

UNITED STATES PATENT OFFICE

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METHOD OF HARDENING PHOTOGRAPHIC GELATIN

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This invention relates to pre-hardened gelatin for photographic emulsions and to a method for hardening gelatin.

It is customary to treat gelatin intended for the manufacture of photographic emulsions with a small amount of hardening agent in order to raise the melting point and to increase the resistance of the emulsion to hot water and processing solutions, particularly under tropical conditions. Compounds which have been used for the purpose of hardening gelatin and emulsions include chrome alum, formaldehyde, and others. In our prior application, Serial No. 745,754, filed September 27, 1934, we disclosed the use of hydroxy aldehydes up to and including pentoses for this purpose.

There are a number of objections to these hardening compounds when employed in the usual way. An excess of the hardening agent ordinarily remains in the gelatin and this excess hardening compound produces undesirable results in the gelatin and in the emulsions made from it. Among these objectionable characteristics are a progressive rise in viscosity of the gelatin at the usual coating temperature so that uncertainties and difficulties in the matter of coating control are introduced; a further objection is the bringing about of a progressive hardening over a period of time after the emulsion is coated and dried. This latter feature is objectionable not only because of the uncertain condition of the material thereby produced unless a very long period of seasoning is resorted to, but also because of the progressive change in the photographic or sensitometric properties, such as the development rate. A further objectionable feature in the use of excess hardening agents, particularly aldehydes, is that the uncombined hardening agent tends to produce fog.

It is therefore an object of the present invention to provide a method for preparing a pre-hardened photographic gelatin having a definite and substantially constant melting point. A further object is to provide a method for eliminating after-hardening of photographic emulsions. A still further object is to provide a method for reducing the tendency of photographic emulsions to fog prior to exposure. Other objects will appear more fully hereinafter.

We have found that the undesirable features referred to above may be attributed in a large measure to the excess or uncombined hardening agent in the gelatin or emulsion. We therefore propose to treat the gelatin in an aqueous bath of a hardening agent for a definite length of time and then wash out the residual uncombined hardening agent.

In carrying out our invention, a solution of gelatin is mixed with an aqueous solution of a hardening agent such as an aldehyde and permitted to stand for an appreciable length of time, for example, from 18 to 72 hours depending on concentration of aldehyde, pH, and temperature of storage. The gelatin may also be immersed in the aldehyde hardening solution in the form of gelatin sheets or noodles. The excess aldehyde or other hardening agent is then washed out of the gelatin with water and the gelatin is mixed with a silver halide emulsion or coated as a separate layer on a photographic support, or in the case of the sheets or noodles, may be dried and retained for future use. The gelatin treated in this way may have a melting point of from 40° C. to 70° C. with a water content of about 10%.

Among the hardening agents which may be used for treating gelatin according to our invention are formaldehyde and other aldehydes, and the hydroxy aldehydes disclosed in our prior application, Serial No. 745,754. These are used in quantities up to 1% of the amount of gelatin. The preferred pH of the hardening solution is 6 to 10.

The following method of procedure, which is by way of example only, illustrates a method of preparing a hardened gelatin having a substantially constant melting point according to our invention:

A 7% gelatin solution at pH 6.44 is treated with 0.3% of formaldehyde (based on the weight of the gelatin). The treated gelatin is allowed to gel and this gel is aged, after coating, for 67 hours at 5° C. The gel is then washed repeatedly with cold water until no trace of formaldehyde can be detected in the wash water (1-2 hours). The plate is dried and melting point studies made. Typical data are given in Table I.

The effect of varying pH and time and temperature of storage are shown by Tables II to IV.

After-hardening of coated plates can be reduced materially by washing the dried plate in water or a 1% urea solution followed by a water wash. Typical data are given in Tables VI to IX.

In the examples given in Tables I to V, the gel was washed and then dried, either before or after coating, after which it was aged. In the examples given in Tables VI to IX, the gel was coated, then dried prior to washing, after which it was aged.

TABLE I

Effect of ageing formaldehyde treated gelatin in the jelly state and of washing and drying on the after-hardening of the dried gelatin

0.3% formaldehyde (on wt. of gelatin)
pH 6.44
Aged 67 hrs. at 5° C. (41° F.) before washing

Age of dried gelatin, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	33° (91.4° F.)	97° (206° F.)	57° (134.6° F.)
3.0		Insoluble	57-58° (134-136° F.)
7.0		do	59-64° (138-147° F.)
16.0		do	70° (158° F.)
27.0		do	72° (162° F.)
64.0	34° (93.2° F.)	do	78° (172° F.)

TABLE II

Effect of ageing of glycol aldehyde treated gelatin in the jelly state and of washing and drying on the after-hardening of the dried gelatin

0.4% glycol aldehyde (on wt. of gelatin)
pH 6.94
Aged 19 hrs. at 25° C. (77° F.) before washing

Age of dried gelatin, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	33° (91.4° F.)	97° (206° F.)	48° (118° F.)
4.0		Insoluble	50° (122° F.)
14.0		do	55° (131° F.)
25.0		do	59° (138° F.)
62.0	34° (93.2° F.)	do	70° (158° F.)

TABLE III

Effect of ageing formaldehyde treated gelatin in the sol state, and of coating, washing, remelting, coating and drying on the after-hardening of the dried gelatin

0.3% formaldehyde (on wt. of gelatin)
pH 8.0
Aged 22 hrs. at 35° C. (95° F.) before washing with water at 5° C. (41° F.)

Age of dried gelatin, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	33° (91.4° F.)	80° (176° F.)	38° (100° F.)
8.0			41° (106° F.)
46.0	33-34° (91.4-93.2° F.)	90° (194° F.)	70° (158° F.)

TABLE IV

Effect of ageing formaldehyde treated gelatin in the sol state, and of coating, washing and drying on the after-hardening of the dried gelatin

0.3 percent formaldehyde (on wt. of gelatin)
pH 8.07
Aged 68 hrs. at 35° (95° F.) before washing

Age of dried gelatin, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	33° (91.4° E.)	75° (167° F.)	45° (113° F.)
3.0			45° (113° F.)
7.0			45° (113° F.)
12.0			45° (113° F.)
49.0	33-34° (91.4-93.2° F.)	97° (206° F.)	68° (154.4° F.)

TABLE V

Effect of ageing formaldehyde treated gelatin in the sol state, and of coating, washing, remelting, coating and drying on the after-hardening of the dried gelatin

0.3% formaldehyde (on wt. of gelatin)
pH 8.07
Aged 68 hrs. at 35° C. (95° F.) before washing

Age of dried gelatin, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	33° (91.4° F.)	75° (167° F.)	45° (113° F.)
3.0			45° (113° F.)
7.0			45° (113° F.)
12.0			45° (113° F.)
49.0	33-34° (91.4-93.2° F.)	97° (206° F.)	74° (165.2° F.)

TABLE VI

Effect of removal of uncombined formaldehyde on the after-hardening of formaldehyde treated X-ray emulsion

Uncombined formaldehyde removed by washing dried emulsion
0.05% formaldehyde (on wt. of gelatin)
pH 6.6

Age of dried emulsion, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	32-34° (89.6-93.2° F.)	33-35° (91-95° F.)	35° (95° F.)
6.0	32-34° (89.6-93.2° F.)	37° (98.6° F.)	35° (95° F.)
23.0	32-34° (89.6-93.2° F.)	39° (102.2° F.)	35° (95° F.)
43.0	32-34° (89.6-93.2° F.)	40° (104.0° F.)	35° (95° F.)
183.0	32-34° (89.6-93.2° F.)	54° (129.2° F.)	36° (96.8° F.)

TABLE VII

Effect of removal of uncombined formaldehyde on the after-hardening of formaldehyde treated X-ray emulsion

Uncombined formaldehyde removed by washing the dried emulsion
0.1% formaldehyde (on wt. of gelatin) pH 6.6

Age of dried emulsion, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0	32-34° (89.6-93.2° F.)	36° (96.8° F.)	37° (98.6° F.)
6.0	32-34° (89.6-93.2° F.)	49° (120.2° F.)	36° (96.8° F.)
23.0	32-34° (89.6-93.2° F.)	79° (174.2° F.)	38° (100.4° F.)
43.0	32-34° (89.6-93.2° F.)	81° (177.8° F.)	38° (100.4° F.)
182.0	32-34° (89.6-93.2° F.)	86° (186.8° F.)	39° (102.2° F.)

TABLE VIII
Effect of removal of uncombined formaldehyde on the after-hardening of formaldehyde treated X-ray emulsion

Uncombined formaldehyde removed by washing the dried emulsion
0.18% formaldehyde (on wt. of gelatin)
pH 6.6

Age of dried emulsion, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0.....	32-34° (89.6-93.2° F.)	39° (102.2° F.)	38° (100.4° F.)
5.0.....	32-34° (89.6-93.2° F.)	66° (150.8° F.)	38° (100.4° F.)
41.0.....	32-34° (89.6-93.2° F.)	76° (168.8° F.)	37° (98.6° F.)
60.0.....	32-34° (89.6-93.2° F.)	89° (192.2° F.)	39° (102.2° F.)

TABLE IX
Effect of removal of uncombined formaldehyde on the after-hardening of formaldehyde-resorcinol treated X-ray emulsion

0.1% formaldehyde
1.5% resorcinol (on wt. of gelatin)
pH 6.6

Age of dried emulsion, days	M. P., °C.		
	Untreated	Treated unwashed	Treated washed
1.0.....	32-34° (89.6-93.2° F.)	40-42° (104-107.6° F.)	40-42° (104-107.6° F.)
6.0.....	32-34° (89.6-93.2° F.)	44° (111.2° F.)	37° (98.6° F.)
23.0.....	32-34° (89.6-93.2° F.)	55° (131.0° F.)	37° (98.6° F.)
43.0.....	32-34° (89.6-93.2° F.)	63° (145.4° F.)	39° (102.2° F.)
72.0.....	32-34° (89.6-93.2° F.)	62° (143.6° F.)	40° (104.0° F.)
98.0.....	32-34° (89.6-93.2° F.)	66° (150.8° F.)	42° (107.6° F.)
182.0.....	32-34° (89.6-93.2° F.)	75° (167° F.)	47° (116.6° F.)

In the preparation of an emulsion according to our invention, the hardening process may be accelerated by heating in a moist atmosphere as described in our co-pending application of S. E. Sheppard, R. C. Houck, and R. H. Lambert, Serial No. 90,000 filed July 10, 1936. According to this method, a gelatino-silver halide emulsion is treated with the hardening agent prior to digestion, the excess hardening agent then washed out, and the emulsion coated on a suitable support and subjected to a heat treatment in a moist atmosphere at 60° to 70° C.

We have referred above to the "melting point" of the gelatin. The melting point of said gelatin varies with the water content and increases as the water content of the gel is reduced. The melting point of gels, as referred to above, is determined in the following way:

A strip of gelatin whose melting point is to be determined is coated on glass and immersed in distilled water and the temperature raised slowly (0.75° C. per minute). The temperature at which the gelatin flows rapidly off the plate is taken as the melting point of the gelatin.

The pre-hardened gelatin made according to our invention may be used in a number of ways in the manufacture of photographic films or plates. When used to produce a hardened photographic emulsion, the pre-hardened gelatin is added to the emulsion preferably after the precipitation of the silver halide. The amount of pre-hardened gelatin added to the emulsion will depend of course upon the melting point of the hardened gelatin and on the desired melting point of the final emulsion. Amounts may be used varying from .05% of the hardened gelatin to 1.0% compared with the amount of emulsion.

The pre-hardened gelatin prepared according to

our invention may also be used as a film overcoating or as a backing layer to reduce the curling tendency of cellulose ester film or to contain an anti-halation material. The pre-hardened gelatin may also be used as substrate between the film support and the emulsion layer or between the film support and other layers of the film.

It is to be understood that the examples referred to above are by way of illustration only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of preparing pre-hardened photographic gelatin which comprises treating unhardened gelatin with an aqueous solution of a hardening agent in an amount up to approximately 1½% of hardening agent based on the weight of gelatin until the desired hardening is obtained, and washing out the residual, uncombined hardening agent prior to coating the gela-

tin on a photographic support.

2. The method of preparing pre-hardened photographic gelatin which comprises treating unhardened gelatin with an aqueous solution of formaldehyde in an amount up to approximately 1½% of formaldehyde based on the weight of gelatin until the desired hardening is obtained, and washing out the residual, uncombined formaldehyde prior to coating the gelatin on a photographic support.

3. The method of preparing pre-hardened photographic gelatin which comprises treating unhardened gelatin with a hardening agent in an amount up to approximately 1½% of hardening agent based on the weight of gelatin until the gelatin attains a melting point of 40° C. to 70° C., and washing out the residual, uncombined hardening agent prior to coating the gelatin on a photographic support.

4. The method of preparing pre-hardened photographic gelatin which comprises treating unhardened gelatin with an aldehyde hardening agent in an amount up to approximately 1½% of hardening agent based on the weight of gelatin until the gelatin attains a melting point of 40° C. to 70° C., and washing out the residual, uncombined aldehyde hardening agent prior to coating the gelatin on a photographic support.

5. The method of preparing pre-hardened photographic gelatin which comprises treating unhardened gelatin with a formaldehyde in an amount up to approximately 1½% of formaldehyde based on the weight of gelatin until the gelatin attains a melting point of 40° C. to 70° C., and washing out the residual, uncombined formaldehyde prior to coating the gelatin on a photographic support.

6. The method of preparing a photographic

emulsion of substantially constant melting point, which comprises treating a gelatino-silver halide emulsion with an aldehyde hardening agent in an amount up to approximately 1½% of hardening agent based on the weight of gelatin, coating the emulsion on a support, drying the emulsion, and washing out the residual, uncombined hardening agent.

7. The method of preparing a photographic

emulsion of substantially constant melting point, which comprises treating a gelatino-silver halide emulsion with an aldehyde hardening agent in an amount up to approximately 1½% of hardening agent based on the weight of gelatin, washing out the residual, uncombined hardening agent, and drying the washed emulsion.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 15, Table IV, under the heading "Untreated" for "33° (91.4° E.)" read --33° (91.4° F.)--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of March, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.