1 min.
d. Stored at 25°C and 45% RH after irradiating with a high frequency for 2 min.

e. Stored at 25°C and 45% RH after irradiating with a high frequency for 5 min.

f. Stored at 25°C and 45% RH after irradiating with a high frequency for 20 min.

g. Immediately after coating and cooling, irradiating with a high frequency for 5 min and then stored at 25°C and 45% RH.

The melting point of the emulsion film of each sample in a 2% aqueous solution of sodium carbonate after storing for 1, 3 and 7 days was determined and the results obtained are shown in Table 1.

TABLE 1

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate							
Storage Time	Sample						
(day)	a	b	c	d	e	f	g
1	40	45	55	68	73	73	37
3	58	70	80	>90	>90	>90	40
7	88	>90	>90	>90	>90	>90	55

As can obviously be seen from the results contained in Table 1, Sample (g) irradiated with a high frequency immediately after coating and cooling was hardened to a lesser extent (i.e., lower melting point) than Sample (a) giving rise to a poor result. However, Samples (b) to (f) were hardened well showing good results.

EXAMPLE 2

20mg of 2-methoxy-4,6-dichloro-s-triazine per g of dried gelatin were added to a gelatin-silver chlorobromide emulsion having silver chlorobromide particles containing 40 mol% of silver chloride (containing 50g of gelatin and 0.38 mol of silver halide per Kg of emulsion), a photographic support was coated with the mixture so that the dried thickness of coating would be 5μ and the procedures (a) to (g) as described in Example 1 were carried out to yield Samples (a) to (f). The melting point of the emulsion film of each sample was determined in a 2% aqueous solution of sodium carbonate and the results as shown in Table 2 were obtained.

TABLE 2

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate						
Storage Time	Sample					
(day)	a	b	c	d	e	f
1	36	40	44	55	60	60
3	43	48	50	65	65	65
7	60	60	63	65	68	68

As can be seen from the results contained in the above table, the hardening of the emulsion film of the samples can be remarkably promoted by irradiation with a high frequency.

EXAMPLE 3

40mg of 2,4-dimethoxy-6-chloro-s-triazine per g of dried gelatin were added to a 5% aqueous solution of gelatin and the same procedure as described in Example 2 was carried out to yield Samples (a) to (f). The melting point of each sample was determined using the same method as described in Example 1 and the results as shown in Table 3 were obtained.

TABLE 3

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate						
Storage Time	Sample					
(day)	a	b	c	d	e	f
1	36	38	42	50	55	55
3	36	38	45	50	55	55
7	36	38	45	50	55	55

As can be seen from the results contained in the above table, the hardening of samples can be remarkably promoted by irradiation with a high frequency.

EXAMPLE 4

Instead of 2,4-dimethoxy-6-chloro-s-triazine used in Example 3, 30mg of 2,4-dichloro-6-hydroxyethylamino-s-triazine were used and the same procedure as described in Example 3 was carried out. The melting point of the gelatin film of each sample in a 2% aqueous solution of sodium carbonate is shown in Table 4.

TABLE 4

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate						
Storage Time	Sample					
(day)	a	b	c	d	e	f
1	36	38	40	50	55	55
3	36	38	42	50	55	55
7	36	38	42	50	55	55

As can obviously be seen from the results contained in the above table, the hardening of the samples irradiated by high frequency was promoted.

EXAMPLE 5

Instead of 2,4-dimethoxy-6-chloro-s-triazine used in Example 3, 10mg of hexahydro-1,3,5-triacryl-s-triazine and 2mg of the sodium salt of 2-oxy-4,6-dichloro-s-triazine per g of dried gelatin were added and the same procedure as described in Example 3 was carried out.

The melting point of the gelatin film of each sample in a 2% aqueous solution of sodium carbonate was determined and the results obtained are shown in Table 5.

TABLE 5

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate						
Storage Time	Sample					
(day)	a	b	c	d	e	f
1	36	40	45	55	55	67
3	45	48	50	60	60	67
7	60	60	60	60	60	67

As can obviously be seen from the results contained in the above table, the hardening of the samples irradiated with high frequency was remarkably promoted.

EXAMPLE 6

Instead of 2-oxy-4,6-dichloro-s-triazine used in Example 1, 4mg of 3-chloro-2-phenoxymalealdehydic acid per g of gelatin were added and the same procedure as described in Example 1 was carried out to yield Samples (a) to (f). The melting point of the emulsion film of each sample in a 2% aqueous solution of sodium carbonate was determined and the results obtained are as shown in Table 6.

TABLE 6

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate

Storage Time	Sample					
(day)	a	b	c	d	e	f
1	38	42	48	60	60	60
3	55	60	64	85	85	85
7	80	80	85	85	85	85

As can obviously be seen from the results contained in above table, the hardening of the sample irradiated with high frequency was remarkably promoted.

EXAMPLE 7

Instead of the sodium salt of 2-oxy-4, 6-difluoro-s-triazine in Example 1, 5mg of 2,3-dihydroxy-1,4-dioxane per g of dried gelatin were added and the same procedure as described in Example 6 was carried out. The melting point of the emulsion film of each sample in a 2% aqueous solution of sodium carbonate was determined and the result obtained are as shown in Table 7.

TABLE 7

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate

Storage Time	Sample					
(day)	a	b	c	d	e	f
1	40	43	50	60	60	60
3	63	65	70	85	85	85
7	85	85	85	85	85	85

As can be seen from the results contained in above table, the hardening of the samples irradiated with high frequency was remarkably promoted.

EXAMPLE 8

4 mg of mucochloric acid per g of dried gelatin were added to a 5% aqueous solution of gelatin. A cellulose triacetate film was coated with this solution so that the dried thickness of coat film would be 5μ, and dried sufficiently to carry out both constant rate and falling rate drying at a wet bulb temperature of 24°C and a dry bulb temperature of 35°C, and the following procedures (a) to (e) were carried out, respectively, to yield Samples (a) to (e):

a. Stored at 25°C and 45% RH for 2 days.

b. Irradiating Sample (a) with a high frequency for 30 sec.

c. Irradiating Sample (a) with a high frequency for 1 min.

d. Irradiating Sample (a) with a high frequency for 3 min.

e. Irradiating Sample (a) with a high frequency for 10 min.

Immediately, the melting point of the gelatin film of each sample in a 2% aqueous solution of sodium carbonate was determined and the results obtained are as shown in Table 8.

TABLE 8

Sample	(a)	(b)	(c)	(d)	(e)
M.P. (°C)	50	55	60	69	72

As can obviously be seen from the results contained in the above table, the hardening of gelatin was remarkably promoted even when a high frequency was applied after the completion of the drying of the gelatin film.

EXAMPLE 9

3mg of the sodium salt of 2-oxy-4,6-dichloro-s-triazine as a hardener per g of dried gelatin were added to a 5% aqueous solution of gelatin, a film of polyethylene terephthalate was coated therewith to form a layer of 8μ in dry thickness, and subjected to the following procedures, to obtain samples (a) to (d).

a. Immediately after coating and cooling, irradiating with a high frequency for 50 sec and then stored at 25°C and 45% RH.

b. After the completion of the constant rate drying at a dry bulb temperature of 35°C and a wet bulb temperature of 24°C irradiated with a high frequency for 1 sec then stored at 25°C, 45% RH.

c. After the completion of the constant rate drying at a dry bulb temperature of 35°C and a wet bulb temperature of 24°C, irradiating with a high frequency for 5 sec then stored at 25°C, 45% RH.

d. After the completion of the constant rate drying at a dry bulb temperature of 35°C and a wet bulb temperature of 24°C stored at 25°C, 45% RH.

The melting point of the gelatin film of each sample after storing for 3 days in a 2% aqueous solution of sodium carbonate was determined and the results obtained are shown in Table 9.

TABLE 9

Melting Point (°C) in 2% Aq. Solution of Sodium Carbonate

Sample	Melting Point
a	43
b	63
c	70
d	58

As can be understood from the results contained in the table, while the irradiation with the high frequency just after the coating gives an inferior effect to the hardening of the gelatin layer, when the irradiation is conducted after the completion of the constant temperature drying, even though for a very short time, the hardening of gelatin is accelerated.

While the invention has been described in detail and in terms of specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modification can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A process for the rapid hardening of gelatin comprising coating a support with an aqueous gelatin solution containing as a hardener at least one of a halogenated diazine compound, a halogenated triazine compound, a compound having an active vinyl radical, a mucohalogen acid or a derivative thereof and a substituted or an unsubstituted 2,3-dihydroxy-1,4-dioxane, drying the coating at a constant rate for a period of time without irradiating and then after completion of the constant rate drying period, irradiating with high frequency microwaves.

2. The process of claim **1,** wherein said hardener is 4-chloro-2, 6-bis(methylsulfonyl)-1,3-diazine, 4-chloro-2-ethylsulfonyl-6-methyl-1,3-diazine, 4,6-bis(methylsulfonyl)-1,3-diazine, 2,4-dibromo-6-methylsulfonyl-1,3-diazine, 2,4,5-tribromo-6-methylsulfonyl-1, 3-diazine, 4,5,6-tris(methylsulfonyl)-1,3-diazine, 4,5-dichloro-6-methyl-2-phenylsulfonyl-1,3-diazine, 2,3-dichloroquinoxaline-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-6-chloro-7-sulfonic acid chloride, N,N-bis(hydroxyethyl)aminodichlorotriazine, the sodium salt of 2,4-dichloro-6-oxy-s-triazine or 2,4-bis(1-aziridinyl)-6-chloro-1,3,5-triazine.

3. The process of claim **1,** wherein said hardener is acrylamide, vinyl sulfone, diacryloylamine, dipotassium 1, 4-di (α-bromoacryloylamino)benzene-2,5-disulfonate, sodium 2,6-di(bromoacryloylamino)-naphthalene-4,6-disulfonate, or N-p-(β-chloroethylamino)-sulfobenzene acrylamide.

4. The process of claim **1,** wherein said hardener is mucochloric acid, mucobromic acid, 3-bromo-2-phenoxymalealdehydic acid, 3-chloro-2-phenoxymalealdehydic acid, 2-(p-carboxyphenoxy)-3-chloromalealdehydic acid, 2-(p-methoxyphenoxy)-3-chloromalealdehydic acid, 2-(p-tert-pentylphenoxy-3-chloromalealdehydic acid, 2-(p-octylphenoxy)-3-chloromalealdehydic acid, 2-(m-pentadecyl)-3-chloromalealdehydic acid, or 3-chloro-2-phenylthiomalealdehydic acid.

5. The process of claim **1,** wherein said hardener is 2,3-diformyl-2,3-dihydroxy-1,4-dioxane, or 2,3-diformyl-2,3-dihydroxy-6-methyl-1,4-dioxane.

6. The process of claim **1,** wherein said hardener is present at a level ranging from 1 to 100mg per g of gelatin on a dry basis.

7. The process of claim **1,** wherein said frequency ranges from 13.56 to 18,000MHz.

8. The process of claim **1,** wherein said frequency is 915MHz or 2450MHz.

9. The process of claim **1,** wherein said irradiating occurs after drying at a constant rate but during drying at a falling rate.

* * * * *