United States Patent

Ishihara et al.

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[54] GELATINOUS PHOTOGRAPHIC COATING COMPOSITION

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[52] **U.S. Cl.** .....**96/114.4,** 106/125, 96/50 PL, 96/84, 96/87 A, 96/114.2

[51] **Int. Cl.**.....**G03c 1/38**

[58] **Field of Search**.....96/114.2, 50, 114.4, 87 A, 96/84; 106/125

[56] **References Cited**

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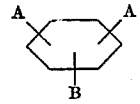
[57] **ABSTRACT**

Light-sensitive photographic materials coated with a dried gelatin emulsion are stabilized against curling and decrease in flexibility under conditions of low relative humidity by incorporating in the gelatin emulsion prior to drying at least 2 percent by weight based on the amount of gelatin of a cyclohexane compound of the general formula

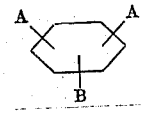


wherein the two A groups may be the same or different and are selected from the group consisting of $-OH$ and $-CH_2OH$ and B is selected from the group consisting of H and $-CH_3$.

4 Claims, No Drawings

GELATINOUS PHOTOGRAPHIC COATING COMPOSITION

This invention relates to a gelatinous photographic coating composition which comprises a cyclohexane compound of the general formula



wherein two A's, same or different, individually mean —OH or —CH_2OH and B means hydrogen or methyl.

It is common to use gelatin as a protective colloid in a light-sensitive silver halide photographic emulsion. However, a light-sensitive gelatino silver halide photographic emulsion when coated on a support and dried usually suffers from decreased flexibility at a low humidity and increased tendency of curling. This often causes fog generation due to physical action or static disorder due to friction electrification during the preparation of a light-sensitive silver halide photographic material or during its storage or use. In order to prevent the above-mentioned undesired tendencies, incorporation of a hygroscopic material such as glycerine or ethylene glycol in a gelatinous emulsion has been proposed in the art. This proposal, however, causes another problem which is raised due to the hygroscopic nature of the additive during the high-temperature storage of a light-sensitive gelatino silver halide photographic material.

It is accordingly the main object of this invention to provide a light-sensitive gelatino silver halide photographic material which is free from the aforementioned disadvantages. Another object of the invention is to provide a light-sensitive gelatino silver halide photographic film which has improved physical properties without sacrificing desired photographic performances.

Typical examples of cyclohexane compounds usable in this invention are

1,4-cyclohexane-diol,
1,4-cyclohexane-dimethanol,
1,3-cyclohexane-diol,
1,2-cyclohexane-dimethanol,
1-methyl-3,4-cyclohexane-diol and
4-hydroxy-cyclohexane-methanol.

Among these, some can exist in the form of either cis- or trans-compounds, which are equally effective for the purpose of the invention. Of course, a cis- and trans-mixture is usable. The above-mentioned hexane compounds can be synthesized by the method described in Journal of the American Chemical Society 76, 771 (1954). These cyclohexane compounds are normally solid and do not show any hygroscopic property unlike glycerine and ethylene glycol. In order to demonstrate this, moisture absorption of various compounds kept for 24 hours under relative humidity of 75 percent are measured. The results are set forth below.

Compound	Moisture absorption (%)
Glycerine	>40%
Ethylene glycol	29%
1,4-Cyclohexane-diol	2%
1,4-Cyclohexane-dimethanol	1%
1,3-Cyclohexane-diol	2%
1,2-Cyclohexane-dimethanol	1%
1-Methyl-3,4-cyclohexane-diol	1.5%

The minimum effective amount of a cyclohexane compound usable in the invention usually 2 percent by weight, based on the weight of a protective colloid (e.g., gelatin). However, the optimum amount of the cyclohexane compound may vary depending on the type of the light-sensitive photographic material as intended. The cyclohexane compound can be also effective even when it is incorporated into a gelatin coating containing a natural or synthetic high-polymeric substance. Further, the cyclohexane compound may exist in any one of the layers constituting a light-sensitive photographic material,

said layers including an emulsion layer, an interlayer, a sublayer, an antihalation layer, a backing layer, a filter layer, a protective layer, etc., with the result that flexibility is improved and curling is prevented, with additional advantages which are decreased fogging, increased antistatic property and improved resistance against pressure or mechanical shocking.

The following examples will serve to show the invention in detail, without limiting the scope of the invention thereto.

Example 1

To a light-sensitive gelatino silver iodobromide emulsion for X-ray film, 15 percent by weight, based on the weight of gelatin, of 1,4-cyclohexane-diol or 1,4-cyclohexane-dimethanol is added in the form of aqueous solution. Immediately thereafter, the emulsion is coated on a cellulose triacetate film base to have a dry thickness of 200μ and then dried. A light-sensitive film having an emulsion coating of 10μ thick is obtained.

Several samples of 6×50 mm. are cut from this film and individually maintained at a relative humidity of 20 and 32 percent to determine curling. The result is set forth in Table 1.

TABLE 1

Sample	Curl cm.$^{-1}$) 20% RH	32% RH
Not added	0.18	0.12
1,4-Cyclohexane-diol	0.06	0.04
1,4-Cyclohexane-dimethanol	0.08	0.06

In the table, "curl" is expressed as an inverse number of radius of curvature. The data clearly indicate the effectiveness of the cyclohexane compounds used herein to improve physical property of the light-sensitive photographic film.

Example 2

To the same emulsion as used in Example 1, 30 percent by weight, based on the weight of gelatin, of 1,4-cyclohexane-diol or 1,4-cyclohexane-dimethanol is added. The emulsion is then coated on a cellulosic triacetate film and dried to form a light-sensitive film.

Several samples are taken from this film. Each film sample is bent six times in a bending machine having the radius of curvature of 3 mm. Then the film sample is exposed to light through an optical wedge and then treated by development as specified in JIS K–7604. Generally, increased fog due to bending is observed at the low-density portion while decreased sensitivity occuring at the bending point is observed at the high-density portion. Pressure tolerance of the light-sensitive photographic film is considered as the inverse number of the density difference ΔD between the bent portion and the unbent portion. The result is set forth in Table 2.

TABLE 2

Sample	Density difference D=0.4	D=0.8	D=1.0
Not added	0.11	0.06	−0.03
1,4-Cyclohexane-diol	0.04	0.03	0.00
1,4-Cyclohexane-dimethanol	0.04	0.04	−0.02

The data clearly indicate that the photographic film according to the present invention is improved in pressure tolerance. $\Delta D>0$ means increase in density, while $\Delta D<0$ means decrease in density.

Example 3

To a high-speed negative, gelatino silver iodobromide emulsion, 1,4-cyclohexane-diol or 1,4-cyclohexane-dimethanol is added at varying amounts. The emulsion is coated on a cellulose triacetate film base and dried. The light-sensitive photo-

graphic film obtained is subjected to sensitometry according to the method specified in JIS K–7604. The result is set forth in TABLE 3.

TABLE 3

Sample	Amount added	Relative speed	Fog
Not added	—	100	0.15
1,4-Cyclohexane-diol	10%	100	0.09
	20%	100	0.04
1,4-Cyclohexane-dimethanol	10%	100	0.11
	20%	100	0.05

The above data clearly indicate that use of the cyclohexane compounds is effective to remarkably reduce fog formation during the preparation of a light-sensitive photographic film, without any adverse effect on the photographic properties.

Example 4

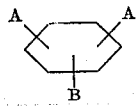
The same emulsion as used in Example 3 is coated on a support and then coated thereon with a 2 percent gelatin liquid containing 20 percent, based on the weight of gelatin, of 1-methyl-3,4-cyclohexane-diol. The resulting photographic film is improved in flexibility and curling as compared with that having a protective layer not containing 1-methyl-3,4-cyclohexane-diol, with decrease of fog formation and without any adverse influence on photographic properties.

Example 5

To each of high-speed, red-, green- and blue-light-sensitive, color-negative photographic emulsions, 20 percent by weight of 1-methyl-3,4-cyclohexane-diol is added. The high-speed, color-negative films prepared by these emulsions are measured in curling test as specified in Example 1. Remarkable improvement in coating properties is observed, without any adverse influence on photographic properties.

What we claim is:

1. A gelatinous photographic coating composition which comprises gelatin and at least 2 percent by weight based on the amount of gelatin of a cyclohexane compound of the general formula



Wherein the two A groups may be the same or different and are selected from the group consisting of —OH and —CH_2OH and B is selected from the group consisting of H and —CH_3, with the proviso that when both A groups are OH and B is H, the A groups are in the 1,2 or 1,4 positions.

2. A gelatinous photographic coating composition as claimed in claim 1 wherein said cyclohexane compound is selected from the group consisting of 1,4-cyclohexanediol, 1,4-cyclohexane-dimethanol, 1,2-cyclohexanedimethanol, 1-methyl-3,4-cyclohexanediol and 4-hydroxy-cyclohexane-methanol.

3. A gelatinous photographic coating composition as claimed in claim 1, wherein said composition is present as a photographic layer coated on a photographic film support.

4. A gelatinous photographic coating composition as claimed in claim 3, wherein said layer is a light-sensitive silver halide photographic emulsion layer, an interlayer, a sublayer, a backing layer, a filter layer or a protective layer.

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