

UNITED STATES PATENT OFFICE

2,494,055

HARDENING OF PHOTOGRAPHIC SILVER
HALIDE GELATIN EMULSIONS WITH
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N. Y., a corporation of DelawareNo Drawing. Application December 10, 1946,
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4 Claims (Cl. 95-7)

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This invention relates to photographic gelatin, and more particularly to the hardening of photographic gelatin and gelatino silver-halide emulsions to yield compositions having an appreciable increase in melting point and good stability on ageing with respect to fog, speed, and gradation.

In the preparation of photographic gelatin dispersions and gelatino silver-halide emulsions, it has been the practice to treat the dispersions and emulsions, prior to coating, with a hardening agent so as to reduce the tendency of the gelatin to soften, or to distend during processing of the photographic material containing the gelatin, particularly at temperatures higher than the temperature specified for processing the particular photographic material. Compounds which have been used for hardening gelatin as such or in silver-halide emulsions are formaldehyde, hydroxy aldehydes, acrolein, glyoxal, and derivatives thereof, and mixtures of an aliphatic aldehyde with an aromatic compound containing at least one nuclear hydroxy substituent group such as phenol, resorcinol, resorcylic aldehyde, and the like. Although formaldehyde and hydroxy aldehydes are satisfactory as hardening agents, these compounds possess the undesirable property of producing excessive fog, desensitization, or flattening of gradation in the processed film. Any hardeners that function by the liberation of formaldehyde will also have these deleterious effects as well as that of "after-hardening." Aliphatic aldehydes, with an aromatic compound containing at least one nuclear hydroxy substituent group, induce some increase in the melting point. They fail, however, to give both an appreciable increase in the melting point and good stability upon ageing in respect to fog, speed, and gradation.

It is an object of the present invention to provide a photographic gelatin or a gelatino silver-halide emulsion having an appreciable higher melting point and much better stability on ageing than gelatin or gelatino silver-halide emulsions per se.

Another object is to provide gelatin layers and gelatino silver-halide emulsion layers in which the gelatin is not subject to the phenomenon known as "after-hardening."

A further object is to provide a gelatino silver-halide emulsion which will not fog on storage.

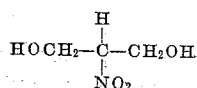
A still further object is to provide a gelatino silver-halide emulsion which will be resistant to relatively high processing temperatures without fogging, loss of speed, and loss of gradation.

Other objects will appear hereinafter.

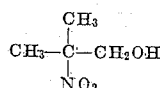
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The foregoing objects are accomplished, according to the present invention, by incorporating in the gelatin or gelatino silver-halide emulsion, a primary aliphatic nitro alcohol of not more than 6 carbon atoms, with or without other compounds which alone possess little or no hardening effect upon gelatin or gelatino silver-halide emulsions, but in conjunction with the nitro alcohol accelerate the hardening action with the elimination of "after-hardening," and also inhibit the tendency of the photographic material to fog on ageing.

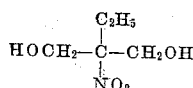
As examples of suitable primary aliphatic nitro alcohols of not more than 6 carbon atoms, the following are illustrative.



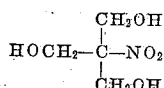
2-nitro-1,3-propanediol



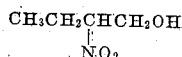
2-methyl-2-nitro-1-propanol



2-ethyl-2-nitro-1,3-propanediol



Tris-(hydroxymethyl)-nitromethane



2-nitro-1-butanol

The compounds which alone possess little or no hardening effect on gelatin or gelatino silver-halide emulsions, and which may be added in conjunction with the nitro alcohol, are 2,4-dihydroxy benzaldehyde (resorcylic aldehyde) and 1,3-benzenediol (resorcinol). The function of 2,4-dihydroxy benzaldehyde in the mixture is to boost or accelerate the hardening action of the nitro alcohol. When resorcinol is added to this combination, the optimum in hardening as well as in photographic properties is obtained. A very desirable increase in melting point of gelatin or gelatino silver-halide emulsions is obtained by the utilization of nitro alcohols alone, said increase in melting point being unaccompanied by

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any tendency for the gelatin or emulsion to undergo the phenomenon of "after-hardening." It has been found that the nitro alcohols depress the speed and gradation of the photographic emulsions a slight amount. Such losses, however, are more than compensated for by the valuable contributions made by the use of the nitro alcohols. Furthermore, if with the nitro alcohols there be added 2,4-dihydroxy benzaldehyde, greater hardness is obtained, the 2,4-dihydroxy benzaldehyde operating as it were to accelerate the hardness attributable to the nitro alcohols. The 2,4-dihydroxy benzaldehyde in addition has the valuable property of reducing the losses in speed and gradation which accompany the use of the nitro alcohols. The results obtained with the nitro alcohols in admixture with the 2,4-dihydroxy benzaldehyde are greatly improved if there also be employed resorcinol. This compound does not detract in the slightest from the hardening effect obtained with the other components and rather surprisingly in cooperation with said other ingredients confers upon the final sensitized emulsions a very excellent stability on ageing with respect to fog, speed and gradation. While, therefore, the invention contemplates the utilization of the nitro alcohols alone to effect hardening while avoiding the phenomenon of "after-hardening," it likewise contemplates the employment with the nitro alcohols of 2,4-dihydroxy benzaldehyde and resorcinol either alone or together. Inasmuch as best results are obtained when all three components are employed, the use of the same represents the preferred embodiment of the invention.

It is to be noted that from the large class of dihydroxy benzaldehydes, 2,4-dihydroxy benzaldehyde is the only one to accelerate the hardening effect of the nitro alcohol without impairing the photographic characteristics of the emulsions, and from the large class of aromatic hydroxy compounds containing at least 1 nuclear hydroxy group, resorcinol was found to be the only one, when in an admixture with a nitro alcohol and 2,4-dihydroxy benzaldehyde, to act as a stabilizing agent so as to impart excellent stability to the emulsion with respect to fog, speed, and gradation.

Where it is desired to increase the melting point of the gelatin in a gelatin dispersion utilized in the preparation of non-curling layers, filter and anti-halation layers, or anti-abrasion layers, a sufficient quantity of the nitro alcohol alone is added. While the exact amount of the nitro alcohol may be varied within wide limits and with due regard to the particular type of gelatin dispersion employed, in general, amounts ranging from 0.05% to 2.5% based on the dry weight of gelatin in the dispersion are preferred. In these amounts, effective hardening is obtained without "after-hardening," i. e., the melting point of the gelatin does not vary with time or with long periods of storage prior to actual use and processing of the photographic material provided with such a layer.

In cases, especially in anti-abrasion layers, where the optimum in hardness is desired, a mixture of the nitro alcohol and 2,4-dihydroxy benzaldehyde is employed. The amount of 2,4-dihydroxy benzaldehyde, to be added to the preceding amounts of the nitro alcohol, may vary from 0.005% to 2.5% based on the dry weight of gelatin.

In hardening gelatin emulsions which are slightly alkaline, i. e., emulsions having a pH greater than 7, generally between 7 and 8.5, the

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exact amounts of the nitro alcohol, 2,4-dihydroxy benzaldehyde, and resorcinol may also be varied within wide limits depending largely upon the desired degree of hardening, stabilizing effect, and gradation. In general, the amounts of the nitro alcohol may vary from 1 to 5 parts by weight, the amount of 2,4-dihydroxy benzaldehyde may vary from 0.1 to 5 parts by weight, and the amount of resorcinol may vary from 1 to 10 parts by weight per 10 kilogram of emulsion containing 8-10% gelatin.

Where it is desired to increase the speed and gradation of a silver-halide emulsion, I prefer to use resorcinol in conjunction with the nitro alcohol and 2,4-dihydroxy benzaldehyde. It is to be understood, however, that these emulsions may also be hardened by mixing therewith prior to coating the nitro alcohol alone or in combination with 2,4-dihydroxy benzaldehyde. In the latter case the melting point of the gelatin rises appreciably without the attendant serious loss of photographic characteristics.

While the following examples describe in detail the methods for accomplishing the aforementioned 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

To ten kilograms of a photographic silver-halide emulsion containing 8-10% gelatin and melting at 35° C., 80 mls. of a 5% aqueous solution of tris-(hydroxymethyl)-nitromethane were added at a temperature of 40° C. A glass plate was coated with a thin layer of this emulsion and dried at room temperature. The emulsion coating did not melt or run off when processed in a bath at a temperature up to 45° C.

EXAMPLE II

Twenty mls. of a 5% aqueous solution of 2-ethyl-2-nitro-1,3-propanediol and 80 mls. of a 5% aqueous solution of 2,4-dihydroxy benzaldehyde were added to 10 kilograms of a photographic silver-halide emulsion, containing 8-10% gelatin and melting at 35° C., at a temperature of 40° C. A glass plate was coated with a thin layer of this emulsion and dried at room temperature. The emulsion layer melted at 47° C., and the film was tougher than the film of Example I.

EXAMPLE III

This example graphically illustrates the results of incorporating tris-(hydroxymethyl)-nitromethane, 2,4-dihydroxy benzaldehyde and resorcinol in an X-ray emulsion containing 8-10% gelatin whereby not only the melting point of the gelatin is increased but excellent photographic properties are obtained. All the parts are in percent by weight based on the weight of the emulsion.

X-ray emulsion

Quantity of Tris-(hydroxymethyl)-nitromethane.....	0	0.023
Quantity of 2,4-Dihydroxy-benzaldehyde.....	0	0.03
Quantity of Resorcinol.....	0	0.07
M. P., °C.....	33	47
Fog.....	0.20	0.16
Speed.....	158	196
Gradation.....	0.75	0.80

EXAMPLE IV

This example shows the effect of fog in a silver-halide emulsion containing 8-10% gelatin by a mixture of 2-nitro-1,3-propanediol, 2,4-dihydroxy benzaldehyde, and resorcinol. All parts are in

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per cent based on the dry weight of the gelatin in the emulsion.

2-Nitro-1,3-propanediol	2,4-Dihydroxy benzaldehyde	Resorcinol	Fog Value
0	0	0	0.20
0.1	0.2	0.3	0.16
0.2	0.2	0.8	0.16
0.2	0.4	0.6	0.14
0.2	0.12	0.48	0.12
0.2	0.24	0.36	0.10

From the foregoing examples, it is clearly apparent that my invention is not only applicable to the preparation of photographic silver-halide emulsions of satisfactory hardening properties, but also to the preparation of gelatin dispersions and dispersions of gelatin substitutes, which are normally capable of being hardened with formaldehyde, especially those which are and have been used in the preparation of various coatings or layers on paper, cloth, film, glass, and other surfaces.

I claim:

1. A photo-sensitive element containing a photographic gelatino silver-halide emulsion layer hardened by means of a primary aliphatic nitro alcohol of 3 to 6 carbon atoms, 2,4-dihydroxy benzaldehyde, and resorcinol.

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2. A photo-sensitive element containing a photographic gelatino silver-halide emulsion layer hardened by means of tris-(hydroxymethyl)-nitromethane, 2,4-dihydroxy benzaldehyde, and resorcinol.

3. A photo-sensitive element containing a photographic gelatino silver-halide emulsion layer hardened by means of 2-ethyl-2-nitro-1,3-propanediol, 2,4-dihydroxy benzaldehyde, and resorcinol.

4. A photo-sensitive element containing a photographic gelatino silver-halide emulsion layer hardened by means of 2-nitro-1,3-propanediol, 2,4-dihydroxy benzaldehyde, and resorcinol.

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